Cyclopentadienyl Nickel Complexes Bearing a Pendant Phosphane Tether

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BY THE NAME OF ALLAH THE
MOST MERCIFUL AND BENIFICIENT

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Mazhar Hussain

Dedicated To My Parents And My

Nadi

To Whom I Owe All That Is Mine

Abstract

Cyclopentadienylnickel-Chelatkomplexe mit Phosphor-Seitenarm

Cyclopentadienylnickel und Phosphan-Nickel-Komplexe wurden im Rahmen früherer Arbeiten untersucht, jedoch wurde nie über Cyclopentadienylnickel-Chelatkomplexe mit Phosphor-Seitenarm berichtet. Im Rahmen dieser Arbeit konnte die Synthese der beiden Komplexe [(Di-*tert*-butylphosphanylethyl)cyclopentadienyl]nickel-(II) und [1-(Di-*tert*-butylphosphanylethyl)indenyl]nickel(II) gezeigt werden. Die Cyclopropanringe des Spiro[2.4]hepta-4,6-dien und des [4,5]Benzospiro[2.4]hepta-4,6-dien wurden mit Hilfe des Nucleophils Lithium-di-*tert*-butylphosphid geöffnet. Die anschließende Addition von wasserfreiem Nickelchlorid ergab über einen anionischen Liganden bei tiefen Temperaturen [(Di-*tert*-butylphosphanylethyl)cyclopentadienyl]chloronickel(II) und das planar chirale [1-(Di-*tert*-butylphosphanylethyl)indenyl]chloronickel(II). Die beiden Komplexe wurden mit Methyllithium umgesetzt und ergaben die Komplexe [(Di-*tert*-butylphosphanylethyl)cyclopentadienyl]methylnickel(II) und das planar chirale [1-(Di-*tert*-butylphosphanylethyl)indenyl]methylnickel(II). Der Komplex [(Di-*tert*-butyl-phosphanylethyl)cyclopentadienyl]chloronickel(II) wurde mit Silbertriflat umgesetzt, und es konnten die Triflatderivate erhalten werden. Die Reaktion von [(Di-*tert*-butylphosphanylethyl)cyclopentadienyl]chloronickel(II) mit verschiedenen Alkinen in Gegenwart katalytischer Mengen CuI in Triethylamin ergab die σ-Alkinyl-Komplexe welche wiederum mit Tetracyanoethylen zu zwei Haupt- und zwei Nebenkonformationen des Butadienylnickel-Chelatkomplexes umgesetzt wurden. Die [4+2]-Cycloadditions-produkte wurden durch die Umsetzung von σ-Alkinylnickel-Chelatkomplexen mit Ethoxycarbonylisothiocyanat erhalten. Die Methyl- und Alkylnickel-Chelate wurden als Katalysatoren in Hydrosilylierungsreaktionen mit Styrol getestet. [(Di-*tert*-butyl-phosphanylethyl)cyclopentadienyl]chloronickel(II), das σ-Acetylid und seine Methyl-derivate zeigen interessante Ergebnisse in der cyclischen Voltammetrie.

Der Komplex [(Di-*tert*-butylphosphanylethyl)cyclopentadienyl]chloronickel(II) wurde mit Silberhexafluoroantimonat, -hexafluorophosphat, -tetrafluoroborat und Natrium-tetraphenylborat in Acetoniril zu den entsprechenden [(Di-*tert*-butyl-phosphanyl-ethyl)cyclopentadienyl(acetonitrile)]nickel(II)-Komplexen umgesetzt. Die Ringöffnung des [4,5]Benzospiro[2.4]hepta-4,6-diens mit Hilfe des Nucleophils Di-*tert*-butylphosphid zum achiralen Di-*tert*-butyl-2-(1′-indenylethyl)phosphan benötigte eine Zeit über fünf Tagen unter Rückfluss, jedoch konnte diese lange Reaktionszeit über eine Mikrowellenreaktion verkürzt werden (200 W, 150 °C, 40 min). Der planar chirale Komplex [1-(Di-*tert*-butylphosphanylethyl)indenyl]chloronickel(II) führte mit CuI als Katalysator und unter Umsetzung verschiedener Alkine in Triethylamin zu den Komplexen [1-(Di-*tert*-butylphosphanylethyl)indenyl]-nickel(II)-σ-acetylid. Die Reaktion mit 1,3-Diethinylbenzol ergab eine Mischung des meso- und des racemischen Produktes im Verhältnis 100:9. Die Reaktion von [1-(Di-*tert*-butylphosphanyl-ethyl)indenyl]chloronickel(II) mit Natriumtetraphenylborat führte zu dem erwarteten Komplex [1-(Di-*tert*-butylphosphanylethyl)indenyl(acetonitrile)]nickel(II).

Cyclopentadienyl- und planar chirale Indenyl-Nicke(II) Komplexe • Di-tert-butylphosphanylethylverbrückter Ligand • Cyclovoltammetrie • [4+2] und [2+2] Cycloadditionsreaktionen • Hydrosilylierungen • Mikrowellen unterstützte Ringöffnung

Abstract

Cyclopentadienyl Nickel Complexes Bearing a Pendant Phosphane Tether

Cyclopentadienyl nickel and phosphane nickel complexes have earlier been investigated, but still no cyclopentadienyl nickel chelate complexes bearing pendant phosphane ligands have been reported. The aim of this research project was mainly to investigate the methodology for the synthesis of [(di-*tert*-butylphosphanylethyl)cyclopentadienyl]nickel (II) and [1-(di-*tert*-butylphosphanylethyl)indenyl]nickel(II) complexes. Cyclopropane rings of spiro[2.4]hepta-4,6-diene and [4,5]benzospiro[2.4]hepta-4,6-diene were cleaved by the nucleophilic attack of lithium di-*tert*-butylphosphide. The addition of anhydrous nickel chloride to the respective anionic ligands at low temperature yielded [(di-*tert*-butylphosphanylethyl)cyclopentadienyl]chloronickel(II) and planar chiral [1-(di-*tert*-butylphosphanylethyl)indenyl]chloronickel(II), which were treated with methyllithium to obtain [(di-*tert*-butylphosphanylethyl)cyclopentadienyl]methylnickel(II) and planar chiral [1-(di-*tert*-butylphosphanylethyl)indenyl]methylnickel(II), respectively, in good yields. [(Di-*tert*-butylphosphanylethyl)cyclopentadienyl]chloronickel(II) was treated with silver triflate to obtain its triflate derivative. The reaction of [(di-*tert*-butylphosphanylethyl)cyclopentadienyl]chloronickel(II) with different acetylenes using the catalytic amount of cuprous iodide in triethyleamine gave the respective σ-alkynyl complexes, which were treated with tetracyanoethylene to obtain two major and two minor conformations of the respective butadienyl nickel chelate complexes. The [4+2] cycloaddition products were obtained by treatment of the σ-alkynyl nickel chelate complexes with ethoxycarbonylisothiocyanate. The methyl and an alkynyl nickel chelates were used as single component catalysts in the hydrosilylation reaction of the styrene. The [(di-*tert*-butylphosphanylethyl)cyclopentadienyl]chloronickel(II), its σ-acetylide and methyl derivatives showed interesting cyclovoltammetry results. The [(di-*tert*-butylphosphanylethyl)cyclopentadienyl]chloronickel(II) was treated with silver hexafluoroantimonate, hexafluorophosphate, tetrafluoroborate and sodium tetraphenylborate in acetonirile to yield cationic [(di-*tert*-butylphosphanylethyl)cyclopentadienyl(acetonitrile)]nickel(II) complexes. The ring cleavage of [4,5]benzospiro[2.4]hepta-4,6-diene by the nucleophilic attack of di-*tert*-butylphosphide needed heating time of five days. To reduce an extended heating time, the reaction was performed under microwave irradiation (Power = 200 W, Temperature = 150 °C, Ramp time = 3 min, Hold time = 40 min) to get the achiral di-*tert*-butyl-2-(1′-indenylethyl)phosphane. The planar chiral complex, [1-(di-*tert*-butylphosphanylethyl)indenyl]chloronickel(II) with cuprous iodide as a catalyst was treated with different acetylenes in triethylamine to obtain [1-(di-*tert*-butylphosphanylethyl)indenyl]-nickel(II) σ-alkynyl complexes. The reaction with 1,3-diethynylbenzene, a mixture of meso and racemic mixture was obtained in the ratio 100:9. The reaction of [1-(di-*tert*-butylphosphanylethyl)indenyl]chloronickel(II) with sodium tetraphenylborate gave [1-(di-*tert*-butylphosphanylethyl)indenyl(acetonitrile)]nickel(II).

Cyclopentadienyl- and Planar Chiral Indenyl -Nickel(II) Complexes • Di-*tert*-butylphosphanylethyl Pendant Ligand • Cyclovoltammetry • [4+2] and [2+2] Cycloaddition Reactions and Conformations • Hydrosilylation Reactions • Microwave Assisted Ring Cleavage

Contents

Abbreviations

APT	Attached proton Test
ATR	Attenuated Total Reflection
br	Broad
BuLi	Butyllithium
tBu	*tert*-Butyl
ca.	Circa
^{13}C NMR	^{13}C nuclear Magnetic Spectroscopy
C	Concentration
Cy	Cyclohexyl
CV	Cyclovoltammetry
Cp	Cyclopentadienyl C5H5
COSY	Correlated Spectroscopy
Conc.	Concentrated
d	doublet
DEPT	Distortionless Enhancement by Polarization Transfer
DCM	Dichloromethane
δ	Chemical Shift
eq.	Equivalent
Et_2O	Diethyl Ether
E°	Standard Potential
EA,*EK*	Anodic, Kathodic Potential
Fig.	Figure
GC	Gas Chromatography
^{1}H NMR	^{1}H Nuclear Magnetic Resonance
L	Ligand
mV	Millivolt
mmol	Millimole
PE	Petroleum Ether
h	Hour

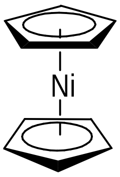
HRMS	High Resolution Mass Spectrometry
Hz	Hertz
iPr	Isopropyl
J	Coupling constant
mL	Milliliter
m	Multiplet
Me	Methyl
min	Minute
MeLi	Methyllithium
IR	Infrared Spectroscopy
MS	Mass Spectrometry
TBME	*tert*-Butylmethyl Ether
tert	Tertiary
NMR	Nuclear Magnetic Spectroscopy
M	Molar
Ph	Phenyl
ppm	Parts Per Million
THF	Tetrahydrofuran
TMS	Trimethylsilane
t	Triplet
s	Singlet
m.p.	Melting Point

Figures

Tables

1 Introduction

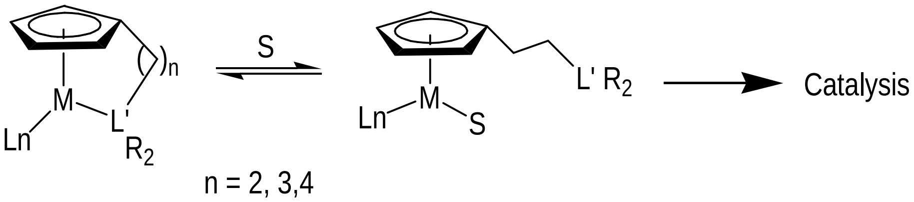
The organometallic chemistry of nickel has a long history dating back to 1890, the preparation of tetracarbonylnickel [$Ni(CO)_4$], and its use in the Mond process for refining nickel metal.[1] In general, the chemistry of nickel is dominated by the divalent Ni^{2+} and zero-valent Ni^0 oxidation states, although examples of compounds of Ni^+, Ni^{3+}, and even Ni^{4+} are known.[2] Nickelocene (**1**) is the only metallocene with 20 valence electrons. It is paramagnetic and easily oxidised to the nickelocinium ion (19 VE) of limited stability. The cyclopentadienyl ligands, especially the first one, are fairly easily displaced from nickelocene. Thus the reactions with phosphanes and phosphates yield NiL_4 [L = PR_3, $P(OR)_3$],[3,4] nitrogen monoxide gives CpNi(NO),[5] and treatment with tetracarbonylnickel results in the formation of dimeric complex [$CpNi(CO)_2]_2$.[6] The cyclopentadienyl ligand is also displaced by allyl magnesium chloride[7] and by azobenzene.[8] The reactivity of nickelocene, and especially the lability of the first cyclopentadienyl group probably arise from the electronic structure of nickelocene, and there is general agreement that the highest occupied MOs have mainly 3d character with the unpaired electron occupying the antibonding e_{1g} orbitals. The first step of the reaction of nickelocene with organolithium or –magnesium compounds is the exchange of one cyclopentadienyl group for an alkyl, vinyl or alkynyl group R leading to the formation of unstable 16 VE species [CpNiR]. This electron poor species came out to be a precursor of many novel organonickel complexes and clusters.



1

Transition metal complexes with hemilabile ligands are an actual topic of organometallic chemistry directed to synthesis, catalysis and material science.[9] The chemistry of transition metal cyclopentadienyl complexes bearing a pendant phosphane ligand has been comprehensively reviewed.[10] Many transition metals and a huge variety of ligand systems have been used to form such chelate complexes and to investigate their reactions in stoichiometric as well as in catalytic reactions. Remarkably, although cyclopentadienyl nickel and phosphane nickel complexes are well established, particularly in catalytic reactions,[11-15] no cyclopentadienyl nickel complexes bearing a pendant phosphane ligand have been reported so far. In contrast, for example, cyclopentadienyl cobalt complexes with pendant phosphane ligands have been investigated in depth.[10,16-25] The cyclopentadienyl ligand and phosphane ligands are quite different. Whereas the cyclopentadienyl ligand is a negatively charged π ligand, phosphanes are electroneutral σ donor ligands, of which a large number of substituent patterns have been investigated.[26] A direct bond between the cyclopentadienyl and phosphane part of the ligands may result in resonance interactions between the phosphane lone pair and cyclopentadienyl π system, which could change the genuine properties of the two components resulting in the different kinds of ligand system. Moreover, the formation of chelate complexes using a direct bridge seems to be unlikely due to the steric congestion.[27]

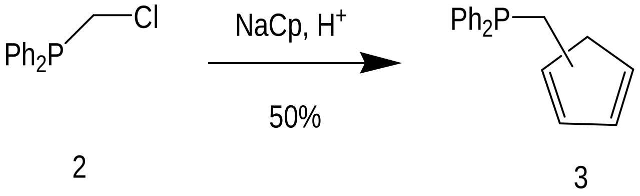
An important class of hemilabile ligands consists of functionalized cyclopentadienyl ligands represented by Cp^L, with ^ denoting the side chain linking the Cp ligand to a functional group L such as NR_2[28] [R = H, Me, ^iPr, $(CH_2)_4$, $(CH_2)_5$], OR[29] [R = Me, $(CH_2)_2$Ind, $(CH_2)_2$Cp, $(CH_2)_2$Ph, $(CH_2CH_2O)_{1-3}$Me, fenchyl, menthyl, isobornyl, Ph, 4-C_6H_4-OMe, ^tBu] PR_2[10] [R = Ph, ^iPr, Me, ^tBu, Cy, p-Tol], SMe,[10] AsR[10] [R = Ph, CH_2CH_2Cp] and C=C.[30] The main role of Cp moiety is to anchor these multidentate ligands to metal centers, while the reversible coordination of L modulates the reactivities of the metal center. In principle a substrate can displace the hemilabile group L from the metal center in order to create a vacant coordination site. On the other hand, since L is never completely separated from the metal, it can recoordinate readily in the absence of substrate to prevent the decomposition of the catalyst (Scheme 1, S = Substrate).



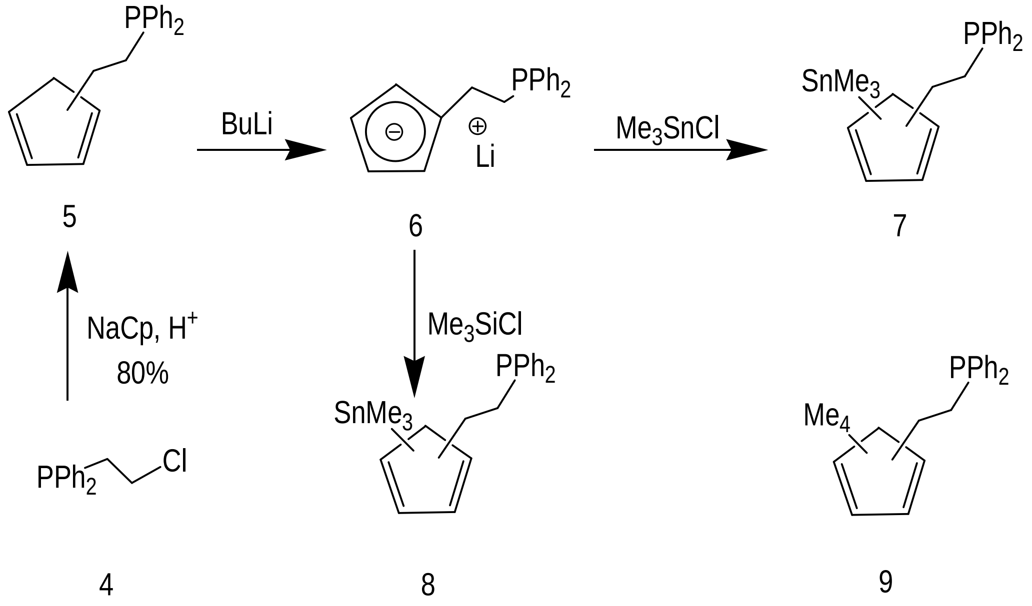
Scheme 1

The potential of this class of compounds in catalysis has spurred research efforts in this area and resulted in the preparation of many transition metal complexes bearing Cp^L type ligands or their indenyl analogues[10]. Examination of the reactivities of some of these has demonstrated the dramatic influence of the hemilabile ligands on fields such as catalyst improvement, stabilization of otherwise unstable species, influence on solubility properties and stereochemical as well as stereoelectronic properties.[26, 30-32]

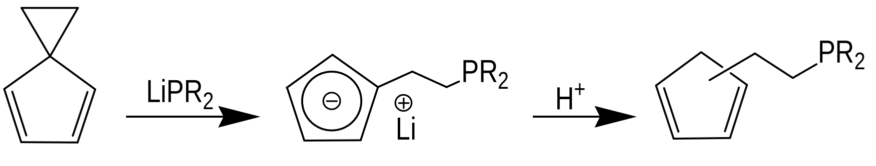
(Phosphanylalkyl)cyclopentadienes and the corresponding cyclopentadienides have been prepared by two main routes, by nucleophilic substitution reactions, in most cases with cyclopentadienyl (Cp) anion as the nucleophile, and by a nucleophilic addition of the respective phosphides to fulvenes or to spiro-anellated cyclopentadienes.[10] Reaction of (chloromethyl)diphenylphosphane (**2**) with sodium cyclopentadienide (NaCp) afforded [(diphenylphosphanyl)methyl]cyclopentadiene (**3**) in 50% yield as a regioisomeric mixture which rapidly polymerizes at room temperature.[33]



Some [(phosphanyl)ethyl]cyclopentadienes were prepared by nucleophilic substitution of the respective 1-chloro-2-phosphanylethanes with cyclopentadienide.[10] Sometimes the cyclopentadienes obtained were immediately deprotonated with base to prevent polymerization, intermolecular Diels-Alder reactions, and formation of mixtures of isomers.[10] The reaction of NaCp with 1-chloro-2-(diphenylphosphanyl)ethane (**4**) gave [(diphenylphosphosphanyl)ethyl]cyclopentadiene (**5**) (80%). Deprotonation with butyllithium afforded cyclopentadienide **6.** Subsequent quench with chlorotrimethylstannane resulted in a mixture of isomeric [(diphenylphosphanyl)ethyl](trimethylstannyl)cyclopentadienes (**7**).[34,35] The corresponding reaction with chlorotrimethylsilane gave cyclopentadienes **8** in 88% yield.[36] In a similar way tetramethyl derivative **9** was prepared from 1-chloro-2-tosylethane by treatment with tetramethylcyclopentadienyl anion followed by lithium diphenylphosphide.[37] However, Jutzi reported the reaction to give almost exclusively isomeric geminal disubstituted cyclopentadiene derivatives when the tetramethylcyclopentadienyl anion was treated with 1-chloro-2-tosylethane.[38]



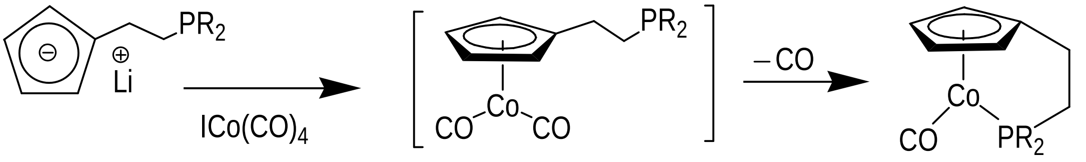
Kauffmann was the first one, who disclosed the cyclopropane ring opening of spiro [2.4]hepta-4,6-diene[39] (**10**) by the attack of a nucleophilic anion.[40] In the course of this ring opening, the nucleophile is attached at the end of ethylene fragment, and the negative charge is implemented in the cyclopentadienyl system with the formation of an aromatic cyclopentadienide. The reaction is rather general and can be used to prepare numerous systems, in which a cyclopentadienide is connected to a nucleophile by an ethylene spacer. Therefore, it is the method of choice to prepare (2-phosphanylethyl)cyclopentadienides by reaction of **10** with the substituted lithium (or potassium[41]) phosphides. Compounds prepared by this route include the cyclopentadienides **6**,[23,24,41] **11**,[42] **12**,[24] **13**,[24,43] and **14**[44] as well as the isomeric [2-(diphenylphosphanyl)ethyl]cyclopentadienes **5**[33,34,45] and di-(*tert*-butyl) derivative **15**[43] (one isomer). Lithium di-*tert*-butylphosphide[40] has been proved one successful tool for nucleophilic ring opening of spiro [2.4]hepta-4,6-diene (**10**).



6 : R = Ph (63%)
11: R = Me (82%)
12: R = ^{i}Pr (83%)
13: R = ^{t}Bu (92%)
14: R = Cy

5 : R = Ph
15 : R = ^{t}Bu

(Phosphanylalkyl)cyclopentadienyl complexes of group 9 metals (cobalt[16-25], rhodium[46] and iridium[46]) are known. In some cases, not only the synthesis and structures of some complexes have been described but a number of reactions have also been investigated. Carbonylcobalt complexes **19-21** were obtained by treatment of anionic ligands **6**, **12**, and **13** respectively, with $ICo(CO)_4$. The reactions proceed via the unchelated intermediates **16**, **17** and **18**. The complexes with *tert*-butyl substituent at the P atom gave the highest yields and were those which gave the best crystals.[23,24]

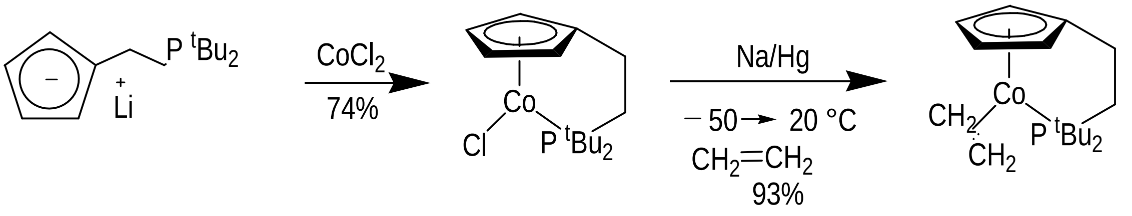


6 : R = Ph
12: R = ^{i}Pr
13: R = ^{t}Bu

16: R = Ph
17: R = ^{i}Pr
18: R = ^{t}Bu

19: R = Ph (24%)
20: R = ^{i}Pr (43%)
21: R = ^{t}Bu (56%)

The corresponding ethene complex **23** was prepared via paramagnetic chloride **22**. This is accessible in 74% yield in analogy to similar chemistry performed by Kölle[47-49] by treatment of anion **13** with $CoCl_2$. **22** was reduced with sodium amalgam at –55 °C in the presence of ethene bubbling through the reaction flask to give **23** in 93% yield.[22,25]



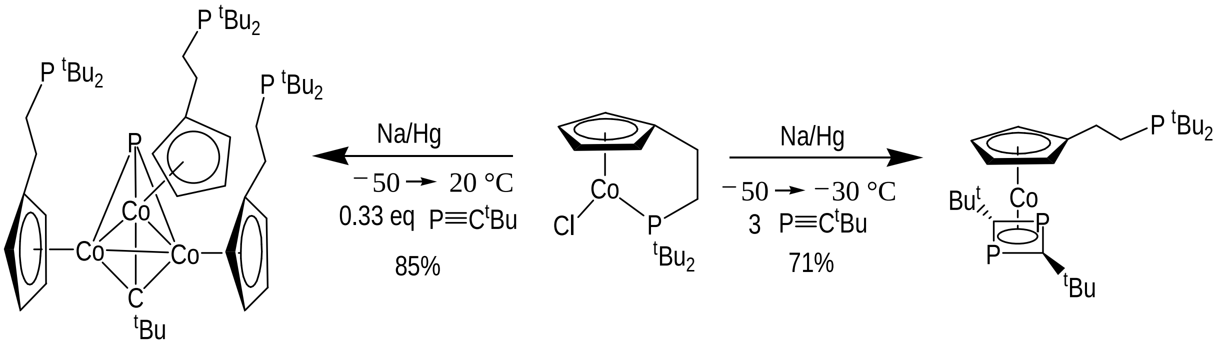
13

22

23

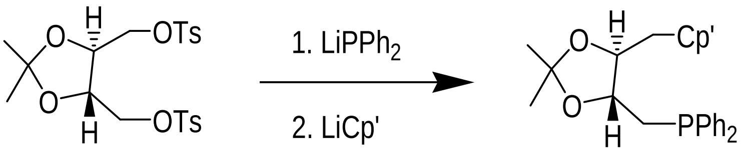
It was found that complexes in which the cyclopentadienyl and the phosphane parts of the ligand system are connected by an ethylene bridge are stable and can be prepared without significant side reactions in high yields.[10] The complex **21** was subjected to a DSC analysis. This showed that **21** melts at 119 °C and decomposes at 175 °C. This means that the compound is quite stable thermally, and this is completely in accord with the result of treatments of **21** with other ligands.[10]

Phosphaalkynes are known to react with **21** and **22** under the similar reaction conditions applied for alkynes.[50-54] Treatment of **22** in the presence of sodium amalgam at low temperature (−50 → −30 °C) with a 3-fold molar excess of *tert*-butylphosphaethyne yields unchelated diphosphate complex **24**, which is in complete accord with the reaction of other cyclopentadienylcobalt complexes with *tert*-butylphosphaethyne.[55-56] However when *tert*-butylphosphaethyne was treated with a 3-fold molar excess of **22** in the presence of sodium amalgam at the temperature (−50 → +20 °C), the μ_3-carbyne-μ_3-phosphidotricobalt cluster **25** is formed in 85% yield.[21]



25 22 24

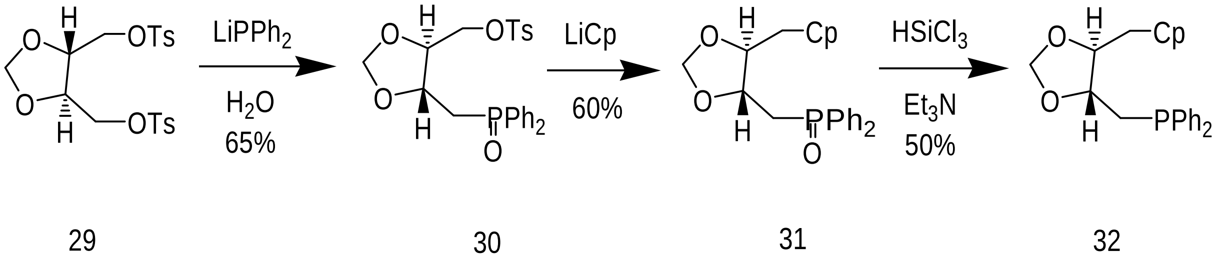
The first enantiomerically pure chiral (phosphanylalkyl)cyclopentadienyl ligands were published by Tani.[57,58] Enantiomerically pure ditosylate **26** derived from L-threitol, was treated subsequently with lithium diphenylphosphide and with cyclopentadienyllithium or indenyllithium to give ligands **27** and **28** respectively.



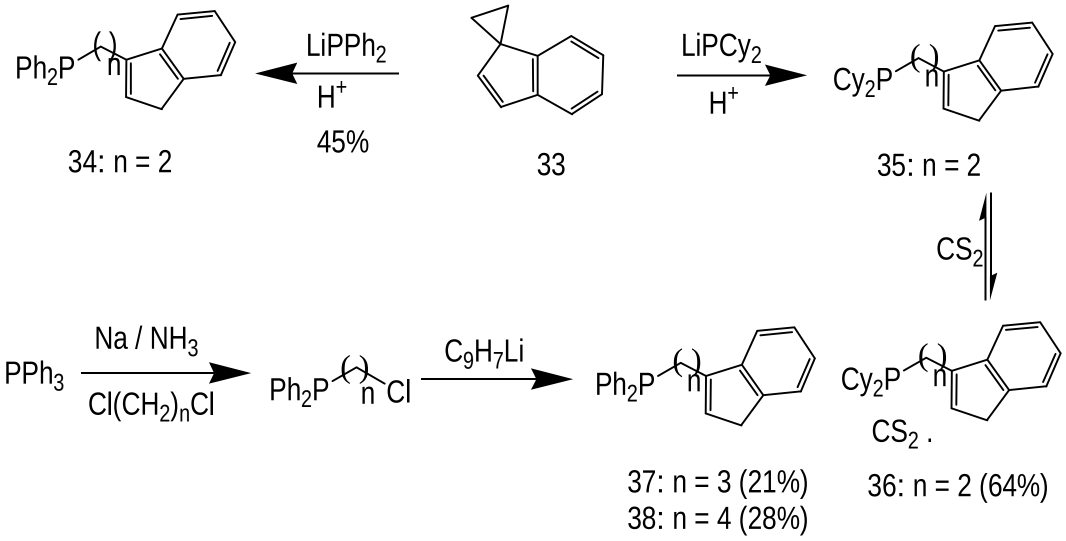
26

27: Cp' = Cyclopentadienyl (27%)
28: Cp' = 1-Indenyl (31%)

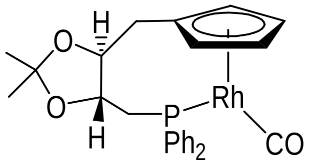
In addition, enantiomerically pure ditosylate **29** was treated with lithium diphenylphosphide to obtain phosphorane **30** (65%). The subsequent substitution of the second tosyl group by lithium cyclopentadienide gave **31** (60%), which was reduced to the desired ligand **32** with trichlorosilane in 50% yield.



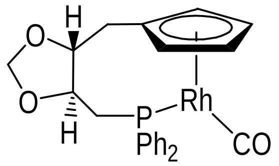
Tani et al.[57-59] prepared several types of [Cp′-P]H ligands starting from [4,5]-Benzospiro[2.4]hepta-4,6-diene (**33**).[60] Treatment with $LiPPh_2$ or with $LiPCy_2$ gave ligands **34** (45%) and **35**, the latter one being stored as its CS_2 adduct **36** (64%), which is air stable. Homologues **37** and **38** were obtained by nucleophilic substitution of 1-chloro-3-(diphosphanyl)propane or 1-chloro-4-(diphenylphosphanyl)butane with indenyllithium in 21% and 28% yield.[61]



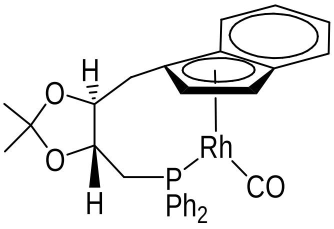
Tani[57,58] treated the optically active [Cp′-P]H ligands **27**, **28** and **32**, in which stereogenic centers are in the spacer, with $[Rh(CO)_2Cl]_2$ to obtain chiral rhodium complexes **39**, **40** and **41**, **42** (20–70%), **41**/**42** forming a 69:31 mixture of two unseparated diastereomers.



39 (22%)



40 (<20%)



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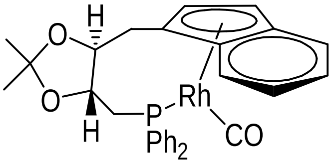
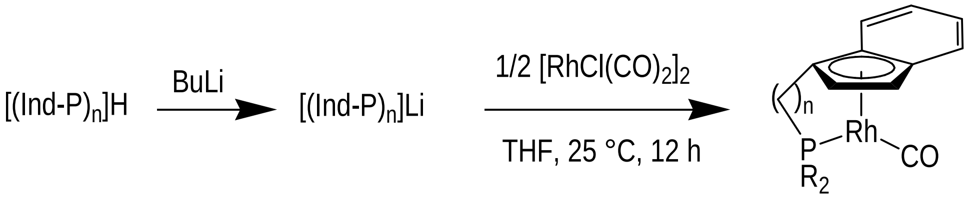


42

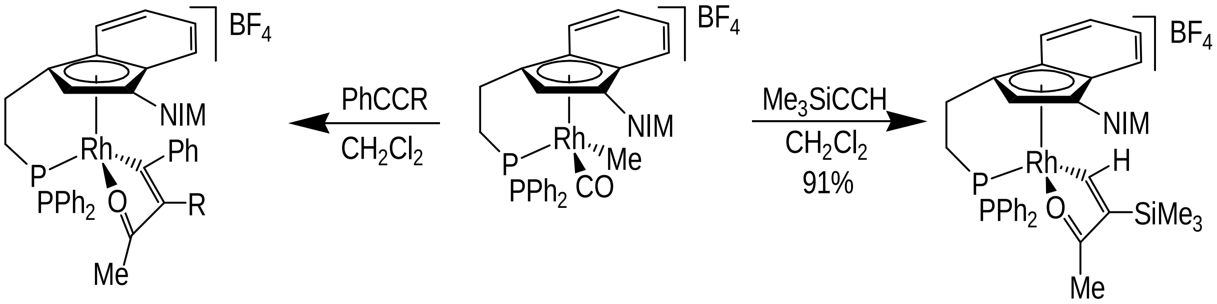
The achiral ligands $[(\text{Ind-P})_n]$H, **34**, **35**, **37** and **38** are those in which indenyl-based planer chirality was induced by Tani[57,61] on coordination to a metal center. The mononuclear Rh(I) complex **43** was obtained in 80% isolated yield as an air stable yellow powder. The complexes **44**, **45**, and **46** were also prepared by similar procedures (**44**, 50%; **45**, 71%; **46**, 64%).



43: R = Ph, n = 2; 44: R = Ph, n = 3
45: R = Ph, n = 4; 46: R = Cy, n = 2

A three-legged piano-stool complex $\text{Cp}'\text{ML}_1\text{L}_2\text{L}_3$ (Cp′ = cyclopentadienyl derivatives, M = metal, L_n = ligand) has a stereogenic center at the metal, if all ligands (L_1-L_3) are different. So far several examples of asymmetric reactions catalyzed by such optically active $\text{Cp}'\text{ML}_1\text{L}_2\text{L}_3$-type complexes have been reported.[62] However, it is too much to say that their progress reaches the level of asymmetric reactions accomplished by organometallic catalysts having chiral ligands.[63] One reason is that easy and convenient methods for the preparation of the optically active complexes that are configurationally stable at the chiral metal center have not been established.[64-66]

A Cp′^P ligand having an indenyl group as the cyclopentadienyl derivative part, which is called the Ind^P ligand generates planer chirality on the indenyl ring upon coordination to the metal. It was demonstrated that the planer chirality was very effective for controlling the central chirality arising at the metal.[59,67] Later it was also reported by Tani[68,69] that the stereogenic center at the metal controlled by the Ind^P ligand was very stable through the stereospecific addition of alkynes to Rh(III) methyl complex **47** and the stereospecific migration of a methyl group between cationic Rh (III) methyl complex **47** and Rh(III) complexes **48**-**50**.

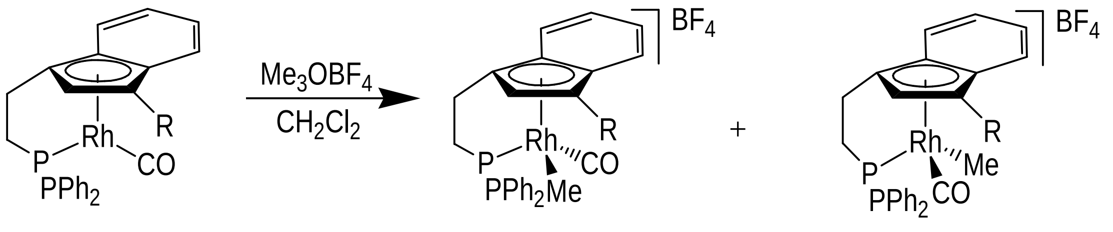


48: R = Me (79%)
49: R = H (92%)

47: NIM = neoisomenthyl

50

Tani[70] reported another method for the generation of metal centered chirality, in which diastereoselective addition of the Meerwein reagent (Me_3OBF_4) to rhodium carbonyl complexes **51a-c** having the Ind^P ligand provides cationic Rh(III) methyl complexes **52a-c** having a stereogenic center at the metal.



a: R = H; b: R = Et;
c; R = Cy (C_6H_{11})

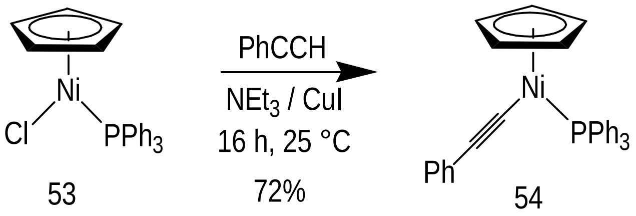
(R^*_{Pl}, R^*_{Rh})

(R^*_{Pl}, S^*_{Rh})

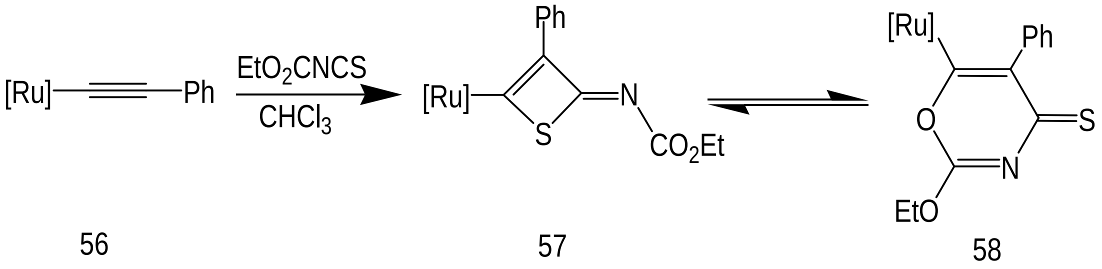
51a-c

52a-c

The synthesis and reactivity of metal acetylide complexes have been the focus of several recent investigations due to their application in organometallic[71-74] and material[75-78] chemistry. Yamazaki et al.[79,80] reported the synthesis of $Ni(C_2Ph)(PPh_3)(\eta\text{-}C_5H_5)$ **54** (60%) by treatment of $NiCl(PPh_3)(\eta\text{-}C_5H_5)$ **53** with PhC_2MgBr. Bruce et al.[81] developed routes for the syntheses of several transition metal σ-acetylide complexes in excellent yields in the presence of organic amines with copper(I) halide as a catalyst.

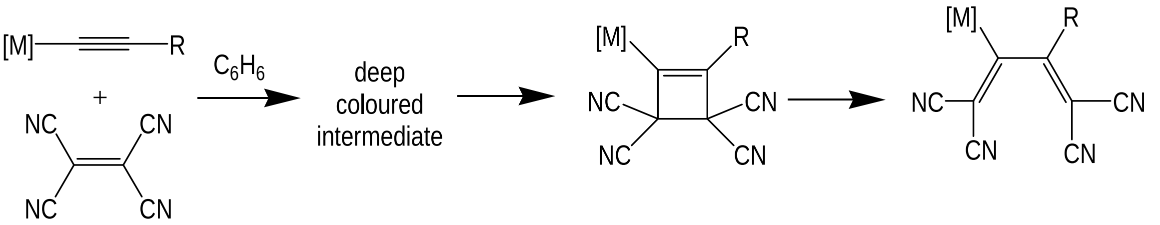


Cycloaddition reactions of metal σ-acetylides with isocyanates take place at several Ni(0) complexes.[82] The other common reaction observed for the σ-acetylides is the [2 + 2] cycloaddition of the triple bond with unsaturated organic substrates.[83] Cycloadditions of organic substrates such as CS_2,[84-86] $(CN)_2C=C(CF_3)_2$, $(CN)_2C=C(CN)_2$,[87-89] and $Ph_2C=C=O$[90] to the σ-acetylide ligand in various metal complexes have been reported. The cycloaddition reaction of an isothiocyanate molecule with the ruthenium σ-acetylide formed an unstable four-membered-ring 2-iminothiete complex. In the presence of an excess of isothiocyanates, expansion of the 2-iminothiete rings by coupling of a second isothiocyanate molecule generated complexes with a six membered–ring 2-imino-1,3-thiazine-4-thione ligand was observed. Reaction of ruthenium σ-acetylide complex **56** with EtO_2CNCS, a more reactive isothiocyanate, were reported.[91] As expected in the initial stage, cycloaddition of C=S bond of EtO_2CNCS to the σ-acetylide **56** afforded the anticipated complex **57** with the four-membered thiete ring which was isomerized to a six membered oxazine ring complex **58** with a thione group.



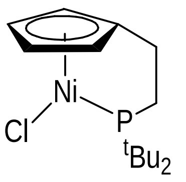
[Ru] = $(C_5H_5)LL'Ru$
LL' = dppe

The first report of a cycloaddition of tetracyanoethylene, $C_2(CN)_4$ to σ-acetylide complexes of iron appeared in 1979[87] and was followed by an initial communication concerning a ruthenium system.[92] These reactions proceed via deeply coloured intermediates which lighten to give σ-cyclobutenyl complexes **60a-f**. These may not be isolable, as the organic ligand more or less rapidly undergoes a ring opening reaction to give the isomeric σ-butadienyl complexes **61a-f**.[93] Cyclobutenyl complexes are believed to be implicated, and have been observed for the analogous reactions of manganese and iron complexes. However they were not seen for the nickel reaction.[94]



59	[M]	60	[M]	61	[M]
a	Mn $(CO)_3$ (dppe)	a	Mn $(CO)_3$ (dppe)	a	Mn $(CO)_3$ (dppe)
b	$Fe(CO)_2$ (C_5H_5)	b	$Fe(CO)_2$ (C_5H_5)	b	$Fe(CO)_2$ (C_5H_5)
c	$Ni(PPh_3)(C_5H_5)$	c	$Ni(PPh_3)(C_5H_5)$	c	$Ni(PPh_3)(C_5H_5)$
d	$Ru(CNBu^t)(PPh_3)(C_5H_5)$	d	$Ru(CNBu^t)(PPh_3)(C_5H_5)$	d	$Ru(CNBu^t)(PPh_3)(C_5H_5)$
e	$Ru(dppe)(C_5H_5)$	e	$Ru(dppe)(C_5H_5)$	e	$Ru(dppe)(C_5H_5)$
f	$W(CO)_3(C_5H_5)$	f	$W(CO)_3(C_5H_5)$	f	$W(CO)_3(C_5H_5)$

The chemistry of cyclopentadienyl complexes of group 9 metals (cobalt[10,16-25], rhodium[10,46] and iridium[10,46]) with pendant phosphane ligands has been deeply investigated. However cyclopentadienyl nickel and phosphane nickel complexes are also well established, particularly in catalytic reactions.[11-15] In the chemistry of cyclopentadienylnickel complexes[95,96] the formation of nickel clusters is frequently observed. However, the chemistry of cyclopentadienyl and indenyl complexes of nickel bearing a pendant phosphane ligand has so far not been investigated and thus needs to be explored. The *tert*-butyl substituent at the P atom is the best selection of ligand which has been proven successful to obtain cobalt complexes[10,16-25] in excellent yield in stoichiometric as well as catalytic reactions. In the course of these studies aimed at extension of our knowledge in the uninvestigated field, we have developed efficient and reproducible syntheses of nickel chelate complexes bearing pendant phosphane ligands. The new methodologies have successfully been applied for the synthesis of [(di-*tert*-butylphosphanylethyl)cyclopentadienyl]chloronickel(II) (**62**) and [1-(di-*tert*-butylphosphanylethyl)-indenyl]chloronickel(II) (**63**) as the principal complexes of this research, from which a number of stoichiometric and catalytic reactions have been performed. The striking point of complex **63** as compared to **62** is its planer chirality.



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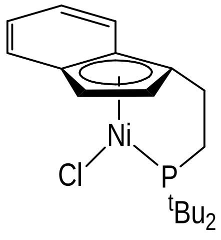


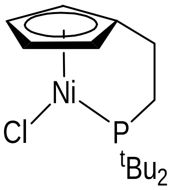
63

2 Results and Discussion

2.1 Synthesis of [(Di-*tert*-butylphosphanylethyl)cyclopentadienyl]chloronickel(II) (62) and its Triflate Derivative 68

Following the extensive research into the chemistry of cyclopentadienyl complexes of many transition metals (e.g. cobalt[10,16-25], rhodium[10,46] and iridium[10,46]), in which the cyclopentadienyl and the phosphane parts are separated from each other by an alkyl chain, the interest has now turned to chelate nickel complexes like **62** bearing a pendant phosphane ligand. Cyclopentadienyl nickel and phosphane nickel complexes are also well established, particularly in catalytic reactions,[11-15] and in many cases, formation of nickel clusters[95,96] has been observed. However, cyclopentadienyl complexes of nickel bearing a pendant phosphane ligand have not been reported so far. Here another significant point to be explored is the chelate formation by the coordination of the phosphanylalkyl chain, thereby avoiding possibly the formation of clusters and instead open alternative reaction paths. The possibility of chelate formation is also a reason for the popularity of ligands with other functional groups in the side chain, for example alkenylcyclopentadienyl[97-101] or aminoalky derivatives.[31,102-104]

Results obtained by the choice of *tert*-butyl substituents at the phosphorous atom as a pendent phosphane ligand, which has been proven successful to obtain cobalt complexes[10,16-25] in excellent yield, encouraged us firstly, to prepare and secondaly, to explore the chemistry of [(di-*tert*-butylphosphanylethyl)cyclopentadienyl]chloronickel(II) (**62**). In a similar way, the synthesis of [1-(di-*tert*-butylphosphanylethyl)indenyl]chloronickel(II) (**63**), the indenyl analogue of nickel chelate **62** showing the planar chirality, has been attempted which would be discussed in the preceding section in detail. The present research is mainly based on the investigation of nickel chelate complexes **62** and **63**.



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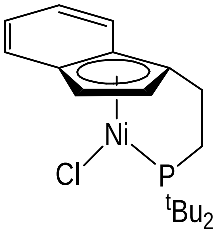
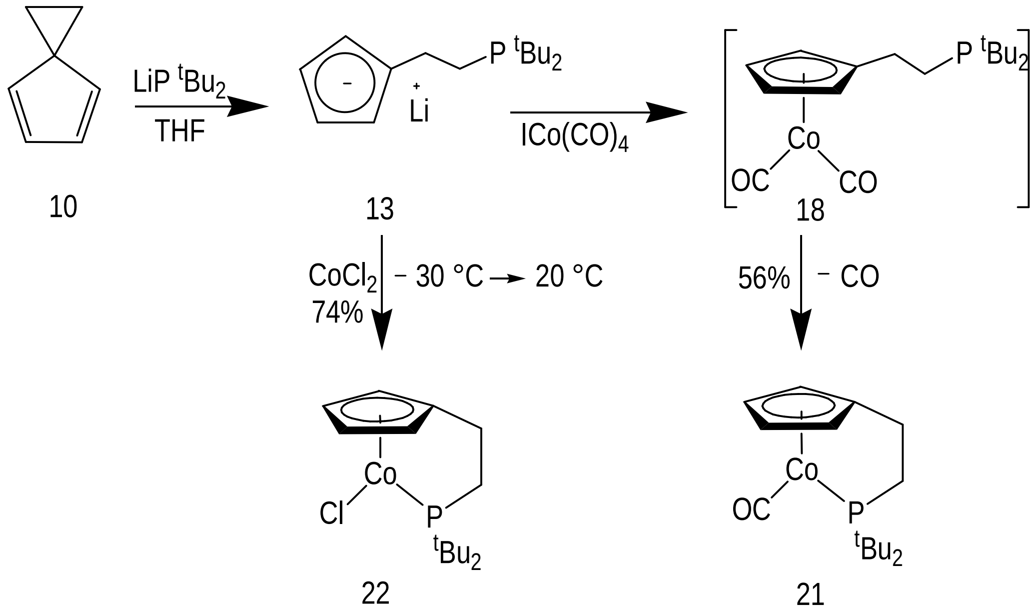


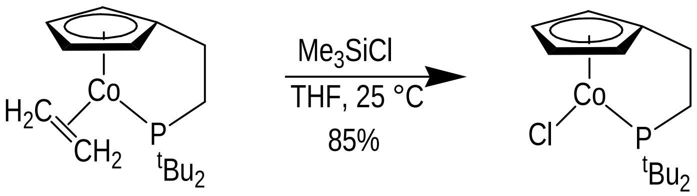
63

Chelate cobalt complexes like **21** are formed by treatment of the anionic (phosphanylalky)cyclopentadienyl ligands with $ICo(CO)_4$.[23,24] The anionic ligand **13** is easily accessible by nucleophilic ring opening of spiro[2.4]hepta-4,6-diene[10] with lithium di-*tert*-butylphosphide.[40] By application of the method introduced by Kölle[47] for the pentamethylcyclopentadienyl ligand, treatment of the resulting anion **13**[24] with anhydrous cobalt(II) chloride at −30 °C and subsequent warming mixture to 20 °C, paramagnetic chloride **22** was obtained in 74% yield as black-purple plates.[22]



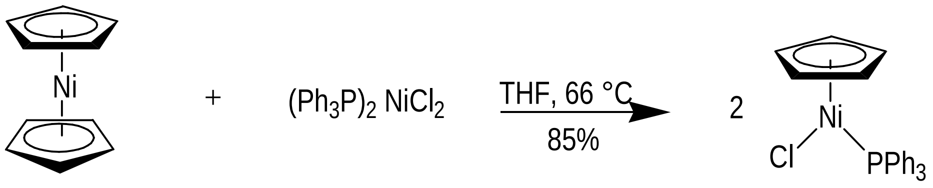
Chloride **22** is well soluble in THF but poorly in all other common solvents. In analogy to similar chemistry by Kölle[47-49] and Okuda,[97,99,100] for some time a dimeric constitution was assumed for **22.**[25] However the ESR spectrum did not only show the signal splitting caused by the cobalt I = 7/2 nucleus but also that caused by the phosphorous I = 1/2 indicating coordination of the phosphane arm, which is in accord with **22**[22] but not with the originally assumed dimeric constitution. The ^{31}P NMR analysis of (phosphanylalkyl)cyclopentadienyl cobalt complexes **19**, **20**, **21** and **23** (δ = 85.2, 108.1, 128.9 and 92.6 ppm) also indicates that phosphorous arm is coordinated at the metal center.[10]

When **23** was treated with chlorotrimethylsilane at 25 °C in THF, a 85% yield of the paramagnetic 17 electron chlorocobalt(II) chelate **22** was obtained. After crystallization from diethyl ether, a crystal structure analysis of **22** was performed, this finally confirmed the constitution of **22.**[105]



23 22

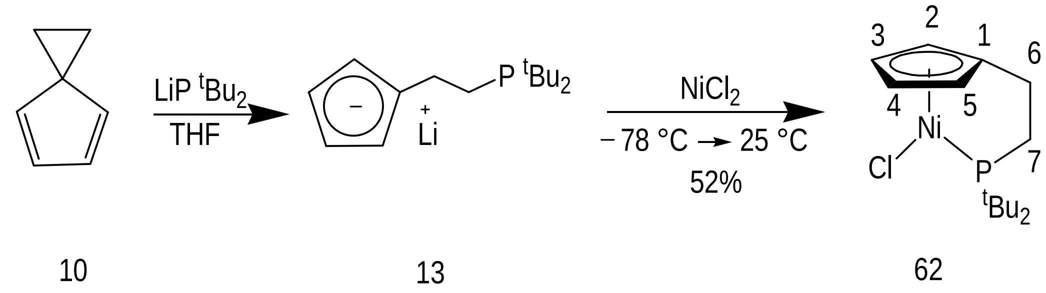
A wide variety of π-cyclopentadienyl complexes of nickel have been reported along with detailed studies of their properties and reactions. These compounds are of the type L(C_5H_5)NiX, where L is a neutral ligand, such as tertiary phosphine, and X can range from halogen to various organic substituents.[106,107] Nearly all the cyclopentadienyl nickel complexes were prepared from nicklocene. Cross et al. reported one of the best methods for the synthesis of cyclopentadienyl nickel complexes, being the disproportionation reaction with a phosphane complex.[108] The X-ray structure analysis of **64** was reported, which is a good example of a two legged piano stool complex, of which many representatives exist.[109]



1 64

2.1.1 [(Di-*tert*-butylphosphanylethyl)cyclopentadienyl]chloronickel(II) (62)

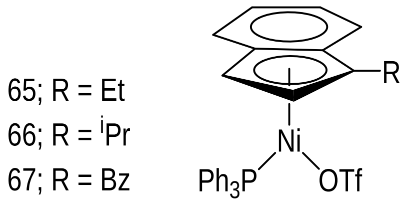
In analogy to the respective cobalt chemistry,[10,16-25] for the preparation of nickel chelate complex **62** the anionic ligand **13** was easily obtained by nucleophilic ring opening of spiro[2.4]hepta-4,6-diene[10] with lithium di-*tert*-butylphosphide.[40] The light brown THF solution of the anionic ligand **13** was treated with anhydrous nickel chloride at –78 °C. The reaction mixture was warmed slowly to 25 °C and stirred for 12 h at the same temperature. The colour of the reaction mixture had changed from brown to purple red. The title complex **62** was crystallized at –20 °C from diethyl ether to obtain in 52% yield as a dark purple red solid.



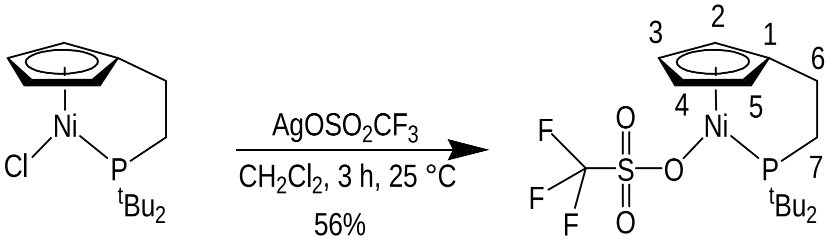
The chelate complex **62** bearing the di-*tert*-butylphosphanylethyl chain as a pendent phosphane ligand is the first nickel chelate complex of its own type. The chloronickel chelate complex **62** is well soluble in THF, ethylacetate, acetone, chloroform and dichloromethane but only slightly soluble in diethyl ether, hexane and toluene. The chelate nickel complex **62** obeys the 18 electron rule and is stable, but if exposed to air for longer periods of time, decomposition has been observed. Complex **62** was fully characterized by IR, ^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectroscopy and EIMS spectrometry, including elemental analysis. The ^{1}H NMR spectrum exhibits one triplet at δ = 1.46 ppm for two methylene protons (6-H). While other two methylene protons (7-H) of the di-*tert*-butylphosphanylethyl part of the ligand show absorption at δ = 2.18 ppm. The spectrum shows one doublet at δ = 1.54 ppm which corresponds to two *tert*-butyl groups. An AA′BB′ spin system was observed for two sets of signals at δ = 5.43 and δ = 5.87 ppm corresponding to H-2(5) and H-3(4) of the Cp ring. In the ^{13}C NMR spectrum the carbon atom C-6 resonates at δ = 25.5 ppm and absorption found at δ = 34.5 ppm is assigned to the carbon atom C-7 of the ethylene bridge. At δ = 30.3 ppm absorption of methyl groups was observed. The quaternary carbon atoms next to phosphorus resonate at δ = 34.8 ppm. The signals resonating at δ = 97.5 and δ = 98.5 ppm correspond to the C-2(5) and C-3(4), respectively. The quaternary carbon atom C-1 of the Cp ring absorbs at δ = 96.7 ppm. The most noticeable feature in the ^{31}P NMR spectrum of the complex **62** is the singlet at δ = 92.9 ppm indicating a coordinated phosphane tether with nickel. The LREIMS mass spectrum exhibits the molecular ion peak [M^{+}] at *m/z* = 330 (76%), which confirms that the **62** is not a dimeric complex. A fragment signal [M^{+} – Cl] was observed at *m/z* = 295 (3%) obtaind by the loss of Cl ligand. All other signals observed in the mass spectrum are in complete accord to the fragmentation pattern of the desired constitution of **62**. Correct elemental analysis data was also obtained. On the basis of these measurements, the assigned constitution of complex **62** is confirmed.

2.1.2 Synthesis of [(Di-*tert*-butylphosphanylethyl)cyclopentadienyl]nickel(II) Triflate (68)

Complexes bearing nonchelating or weakly nucleophilic ligands such as triflate have been investigated as precursors to highly reactive cationic intermediates.[110-112] Zargarian et al.[113] reported the preparation and characterization of the triflate derivatives **65-67** and reported the displacement of the OTf moiety to get corresponding cationic complexes.



Such an easy displacement of triflate moiety to get the cationic complexes encouraged us to prepare [(di-*tert*-butylphosphanylethyl)cyclopentadienyl]nickel(II) triflate (**68**). Complex **62** was treated in dichloromethane with an excess of silver triflate. The dark purple solution had changed to reddish brown. After stirring the reaction mixture at 25 °C for 3 h, the unconsumed silver triflate, along with the silver chloride as the side product, was filtered out. The product was crystallized from a mixture of dichloromethane and hexane at –20 °C to get the title complex **68** in 56% yield as a reddish brown solid.



62

68

The desired complex **68** is soluble only in polar solvents indicating the more ionic nature of the complex. It was observed that the proposed triflate complex **68** is not sufficiently stable as complex **62**. In solution, immediate decomposition of **68** was observed. However, in solid phase after 1 h decomposition of the complex starts. The ^1H NMR, ^{13}C NMR and ^{31}P NMR spectra could not be obtained successfully due to solution phase instability of complex **68**. The triflate complex **68** was characterized by IR spectroscopy and EIMS and HRMS spectrometry. The IR spectrum of nickel chelate complex **68** shows characteristic absorption bands at 1396, 1373, and 1160 cm^{-1} which correspond to SO_2—O group. The EIMS mass spectrum of triflate chelate complex **68** shows molecular ion peak [M^+] at *m/z* = 444 (20%). The fragment peak [$M^+ - CF_3SO_3$] at *m/z* = 295 (9%) was obtained by the cleavage of triflate unit from nickel. All the fragment peaks observed in the spectrum are in complete accord to the fragmentation pattern. The HRMS mass spectrum of **68** was also measured which is in close agreement to the desired molecular formula. Finally the assigned constitution of **68** was confirmed by an X-ray structure determination. Recrystallization of **68** from a mixture of dichloromethane and hexane at –20°C gave reddish brown crystals suitable for an X-ray structure analysis indicating that complex **68** crystallizes in the monoclinic crystal system with space group *P 21/c*. Some selected bond lengths and bond angles are listed in table **1** and **2**. The solid state structure analysis data of triflate complex **68** represents the first example of a nickel chelate complex bearing a phosphanylalkyl group as a pendent ligand. The ORTEP diagram of **68** is depicted in figure 1.

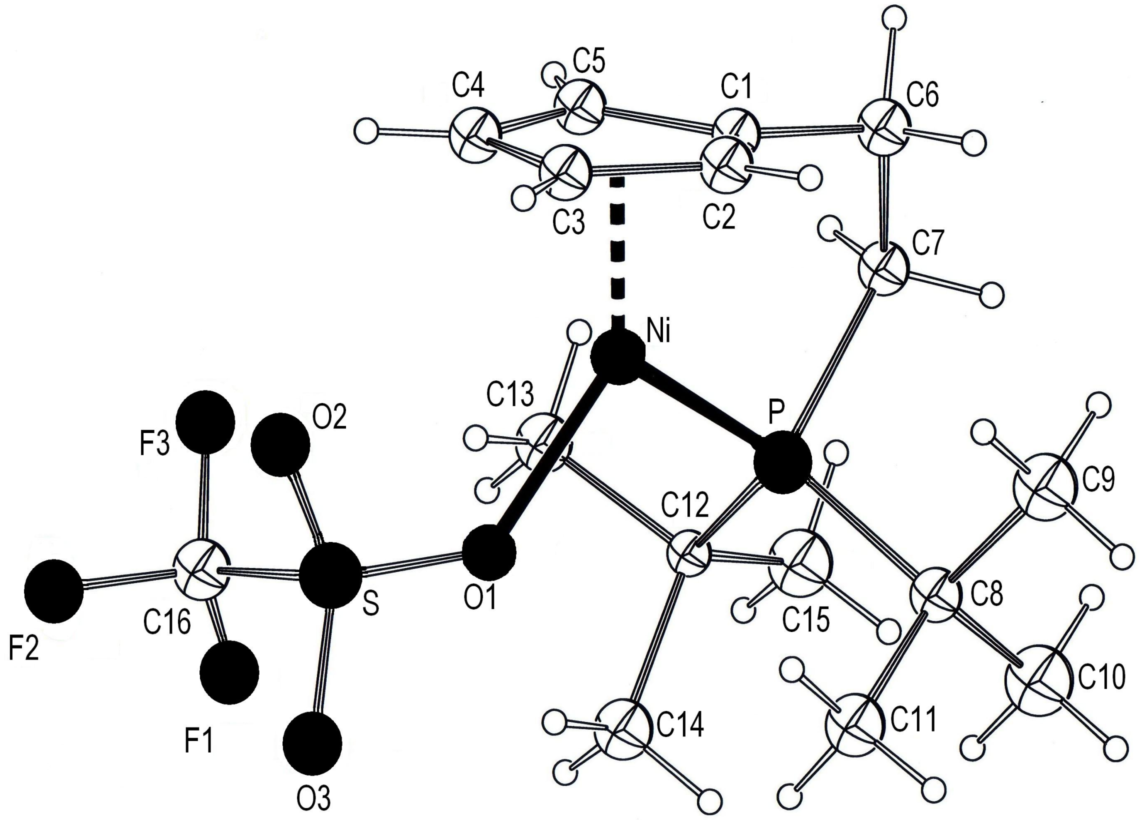


Fig. 1: Structure of **68** in the crystal.

Table: 1. Selected bond lengths for **68**.

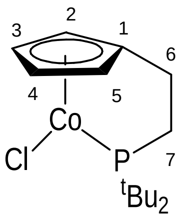
Bond	**Bond length in [Å]**	**Bond**	**Bond length in [Å]**
Ni-O1	1.951(9)	C2-C3	1.39(2)
Ni-C1	2.028(13)	C3-C4	1.42(2)
Ni-C5	2.117(14)	C4-C5	1.36(2)
Ni-C2	2.13(2)	C1-C2	1.42(2)
Ni-C3	2.13(2)	C1-C5	1.42(2)
Ni-C4	2.158(14)	Ni-P	2.181(5)

Table**:** 2. Selected bond angles for **68**.

Bond angle	**[°]**	**Bond angle**	**[°]**
O1-Ni-C1	171.8(5)	C6-C1-Ni	119.8(9)
C1-Ni-C2	39.9(5)	C1-Ni-P	86.9(5)
C5-Ni-C2	65.3(6)	C7-P-Ni	102.9(5)
C1-C6-C7	110.7(12)	O1-Ni-P	101.3(3)

The over all geometry of the structure of complex **68** suffers somewhat from a dynamic disorder of the (di-*tert*-butylphosphanyl)ethyl moiety, as indicated by the large anistropic displacement parameters. This has also been observed for some cobalt complexes[105] and is due to the staggered conformation of the ethylene bridge. All the bond lengths and bond angles are within the expected range. The Ni─O1 bond length [1.951(9) Å] shows that the triflate moiety is strongly bonded to the nickel atom. The Ni─P bond length [2.181(5) Å] shows the strong interaction of the hindered di-tert-butylphosphane ligand to the nickel center. The Ni─C1 bond length [2.028(13) Å] is shorter and Ni─C4 bond length [2.158(14) Å] is longer than that of the other Cp carbon atoms to the nickel indicating that the coordination of the Cp ring is distinctly off-center with the Ni closest to C1 and far from C4. The bond angles O1─Ni─C1 [171.8(5)°], O1─Ni─P [101.3(3)°] and C1─Ni─P [86.9(5)°] indicate that phosphane region is sterically highly shielded and that the triflate ligand is repelled far from the phosphane part.

After getting the crystal structure analysis data of complex **68**, the assigned constitution of complex **68** and its parent chelate complex **62** are confirmed. The comparative study of the crystal structure of nickel chelate **68** with the nickel complexes **64**[109] and **66**[113] and, those of the cobalt chelate complexes particularly complex **22**[105] having phosphane side arm connected to cyclopentadienyl through the ethylene bridge like complex **68** gave some interesting information about the structure of complex **68**. Some comparative bond lengths are listed in table 3.



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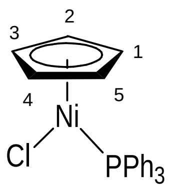

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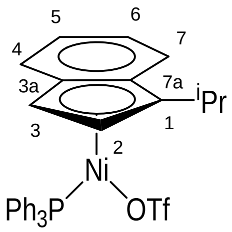

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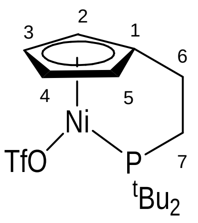


68

Table**:** 3. Selected bond lengths in Å for **22**, **64**, **66** and **68**.

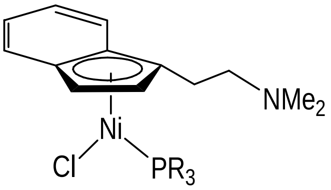
Bond	**22**[105]	**64**[109]	**66**[113]	**68**
Ni(Co)-C1	2.020(6)	2.103(4)	2.131(2)	2.028(13)
Ni(Co)-C2	2.072(6)	2.154(4)	2.064(2)	2.13(10)
Ni(Co)-C3	2.109(5)	2.096(4)	2.024(2)	2.13(11)
Ni(Co)-C4,C3a	2.103(6)	2.147(4)	2.311(2)	2.158(14)
Ni(Co)-C5,C7a	2.097(6)	2.081(4)	2.335(2)	2.117(14)
Ni(Co)-O1,Cl	2.195(2)	2.176(1)	1.9404(16)	1.951(9)
Ni(Co)-P	2.204(2)	2.160(1)	2.1973(6)	2.181(5)

All the bond distances of the complexes **68** fall within the range of expected values. However, there is bond length difference as shown in the table **3**. The Ni─C1 bond length [2.028(13) Å] in **68** is shorter than the Ni─C2-5 bond lengths. Obviously the Ni atom is closer to C1 than the other Cp carbon atoms and Cp ring coordinated to the nickel is significantly off-center in complex **68**. The same bond length differences from metal to Cp carbon atoms were found in the chelate cobalt complex **22**[105] bearing the di-*tert*-butylphosphanylethyl linker. The Ni─O1 bond [1.951(9) Å] in **68** is longer than the Ni─O1 bond [1.9404(16) Å] in **66**[113] indicating that triflate unit faces steric hindrance to approach to Ni atom due to the di-

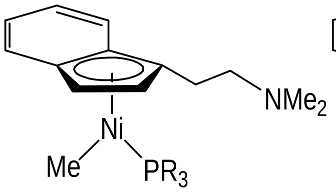
tert-butyl groups on phosphorus atom. This steric bulk also affects significantly as the Ni─P bond length [2.181(5) Å] in **68** is larger than Ni─P [2.160(1) Å] in **64**.[109] The O─Ni─P bond angle [101.3(3)°] in **68** is larger than the O─Ni─P bond [96.41(6)°] in **66**[113] indicating that due to the chelate formation by the ethylene bridge and steric hindrance of *tert*-butyl groups, triflate is pushed away from the phosphorus atom.

2.2 Synthesis of [(Di-*tert*-butylphosphanylethyl)cyclopentadienyl]alkyl- and -alkynyl nickel(II)

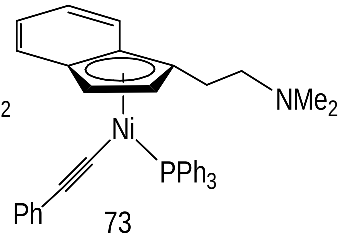
Zargarian et al.[114] reported the synthesis of indenyl chloro complexes **69-71**, the neutral complexes **72-74** and cationic species **75-77** which have been fully characterized, including solid state structures determinations by X-ray crystallography for complexes **70**, **72-74** and **77**.[114] The cationic complexes **70**, **72-74** and **77** are single–component catalysts for the polymerization of styrene, giving polystyrene, and hydrosilylation catalysts of styrene and 1-hexene with $PhSiH_3$ and Ph_2SiH_2. The nature of the phosphane ligand has an important influence on the binding of the tether to the Ni centre and the catalytic reactivities, the PMe_3 analogue **76** being the most active catalyst.



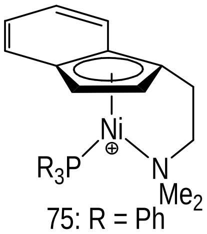
69: R = Ph
70: R = Me
71: R = Cy



72: R = Ph
74: R = Me

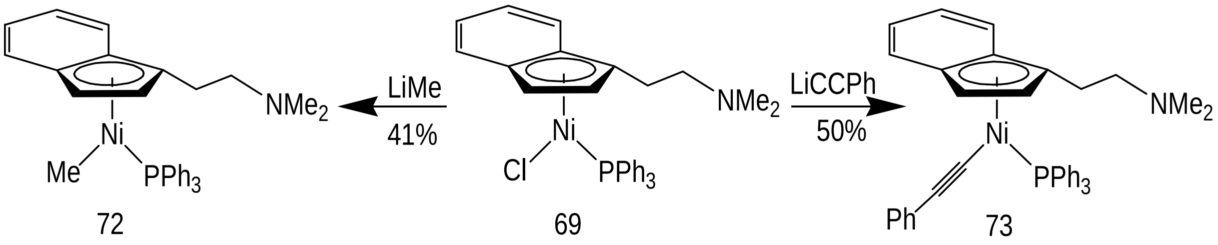


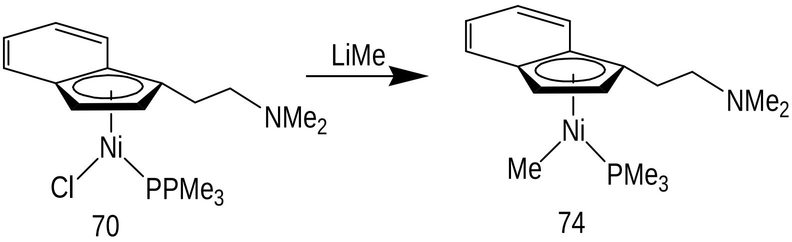
73



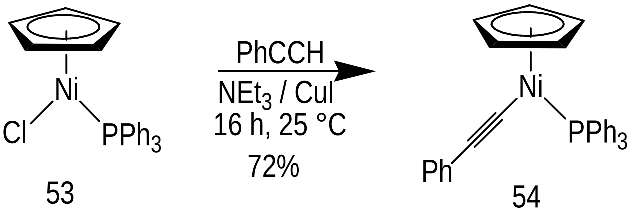
75: R = Ph
76: R = Me
77: R = Cy

Inspection of the structural data showed that replacing the Cl atom by strongly donating ligands such as CCPh and Me reinforces the Ni─P and Ni─Ind interactions. The chloro complexes **69-71** have been used to prepare the new nickel complexes **72-74**. The Ni─Me derivatives **72** and **74** were obtained by reacting MeLi with **69** or **70**, respectively, while the Ni─CCPh derivative **73** was prepared in a similar manner by the metathetic reaction between **69** and LiCCPh.[114]



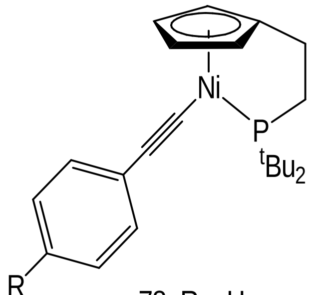


Bruce et al.[81] developed routes for the syntheses of several transition metal σ-acetylide complexes in excellent yields in the presence of organic amines with copper(I) halide as a catalyst. He reported 72% yield of the alkynyl complex **54** starting from $NiCl(PPh_3)(\eta\text{-}C_5H_5)$ **53** and phenyl acetylene in the presence of triethyl amine with CuI as a catalyst. Whittall et al.[115] reported the X-ray structure analysis data of **54**, which crystallizes as a dark green blocks in a triclinic crystal system.

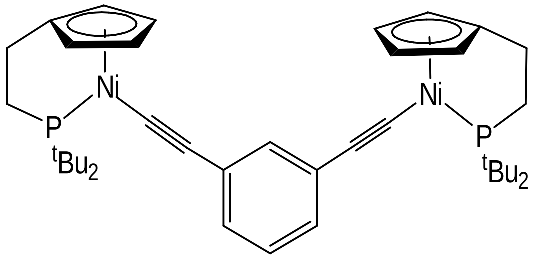


Whittall[116] was the first one who published the results of the cyclic voltammetric investigations for nickel acetylide complex **54** and its various analogues. He reported that all complexes underwent a one electron oxidation assigned to the $Ni^{II/III}$ couple. He added that the replacement of the electron withdrawing Cl by C≡CPh in progressing from **53** to **54** leads to a decrease in the oxidation potential. Cyclic voltammetry measurements of complexes **69**-**77** showed that they undergo irreversible reductions at potentials ranging from −1.16 to −2.33 V. Inspection of electrochemical data shows that the cationic species **75**-**77** are more easily reduced than the neutral complexes **72**-**74**. The reduction potential for the Ni─CCPh derivative **73** is intermediate between those of its chloro **69**-**71** and cationic analogues **75**-**77**.[114]

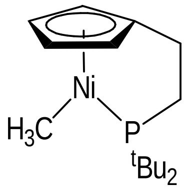
The efficiency of complexes **72-77** in hydrosilylation and polymerization reactions and the interesting cyclic voltammetry results of complexes **54**[116] and **69-77**[114] encouraged us to prepare the novel alkynyl nickel chelate complexes **78-80** and new alkyl chelate complex **81** bearing the bulky phosphanylalkyl chain. The synthetic methodology employed by Bruce[81] for the preparation of complex **54** has been successfully utilized for the preparation of **78-80**. For the synthesis of alkyl chelate complex **81**, the method applied for the synthesis of complexes **72** and **74** by Zargarian[114] was followed.



78: R = H
79: R = CH$_3$



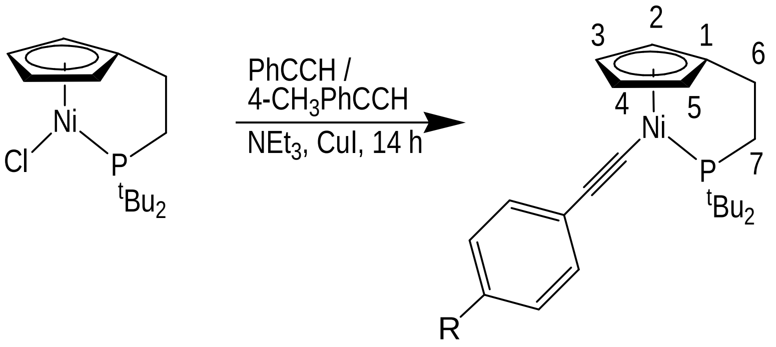
80



81

2.2.1 Synthesis of Alkynyl Chelate {[(Di-*tert*-butylphosphanylethyl)cyclopentadienyl]nickel(I1) Complexes 78 and 79

By the application of the method introduced by Bruce,[81] for the syntheses of **78** and **79**, complex **62** in two separate reaction flasks was suspended in triethylamine along with the catalytic amount of CuI. At 25 °C upon the addition of an excess of phenyl ethyne and 1-ethynyl-4-methylbenzene for **78** and **79** respectively, the reactions started and colour changed from dark purple to brown. After stirring the reaction mixtures for 14 h, the purification was done by column chromatography over SiO$_2$, using petroleum ether / ethyl acetate as eluent (10: 1) to obtain alkynyl complexes **78** and **79** in 58% and 91% yield, respectively, as deep brown solids.



62

78: R = H, (58%)
79: R = CH_3, (91%)

The novel alkynyl nickel chelate complexes **78** and **79** are significantly more stable than **62,** presumably because the alkynyl ligand is more strongly electron donating to the nickel centre than the chloro ligand thus stabilising the alkynyl complexes. **78** and **79** are well soluble in organic solvents (diethyl ether, THF, hexane, dichloromethane and chloroform). The chelate nickel complexes **78** and **79** were fully characterized by IR, ^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectroscopy as well as EIMS, MS (ESI) and HRMS (ESI) spectrometry. In the IR spectra of **78** and **79**, the most noticeable feature is the $\tilde{\nu}$ (C≡C) vibration, which is observed at 2090 and at 2086 cm^{-1} respectively. ^{1}H NMR spectra of **78** and **79** exhibit dublet of triplet with an increased chemical shift of the two methylene protons 6-H at δ = 2.01 and δ = 2.02 ppm respectively. The second set of methylene protons 7-H absorb at δ = 2.49 and δ = 2.48 ppm showing the multiplicity dublet of dublet. All other signals observed in the ^{1}H NMR spectra are in complete accord with the proposed constitutions of complexes **78** and **79**. In the ^{13}C NMR spectra of **78** and **79** the characteristic signals are the absorptions of two carbon atoms (C≡C). The α-carbon atoms resonate at δ = 90.3 and δ = 88.0 ppm. While the signals for β-carbon atoms for complexes **78** and **79** are observed at δ = 117.1 and δ = 117.0 ppm. Another significant absorption signals are of carbon atoms C-1 in the ^{13}C NMR spectra of **78** and **79**, which are found at δ = 108.1 and δ = 107.9 ppm. The ^{31}P NMR spectra of **78** and **79** exhibit one singlet at δ = 104.8 and δ = 104.5 ppm respectively indicating that phosphane side arm is coordinated to nickel and the higher chemical shifts show that the phosphorus is more electron deficient than the respective phosphorus in **62** absorbing at δ = 92.6 ppm. The mass spectrum of complex **78** exhibits the molecular ion base peak [M^+ + 1] at *m/z* = 397 (100%). A fragment peak [$M^+ - C_4H_8$] was observed at *m/z* = 340 (34%) obtaind by the loss of one *tert*-butyl group. The MS (ESI acetonitrile) mass spectra of **78** and **79** exhibit the molecular ion peaks [M^+ + H] at *m/z* = 397 (14%) and *m/z* = 411 (12%). The spectra exhibit the base peaks

[M^+ – ArCC + CH_3CN] at *m/z* = 336 (100%) which, are obtained by the loss of alkynyl part of the ligand followed by the reaction of the resulting fragment with acetonitrile. The HRMS (ESI acetonitrile) spectra were also obtained which are in accord with the other analytical data. All the spectroscopic data confirm the assigned constitutions of **78** and **79**. Finally the assigned constitutions are also supported by solid state structure determination of alkynyl complex **79**. The ORTEP diagram of complex **79** is depicted in figure.3.

Recrystallization of **79** from hexane at –20°C gave deep brown crystals suitable for an X-ray structure analysis. **79** crystallizes in the orthorhombic crystal system with space group *P c c n*. The crystallographic data is studied at 300 K and is in complete accord with the assigned constitution of complex **79**. Some selected bond lengths and bond angles are listed in tables 4 and 5.

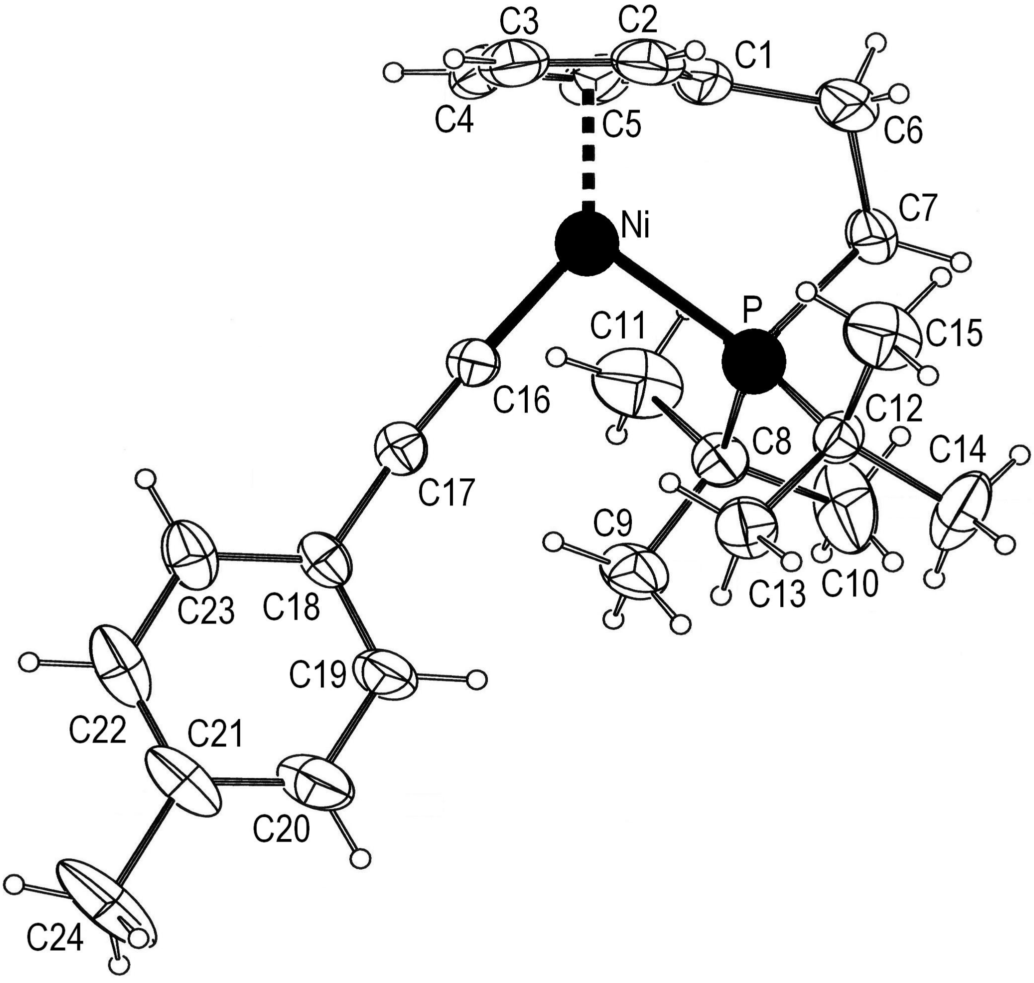


Fig. 2: Structure of **79** in crystal.

Table: 4. Some Selected bond angles for **79**.

Bond angle	**[deg]**	**Bond angle**	**[deg]**
C16-Ni-C1	171.1(2)	C1-Ni-P	88.12(14)
C1-Ni-C4	65.8(2)	C16-Ni-P	99.43(11)
C3-Ni-C4	38.4(2)	C7-C6-C1	113.0(4)
C17-C16-Ni	176.8(3)	C6-C1-Ni	117.1(3)

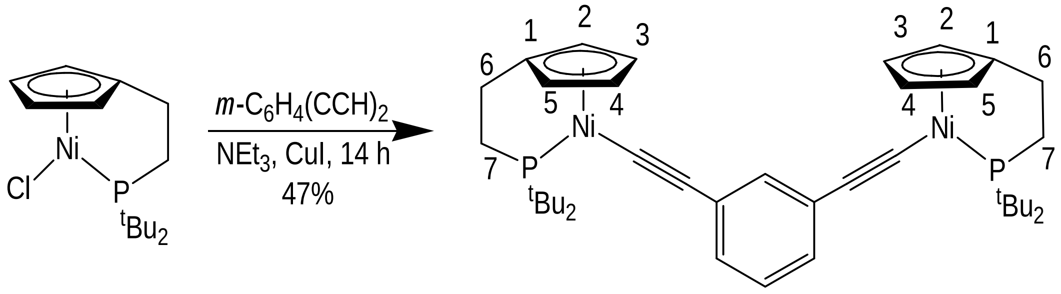
Table: 5. Some Selected bond lengths for **79**.

Bond	**Bond length in Å**	**Bond**	**Bond length in Å**
Ni-C16	1.841(4)	C2-C3	1.360(7)
Ni-C1	2.034(4)	C3-C4	1.399(7)
Ni-C5	2.121(4)	C4-C5	1.392(6)
Ni-C2	2.123(5)	C1-C2	1.407(7)
Ni-C3	2.115(4)	C1-C5	1.437(7)
Ni-C4	2.143(4)	Ni-P	2.1441(10)
C16-C17	1.207(5)	C1-C6	1.511(6)

The structure in the crystal of complex **79** shows the staggered conformation of the ethylene bridge. Some cobalt complexes[105] bearing a pendant phosphanylalkyl chain shows this conformation of ethylene bridge. All the bond lengths and bond angles fall within the expected range. The Ni─C16 bond length [1.841(4) Å] is in the typical range of σ-alkynyl bonds indicating that the more strongly donating acetylide part of ligand is strongly bonded to the nickel center. The Ni─P bond length [2.1441(10) Å] also shows the strong interaction of the hemilabile hindered di-*tert*-butylphosphane ligand to the nickel center. The Ni─C1 bond length [2.034(4) Å] is shorter than the other Cp carbon atoms to Ni atom indicating that the Ni atom coordinating to Cp ring is not in the center resulting the nickel atom closer to C1. The C16-C17 bond length 1.207(5) Å is shorter showing the typical value of the triple bond (C≡C). The repulsive interaction between bulky di-tert-butylphosphanyl group and phenyl ring causes the triple bond (C≡C) to be not linear with a bond angle C17─C16─Ni bond angle [176.8(3)°]. The bond angles C16─Ni─C1 [171.1(2)°], C16─Ni─P [99.43(11)°] and C1─Ni─P [88.12(14)°] show that the region around the phosphorous is highly shielded and that thealkynyl part of ligand is repelled away from the phosphane part.

2.2.2 1,3-Bis{[(di-*tert*-utylphosphanylethyl)cyclopentadienyl]nickel(II)ethynyl}-benzene (80)

Following the method introduced by Bruce,[81] the synthesis of alkynyl complex **80** can be accomplished via a reaction of **62** with 1,3-diethynylbenzene in the presence of triethylamine and CuI. The complex **62** along with catalytic amount of CuI, was suspended in triethylamine. After the addition of 1,3-diethynylbenzene at 25 °C, a change of colour from dark purple to violet brown was observed. After 14 h the alkynyl complex was extracted with diethyl ether. The extract was chromatographed over SiO_2 eluting with petroleum ether / ethyl acetate (10: 1) to obtain the title bimetallic complex **80** in 47% yield as a deep brown solid.



62

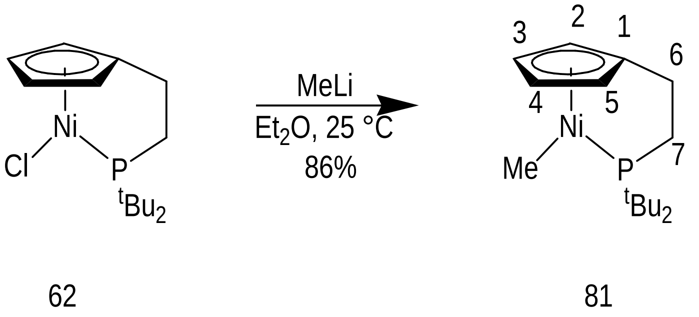
80

The bimetallic complex **80** is an air stable for 2 to 3 h. Complex **80** is well soluble in chloroform, dichloromethane, acetone and diethylether. **80** was fully characterized by IR, ^1H NMR, ^{13}C NMR and ^{31}P NMR spectroscopy and MS (ESI), and HRMS (ESI) spectrometry. The significant feature in the IR spectrum of **80** is the $\tilde{\nu}$ (C≡C) vibration, which is observed at 2082 cm^{-1}. In ^1H NMR spectrum of **80** the distinguishing point is the higher chemical shift value of the proton of the ethylene bridge than the respective protons in **62**. Two methylene protons 6-H absorb at δ = 2.03 ppm as a dublet of triplet. While for 7-H protons, one dublet of dublet was observed at δ = 2.47 ppm. The ^{13}C NMR spectrum of **80** shows the absorption of two quaternary carbon atoms C-1 of two Cp rings at δ = 108.5 ppm which is higher than the respective one in the starting complex **62** indicating the pronounced electronic effect of alkynyl moiety on the Cp ring. The most characteristic point in the ^{13}C NMR spectrum of **80** are the (C≡C) absorptions, which are observed at δ = 93.5 and δ = 116.3 ppm for α and β carbon atoms respectively. The ^{31}P NMR spectrum shows one singlet at δ =105.2 ppm indicating that phosphorus is coordinated to the nickel center and is more deshielded than in **62**. The MS (ESI acetonitrile) mass spectrum exhibits the molecular ion peak $[M^+ + H]$ at *m/z* = 715 (19%). The spectrum exhibits the base peak $[M^+ - CH_3PhCC + CH_3CN]$ at *m/z* = 336

(100%), which is obtained by the cleavage of acetylide linkage followed by the reaction of the resulting fragment with acetonitrile. In addition to this, the HRMS (ESI acetonitrile) spectrum was obtained which is also in agreement with all analytical data. All the analytical data are in complete accord with the assigned constitution of **80**.

2.2.3 [(Di-*tert*-butylphosphanylethyl)cyclopentadienyl]methylnickel(II) (81)

Following the method introduced by by Zargarian[114] applied for the synthesis of complexes **72** and **74,** the synthesis of alkyl complex **81** was accomplished via a metathetic reaction between **62** and methyllithium. For the ligand exchange reaction, **62** was treated with MeLi at 25 °C in diethyl ether. After one hour stirring, the colour of the solution had changed from dark purple to dark brown. After filteration through celite complex was purified by crystallization from hexane at −20 °C to obtain **81** in 86% yield as a green solid.



In contrast to complex **62**, the complex **81** is more stable in the solid phase and can be handled in the air for some time. It is, however, observed that **81** is comparatively less stable than alkynyl complexes **78**, **79** and **80**. The methyl chelate **81** is well soluble in diethyl ether, THF, chloroform and dichloromethane. In solution phase, decomposition of **81** was observed after 20 min. This new alkyl nickel chelate complex **81** is fully characterized by IR, ^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectroscopy, and LREIMS and HREIMS spectrometry. The significant feature in the ^{1}H NMR and ^{13}C NMR spectra of **81** is the absorption of methyl group connected to Ni, which is observed at $\delta = -1.07$ and $\delta = -43.5$ ppm respectively. All other signals in ^{1}H NMR and ^{13}C NMR are well assigned and satisfy the proposed structure of **81**. In the ^{31}P NMR spectrum absorption of phosphorus atom as one singlet at $\delta = 90.0$ ppm indicates its coordination to the nickel center. The low resolution mass spectrum exhibits the molecular ion peak [M^{+}], m ⁄z = 310 (40%). A fragment signal at *m⁄z* = 295 (32%) corresponds to [M^{+} – CH$_3$]. The high resolution mass spectrum of **81** was obtained which is in complete accord with the assigned formula. Finally the constitution of **81** is confirmed by X-ray diffraction study.

A saturated solution of a part of **81** in boiling hexane was placed at −20°C to obtain the needle like green crystals suitable for X-ray structure analysis. The structure indicates the hexagonal crystal system with the space group *P* 61 which was studied at 300 K. Some selected bond lengths and bond agnles are listed in tables 6 and 7. The X-ray diagram of 81 is depicted in figure 3.

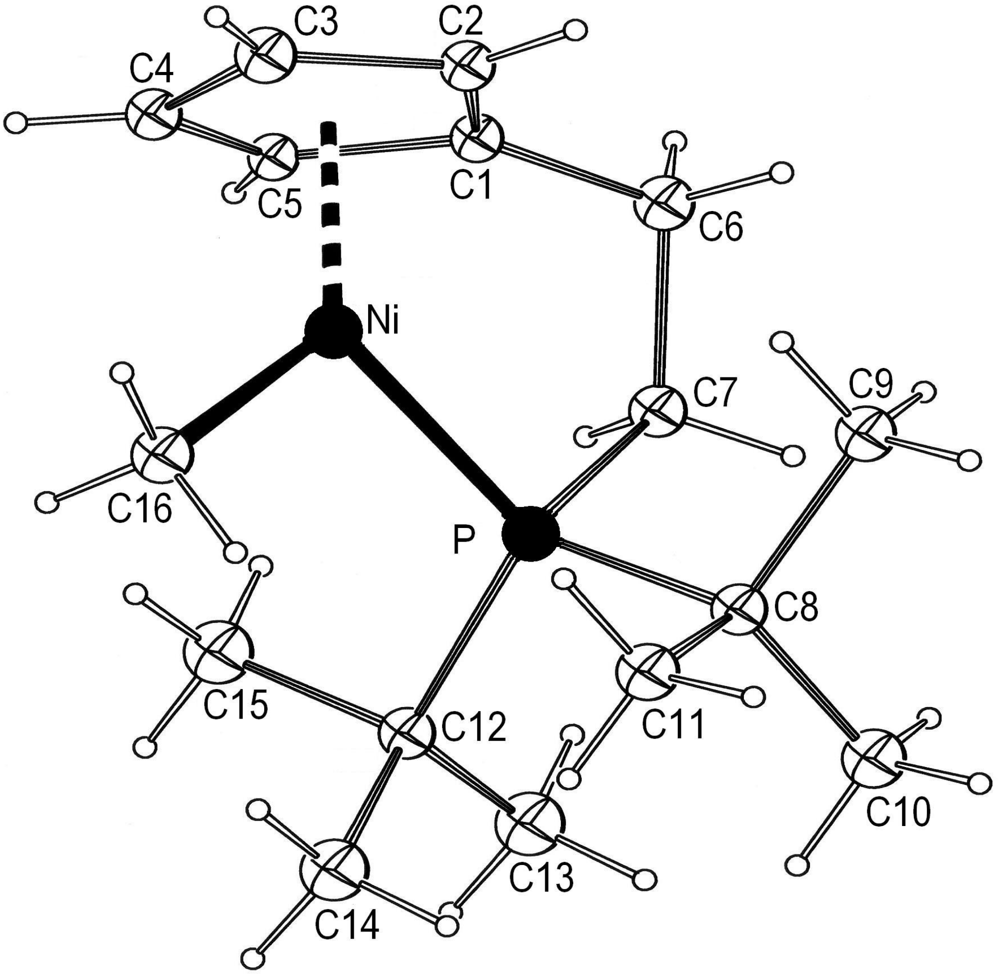


Fig. 3: Structure of **81** in the crystal.

Table 6. Selected bond lengths in Å for **81**.

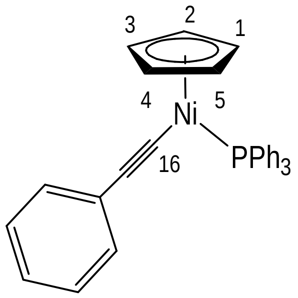
Bond	**Bond length in Å**	**Bond**	**Bond length in Å**
Ni-C1	2.099 (11)	Ni-P	2.145 (4)
Ni-C2	2.132 (10)	C2-C3	1.414 (13)
Ni-C3	2.110 (11)	C3-C4	1.409 (13)
Ni-C4	2.104 (10)	C4-C5	1.327 (14)
Ni-C5	2.152 (10)	C1-C2	1.377 (13)
Ni-C16	1.972 (11)	C1-C5	1.449 (12)

Table 7. Selected bond angles in [deg] for **81**.

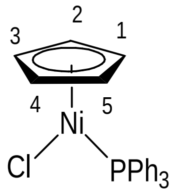
Bond angle	**[°]**	**Bond angle**	**[°]**
C16-Ni-C1	166.6(5)	C16-Ni-P	104.6(4)
C1-Ni-C4	64.6(4)	C6-C1-Ni	116.7(7)
C4-Ni-C3	39.1(4)	C1-Ni-P	88.8(3)
C1-C6-C7	111.4(9)	C7-P-Ni	102.6(3)

The ethylene bridge in the structure of **81** causes a disorder in the geometry of complex **81**. This happened due to the staggered conformation of the ethylene bridge in the structure of **81**. Some cobalt cyclopentadienyl complexes bearing a pendant phosphane ligands are also known having the steggered conformation of ethylene bridge.[105] All the bond lengths and bond angles are within the expected range. The Ni─C16 bond length [1.972 (11) Å] exhibits the typical value of σ-methyl bond indicating that methyl group is strongly bonded to the nickel center. The Ni─P bond length [2.145 (4) Å] also shows the strong bond of the strongly hindered di-tert-butylphosphane ligand to the nickel center. The Ni─C1 bond length [2.099 (11) Å] is shorter than the other Cp carbon atoms to nickel indicating that the coordination of the Cp ring is off-center which results that the nickel atom is closer to C1. The bond length C4─C5 [1.327 (14) Å] is shorter that the other Cp carbon bonds due to the off-center coordination of nickel to the Cp ring. The bond angles C16─Ni─C1 166.6°(5), C(16)─Ni─P 104.6°(4) and C1─Ni─P 88.8°(3) indicate that the region around the phosphorus is shielded and methyl ligand is well accessible.

In the literature very few examples of solid state structure analysis of nickel complexes with phosphanylalkyl chain[109,115] exist. A comparative X-ray structure analysis of the Cp nickel complexes with or without phosphanylalkyl chain is described. Some comparative bond lengths are given in table 8.



54



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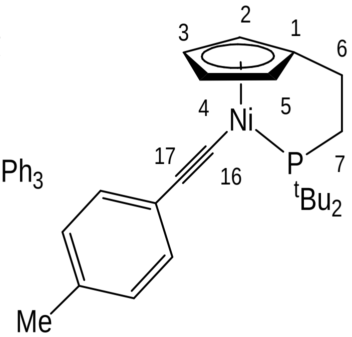
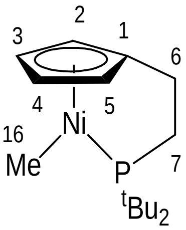


79



81

Table: 8. Selected bond lengths in Å for **54, 64, 79** and **81**.

Bond	**54**[115]	**64**[109]	**79**	**81**
Ni-C1	2.063(3)	2.081(4)	2.034(4)	2.099(11)
Ni-C2	2.118(3)	2.103(4)	2.123(5)	2.132(2)
Ni-C3	2.098(3)	2.096(4)	2.115(4)	2.110(2)
Ni-C4	2.135(3)	2.147(4)	2.143(4)	2.104(10)
Ni-C5	2.142(3)	2.154(4)	2.121(4)	2.152(10)
Ni-C16(Cl)	1.856(3)	2.176(1)	1.841(4)	1.972(11)
Ni-P	2.1350(9)	2.160(1)	2.1441(10)	2.145(4)

All the bond distances of the complexes **79** and **81** fall within the range of expected values. There is a significant bond length difference as shown in the table **8**. The Ni─alkynyl bond length [1.841(4) Å] in **79** is shorter than the Ni─alkyl bond length [1.972(11) Å] **81**, presumably because of the greater *sp* character of the alkynyl carbon atom. The Ni─C1 bond length [2.099 (11) Å] in **81** is shorter than that of the other Cp carbon atoms to the nickel which indicates that the coordination of the Cp ring is off-center with the Ni atom resulting the metal closer to C1. The same trend of coordination of the Cp ring to the Ni center is observed in **79**, however the Ni─C1 bond length [2.034(4) Å] in **79** is shorter than the Ni─C1 bond length [2.099 (11) Å] in **81** indicting that the Cp ring is more strongly coordinated to nickel center in **79** because of the more strongly electron donating alkynyl ligand. This strong coordination of nickel is the reason that alkynyl complexes are more stable than the respective alkyl **81** and chloro **62**. The Ni─P bond [2.1350(9) Å] in **54**[115] is shorter than Ni─P bond [2.1441(10) Å] in **79** and the respective bond [2.145(4) Å] in **81**. This is due to the repulsive interaction of *tart*-butyl groups on the phosphorus atom in **79**. The C16-Ni-P bond angle [104.6°(4)] in **81** is larger than the corresponding angle C16-Ni-P [99.43°(11)] in **79** indicating the alkynyl ligand bending more toward the phosphane part of the ligand reflecting the large steric bulk of the methyl group as compared to the linear alkynyl group. The chelate formation by the ethylene bridge results the bond angle C16-Ni-P bond angle [104.6°(4)] in **81** and C16-Ni-P [99.43°(11)] in **79** larger from the (Cl)─Ni─P bond angle [96.08°(4)] in **64.**[107] In short it is concluded that the staggered conformation of ethylene in the structures of **79** and **81** causes some slight ring slippage to stabilize the respective chelate**.**

The replacement of Cl ligand by the electron donating alkyl or alkynyl ligand increases the stability of the nickel complexes. The ^{31}P NMR spectra of alkynyl complexes **78-80** show downfield shifts at δ = 104.8, δ = 104.5 and δ = 105.2 ppm, respectively, while the respective absorption in the ^{31}P NMR spectrum of chloro complex **62** at δ = 92.9 ppm. This significant downfield shift indicates the strong interaction between nickel and phosphane ligand and more stability of alkynyl complexes **78-80**. The complex **81** having weakly methyl electron donating ligand as compared to alkynyl ligand shows upfield phosphorus shift at δ = 90.0 ppm than the respective absorption in the ^{31}P NMR spectrum of **62** at δ = 92.9 ppm indicating weak coordination of phosphorus side arm to nickel.

2.2.4 Cyclovoltammetry of 62, 79, 80 and 81

Cyclic voltammetry has proven to be a powerful tool in order to investigate the electronic influence of substituents at the Cp-ring system of transition metal complexes. The nickel chelates **62**, **78**, **80** and **81** prepared in this study were investigated by cyclic voltammetry. The cyclovoltammogram of complexes **62**, **79**, **80** and **81** were recorded in dichloromethane, reference electrode Ag/AgCl (Alfa), counter electrode Pt wire, 0.2 M tetrabutylammonium hexafluorophosphate potential normalized to ferrocene/ferrocenium ion (E_0 = 4.9 V vs Ag/AgCl). The concentration of solution in all cases was 1 mmol/l.

The voltammograms of **62** shows reversible oxidation at 0.35 V. Whittall[116] reported the oxditation potential of nickel complex **53**, an analogue without an ethylene bridge at 0.86 V. This significant decrease in the oxidation potential is caused by the chelate formation by the phosphanylalkyl part of ligand in **62**. When the Cl ligand in **62** was replaced with alkynyl ligand to get the complex **79** a reversible oxidation at 0.038 V and an irreversible reduction at −1.935 V are observed. This decrease in the oxidation potential has also been observed by replacement of the electron withdrawing Cl by C≡CPh in progressing from **53** to **54**.[116] However, this decrease in the oxidation potential leading from **62** to **79** is more as compared to the respective decrease in the oxidation potential in progressing from **53** to **54**.[116] The cyclic voltammetry data obtained are summarized in table 9.

Table**:** 9. Cyclic voltammetry of complexes **62, 79, 80** and **81**.

Complexes	V(V/s)	E_A (V)	E_K(V)
62	0.05	0.35	0.196
62	0.1	0.313	0.205
62	0.2	0.322	0.179
62	0.5	0.321	0.153
79	0.1	0.038	−0.064, −1.935
79	0.5	0.066	−0.05
80	0.1	0.3802	0.1312, −1.7574
80	0.2	0.2734	0.1284, −1.744
80	0.5	0.2824	0.1314, −1.7874
81	0.1	−0.16	−0.253
81	0.2	−0.065	−0.313, −1.521
81	0.5	−0.019	−0.359, −1.521

The cyclic voltammetry measurements of complex **80** showed that it undergoes reversible oxidation at 0.3802 V and irreversible reduction at −1.7574 V indicating no significant difference in oxidation potential than **62**. However, an interesting feature to be noted is the replacement of the Cl ligand in **62** with methyl group to get **81** which showed reversible oxidation at −0.161 V with scan rate 0.1 V/s. Some representatives of CV plots of **62**, **78**, **80** and **81** are given in figures 4, 5, 6 and 7, respectively.

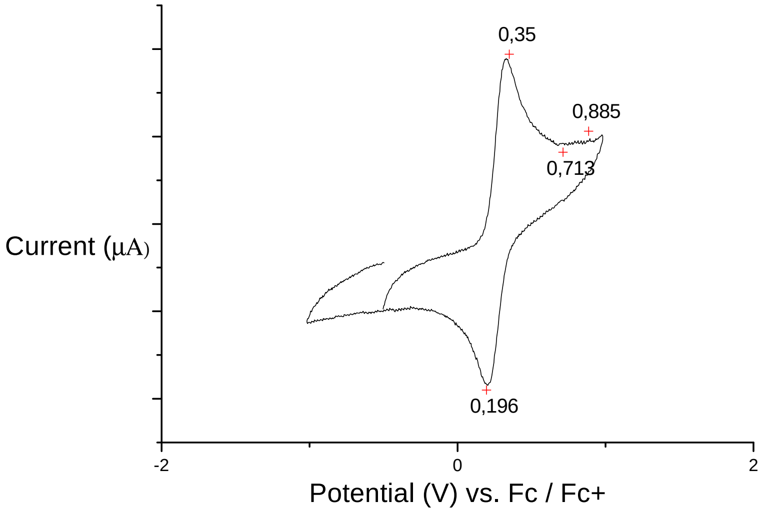


Fig. 4: CV plot of **62**. 0.05 V/s, T = 20 °C,
c = 1.0 mmol/l, c_{TBAHFP} = 0.2 mol/l, 1 scan, DCM.

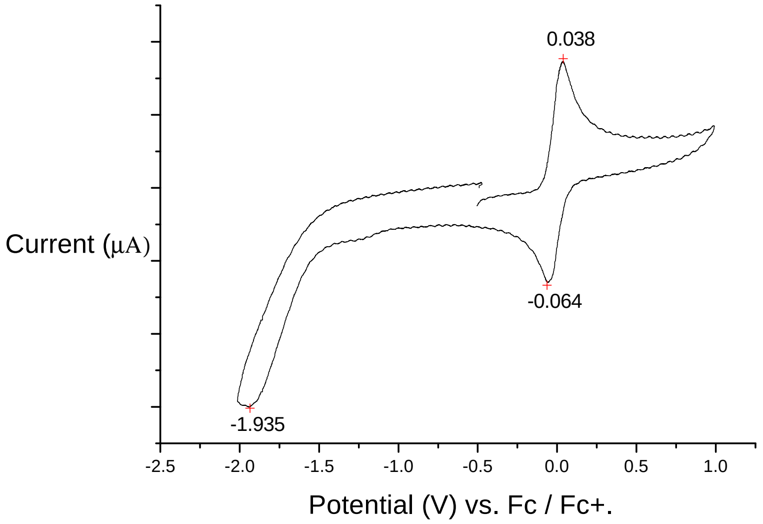


Fig. 5: CV plot of **79**. 0.1 V/s, T = 20 °C,
c = 1.0 mmol/l, c_{TBAHFP} = 0.2 mol/l, 1 scan, DCM.

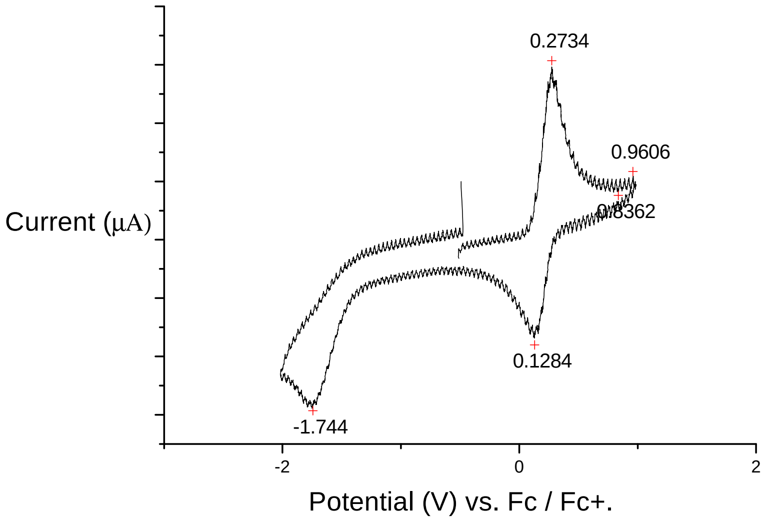


Fig. 6: CV plot of **80**. 0.1 V/s, *T* = 20 °C, *c* = 1.0 mmol/l, c_{TBAHFP} = 0.2 mol/l, 1 scan, DCM.

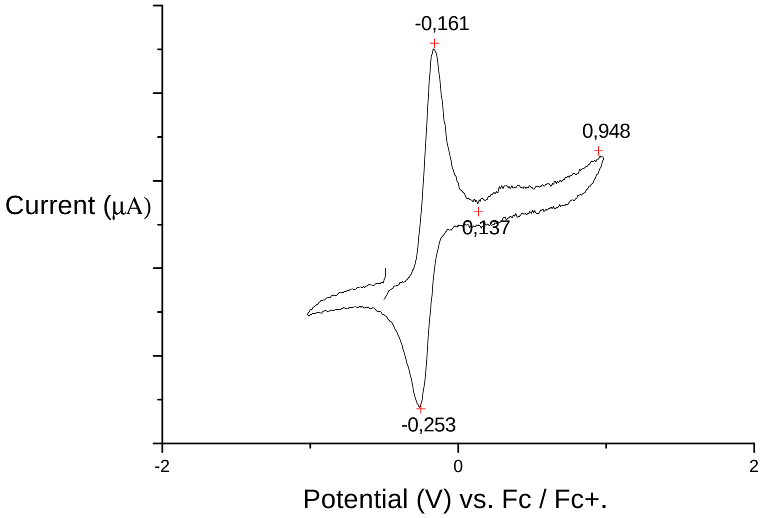
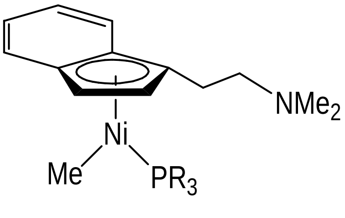


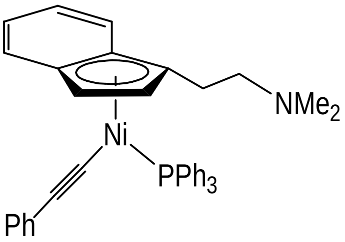
Fig. 7: CV plot of **81**. 0.1 V/s, *T* = 20 °C, *c* = 1.0 mmol/l, c_{TBAHFP} = 0.2 mol/l, 1 scan, DCM.

2.2.5 Dehydropolymerization of $PhSiH_3$

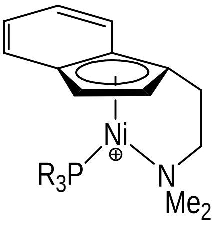
Complexes **72-74**[114] were reported as catalysts in the oligomerization of $PhSiH_3$ to get thick oils consisting of mixtures of cyclic and linear polysilane, as identified by ^1H NMR spectra showing broad peaks at δ = 5.6-5.1 ppm (cyclic) and at δ = 4.8-4.4 ppm (linear).[114] The cationic complexes **75-77** were used as catalyst in the hydrosilylation of styrene and 1-hexene. The analysis of the reaction products obtained confirmed the formation of $Ph(PhSiH_2)CHCH_3$ promoted by **75 -77** as the precatalyst.[114]



72: R = Ph
74: R = Me

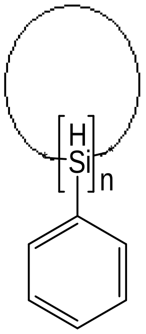


73

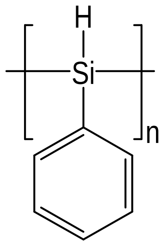


75: R = Ph
76: R = Me
77: R = Cy

Having the nickel chelate complexes **78-81** in hand prompted us to study the efficiency of neutral complexes bearing a pendant di-*tert*-butylphosphanylethyl moiety along these lines of reaction, beginning with the reactivity of the complexes **79** and **81** in the oligomerization of $PhSiH_3$. Thus the addition of neat $PhSiH_3$ (200 equiv) to solid samples of **78** and **81** caused an immediate evolution of gas (presumably H_2). Stirring the phenylsilane ($PhSiH_3$) for 1 day with **81** gave thick oil consisting of mixture of cyclic and linear polysilanes presumably **82** and **83**, respectively, while from the respective reaction with alkynyl nickel complex **79** as a catalyst, the thick oil was obtained after stirring for 2 days. The ^1H NMR spectra show absorption peaks for Si—H at δ = 5.17-5.19 ppm for cyclic oligomers like **82** and at δ = 4.40-4.56 ppm for linear oligomers like **83**. The ^1H NMR spectra cannot determine the degree of oligomerization; however, an indication about the oligomerization can be obtained. On the basis of ^1H NMR spectra, we can just suggest the constitutions of cyclic and linear oligomers like **82** and **83**, respectively obtained by the oligomerization reaction. The cyclic to linear oligomer ratio was determined for each case by integration of these peaks (ca. 80:20 for reaction with **81** and ca. 60:40 for reaction with **79**), while the monomer conversion was determined relative to the $PhSiH_3$ signal at δ = 4.19 ppm (ca. 94% for the reaction of **81** and ca. 85% for reaction of **79**). The reaction with nickel chelate **81** is completed with 1 day and complex **79** needed 2 days of reaction time, while the completion of reaction with **72** and **74** have been reported in 3 days.[114] It is concluded that the nickel chelates bearing a pendant phosphane ligand seem to be more active in the oligomerization of phenylsilane as compared to the reported one.[114]



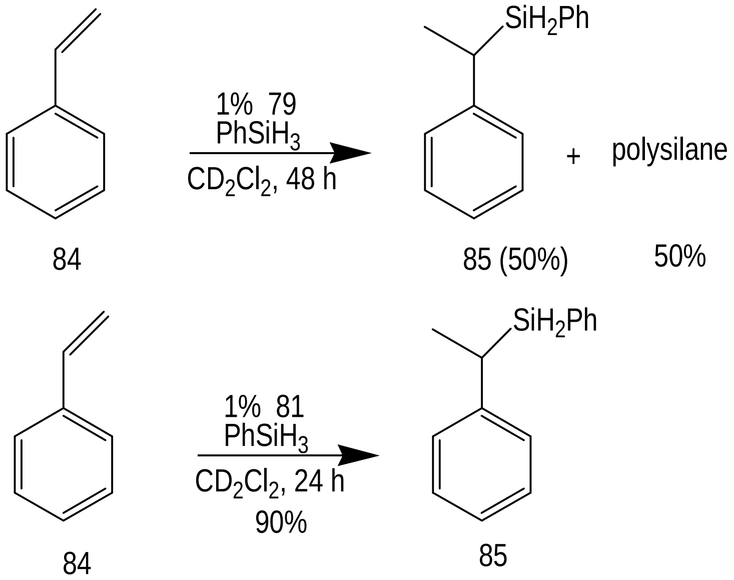
82



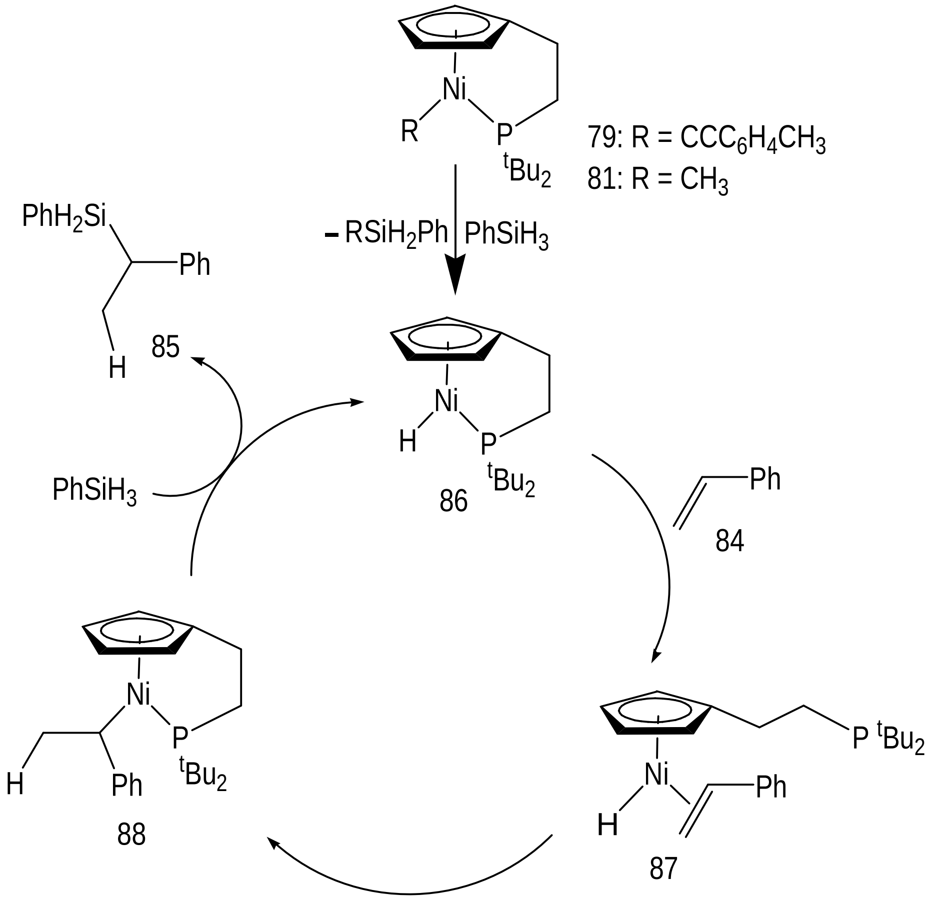
83

2.2.6 Hydrosilylation of Styrene

The efficiency of **79** and **81** in the oligomerization of $PhSiH_3$ encouraged us to examine in the hydrosilylation of styrene **84**. In two separate reactions complexes **79** and **81** were dissolved in CD_2Cl_2 at 25 °C. Upon the addition of styrene **84** no reaction was observed. After the addition of phenylsilane the slow colour change from light green to orange red was observed. The reactions were monitored by ^1H NMR spectroscopy. After stirring the reaction mixture with **81** for 24 h, the ^1H NMR spectrum showed the completion of the reaction. The respective ^1H NMR spectrum of reaction with **79** showed disappearance of phenylsilane after 48 h. However, in case of reaction with **79** the ^1H NMR spectrum showed conversion of 50% of phenylsilane to polysilane. The solutions were filtered through silica gel and solvent was removed at reduced pressure to obtain the hydrosilylation product **85** in 90% yield for reaction with **81** and 49% yield for reaction with **79**. The hydrosilylation product **85** was characterized by ^1H NMR, ^{13}C NMR spectroscopy and GCMS. All the analytical data were in complete accord with those in the literature.[114]



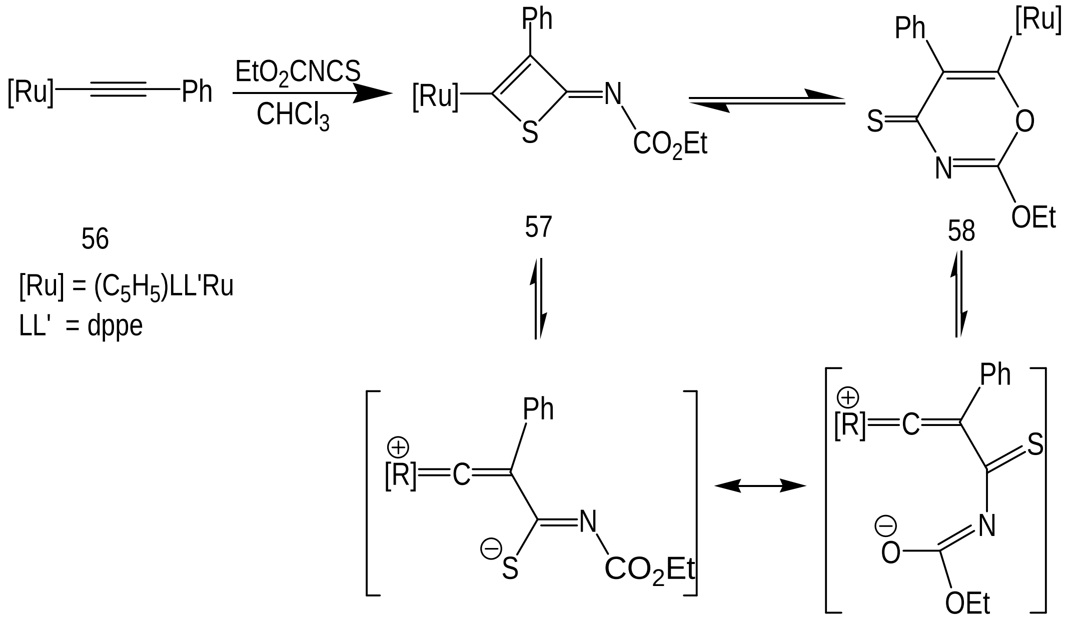
It is postulated that in either case a Ni─H intermediate is the active catalyst during the course of the reaction.[114] The mechanism of the hydrosilylation of styrene has already been proposed[117] using triphenylphosphane indenyl nickel with or without an amine tether. It is suggested that Ni─H intermediate formed from **72-77** is stabilized by phosphane as well as by the amine tether.[114,117] So it is suggested that during the course of reaction the decoordinated phosphane ligand has a minimum chance to coordinate again to the metal center. In the literature all the reports show that the hydrosilylation reaction has been promoted by cationic nickel species.[114,117] The neutral nickel chelates like **79** and **81**, contaning di-*tert*-butylphosphane as a pendant ligand, need to be checked in the hydrosilylation reaction of olefins and acetylene. It is investigated that the complexes **79** and **81** can catalyze in a better way because di-*tert*-butylphosphanyl part of the ligand can not leave the Ni─H intermediate during the course of reaction. The mechanism involves the insertion of styrene into the Ni─H bond of an intermediate **86** to give a π-complex **87**, which further yields new Ni─alkyl species **88**. The species **88** reacts with a second molecule of $PhSiH_3$ to liberate the hydrosilylation product **85** and regenerates Ni─H intermediate **86** (Scheme 2).



Scheme 2

2.3 [4+2] Cycloaddition Reactions of EtO_2CNCS to σ-Alkynyl 78 and 79

The cycloaddition reaction of an isothiocyanate molecule with the ruthenium σ-acetylide **56** results an unstable four-membered-ring 2-iminothiete complex **57**. In the presence of an excess of isothiocyanates, expansion of the 2-iminothiete ring by coupling of a second isothiocyanate molecule generated complex with a six membered 2-imino-1,3-thiazine-4-thione ligand. In the initial stage within 1 h, cycloaddition of C=S bond of EtO_2CNCS to the σ-acetylide **56** afforded the anticipated complex **57** with the four membered thiete ring. From the reaction of **56** with 1.1 equiv of EtO_2CNCS for 1 day in $CHCl_3$, a mixture containing **57** and **58** in a 1:3 ratio was isolated.[91] The isomerisation could involve opening of the four membered 2-iminothiete ring to form zwitterionic vinylidene with the anionic charge delocalized between the sulphur atom and the oxygen atom of the carbonyl group (scheme 3). The zwitterionic vinylidene with a more electronegative oxygen atom makes **58**, with six membered oxazine ring containing a thione group, the predominant species after ring closure. The formation of **57** may involve a fast concerted [2+2] cycloaddition. Transformation takes 1 day to establish the equiblrium of **57** and **58** in a ratio 1:3.

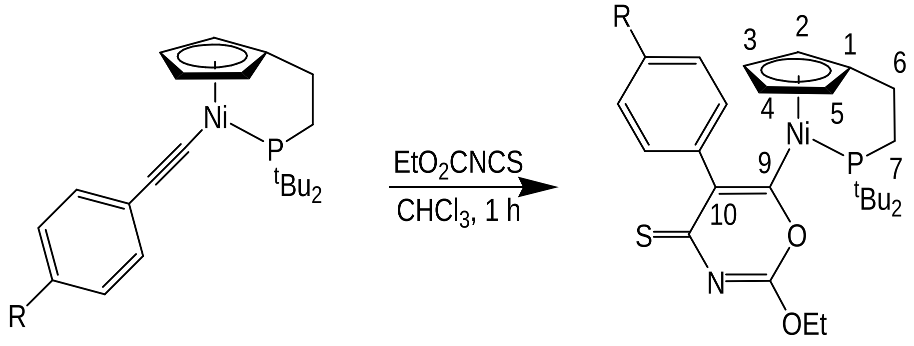


scheme 3

Cycloaddition reactions of several nickel σ-acetylide complexes[82] with isocyanates have been reported. Having the σ-acetylides of Ni^{2+} with the activated C≡C bond at hand prompted us to check the efficiency of activated C≡C bond of the complexes **78** and **79** along these lines of reactions with EtO_2CNCS to get the respective cycloaddition products.

2.3.1 [4+2] Cycloaddition Reaction of EtO_2CNCS to the Triple Bonds of 78 and 79

The synthesis of **89** and **90** can be accomplished by following the method introduced for the treatment of EtO_2CNCS with ruthenium σ-acetylide **56**.[91] Treatment of alkynyl complexes **78** and **79** in two separate reaction flasks with 1.2 equiv of EtO_2CNCS at 25 °C results an immediate colour change from deep brown to orange. The reaction was complete within 1 h and afforded the complexes **89** and **90** with a six membered 2-imino-1,3-thiazine-4-thione ligand in 85% and 90% yield respectively as orange coloured solids.



78: R = H
79: R = CH_3

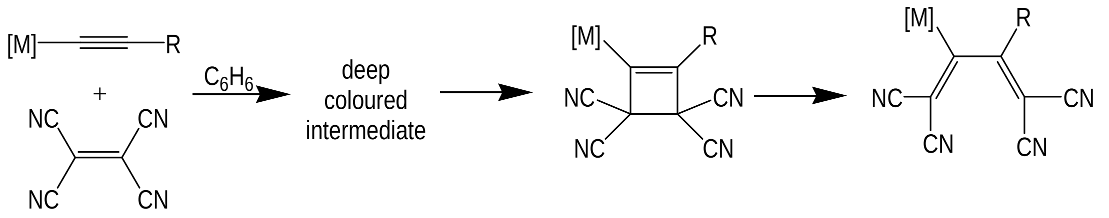
89: R = H, 85%
90: R = CH_3, 90%

The title complexes **89** and **90** are soluble in all common organic solvents (diethyl ether, THF, Chloroform, dichloromethane and hexane). Both complexes are stable when exposed to air for half an hour. It is reported that by treating the σ-acetylide of ruthenium complex **56** with EtO_2CNCS and stirring for 1 h, cycloaddition of the C=S bond occurs affording the complex **57** with the four-membered thiete ring.[91] However, the σ-acetylide nickel chelate complexes **78** and **79** yield six membered oxazine ring within only 1 h reaction time indicating that the triple bonds in the complexes **78** and **79** are more activated than the respective bond in the ruthenium analogue **56**. The complexes **89** and **90** are fully characterized by IR, ^1H NMR, ^{13}C NMR and ^{31}P NMR spectroscopy, and LREIMS and HREIMS spectrometry. The noticeable feature in the IR spectra of **89** and **90** is the absorption of the C=S group. The IR spectra of **89** and **90** exhibit absorption bands at 1259 cm^{-1} indicating the absorption of the C=S moiety. The expected reaction products resulting from the cycloaddition of C=S, 2-iminothiete four membered rings like the analogue of **57**, do not show any absorption in this region. Other characteristic absorptions of C=N moiety of **89** and **90** in each IR spectrum are observed at 1670 cm^{-1} and 1669 cm^{-1} respectively.

The ^1H NMR spectra are well assigned and fully satisfied to the proposed structures including the absorptions of ethyl groups of the complexes **89** and **90** at $\delta = 1.35$ and $\delta = 4.23$ ppm, and $\delta = 1.31$ and $\delta = 4.23$ ppm respectively. The oxazine rings are confirmed only by ^{13}C NMR spectra which show the characteristic signal for the C=S groups at $\delta = 211.7$ and $\delta = 209.1$ ppm for **89** and **90**. The signals observed at $\delta = 150.3$ and $\delta = 150.5$ ppm correspond to the carbon atom (C-10) of **89** and **90** respectively. While the carbon atom (C-9) shows absorptin at $\delta = 165.4$ and $\delta = 165.2$ ppm. The C=N groups of **89** and **90** absorb at $\delta = 160.6$ ppm. All the other carbon atoms show the typical absorption signals in the ^{13}C NMR spectra of **89** and **90**. The characteristic features are the absorptions in ^{31}P NMR spectra of **89** and **90** showing the singlet at $\delta = 101.2$ and $\delta = 101.2$ ppm which indicate that phosphorous atoms are coordinated to the nickel. The MS (ESI acetonitrile) mass spectrum of **89** shows the molecular ion peak, the base peak, [M$^+$ + H] at *m/z* = 528 (100%). While the respective spectrum of the complex **90** exhibits molecular ion peak which is also the base peak, [M$^+$ + H] at *m/z* = 542 (100%). The spectra show the fragment peaks [$C_{15}H_{26}NiP$ + CH_3CN] at *m/z* = 336 (38%) and *m/z* = 336 (71%) for **89** and **90** respectively, which are obtained by the cleavage of the oxazine linkage from nickel followed by the reaction of the resulting fragment with acetonitrile. In addition to this, the HRMS (ESI acetonitrile) spectra were also obtained which are in close agreement to the assigned molecular formula of complexes **89** and **90**. All the analytical data confirm the assigned constitutions of complexes **89** and **90**.

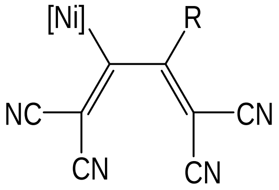
2.4 [2+2] Cycloaddition Reactions of $(CN)_2CC(CN)_2$ to the Triple Bonds of σ-Alkynyl Complexes 78-80

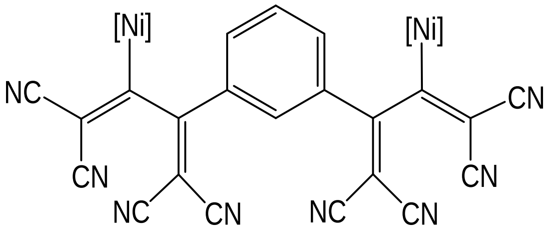
Solar[87] was the first one who reported the cycloaddition of tetracyanoethylene, $C_2(CN)_4$ to σ-acetylide complexes of iron, and this was followed by an initial communication concerning a ruthenium system.[92] These reactions proceed via deeply coloured intermediates which lighten to give σ-cyclobutenyl complexes **60a-f**. The σ-cyclobutenyl complexes **60a-f** may not be isolable, as the organic ligand more or less rapidly undergoes a ring opening reaction to give the isomeric σ-butadienyl complexes **61a-f**.[93] Cyclobutenyl complexes are believed to be involved, and have been observed for the analogous reactions of manganese and iron complexes. However these cyclobutenyl complexes were not observed for the nickel reaction.[94]



59	[M]	60	[M]	61	[M]
a	Mn $(CO)_3$ (dppe)	a	Mn $(CO)_3$ (dppe)	a	Mn $(CO)_3$ (dppe)
b	$Fe(CO)_2$ (C_5H_5)	b	$Fe(CO)_2$ (C_5H_5)	b	$Fe(CO)_2$ (C_5H_5)
c	$Ni(PPh_3)(C_5H_5)$	c	$Ni(PPh_3)(C_5H_5)$	c	$Ni(PPh_3)(C_5H_5)$
d	$Ru(CNBu^t)(PPh_3)(C_5H_5)$	d	$Ru(CNBu^t)(PPh_3)(C_5H_5)$	d	$Ru(CNBu^t)(PPh_3)(C_5H_5)$
e	$Ru(dppe)(C_5H_5)$	e	$Ru(dppe)(C_5H_5)$	e	$Ru(dppe)(C_5H_5)$
f	$W(CO)_3(C_5H_5)$	f	$W(CO)_3(C_5H_5)$	f	$W(CO)_3(C_5H_5)$

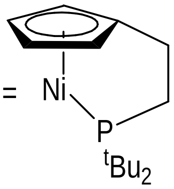
Bruce[93] prepared several metal butadienyl complexes by treating tetracyanoethylene with σ-alkynyl metal complexes. He also reported the X-ray diffraction study of complex **61c**, and it is described that the coordination of nickel to the Cp ring in butadienyl nickel complex **61c** is at the point of center. The X-ray structure analysis of alkynyl nickel chelate complex **79**, being discussed in the preceding section 2.2, has shown that the coordination of nickel to the Cp ring is off-center caused by the staggered conformation of the ethylene bridge. The interest has now been turned to check the efficiency of the σ-acetylide nickel chelate complexes **78-80**, bearing very bulky di-*tert*-butylphosphane as a pendant ligand separated from the Cp ring by the ethylene bridge with staggered conformation, toward the cycloaddition with tetracyanoethylene $(CN)_2CC(CN)_2$. The present study has also been focussed on the influence of *tert*-butyl substituented phosphane, connected by an ethylene bridge, on the geometry of the cycloaddition reaction products **91-93**.





91: R = C_6H_5
92: R = 4-$CH_3C_6H_4$

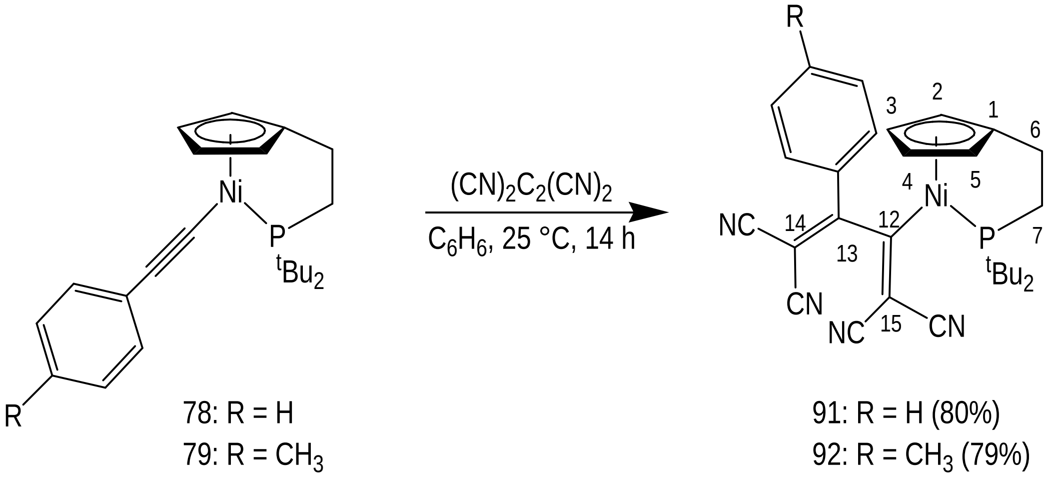
[Ni] =



93

2.4.1 [2+2] Cycloaddition Reaction of Tetracyanoethylene to the Triple Bonds of σ-Alkynyl Nickel Chelate Complexes 78 and 79

The complexes **91** and **92** were prepared by the treatment of tetracyanoethylene $(CN)_2C_2(CN)_2$ with metal σ-acetylide. In two different reaction flasks alkynyl nickel chelate complexes **78** and **79** were dissolved in benzene and treated with an excess of tetracyanoethylene $(CN)_2C_2(CN)_2$ at 25 °C. An immediate colour change from brown to dark red was observed. After stirring for 14 h, the reaction mixtures were chromatographed through silica gel (SiO_2) using petroleum ether and ethyl acetate (10:1) as eluent to obtain the products in 80% and 79% yields identified spectroscopically butadienyl nickel complexes **91** and **92** as dark brown solids.



78: R = H
79: R = CH_3

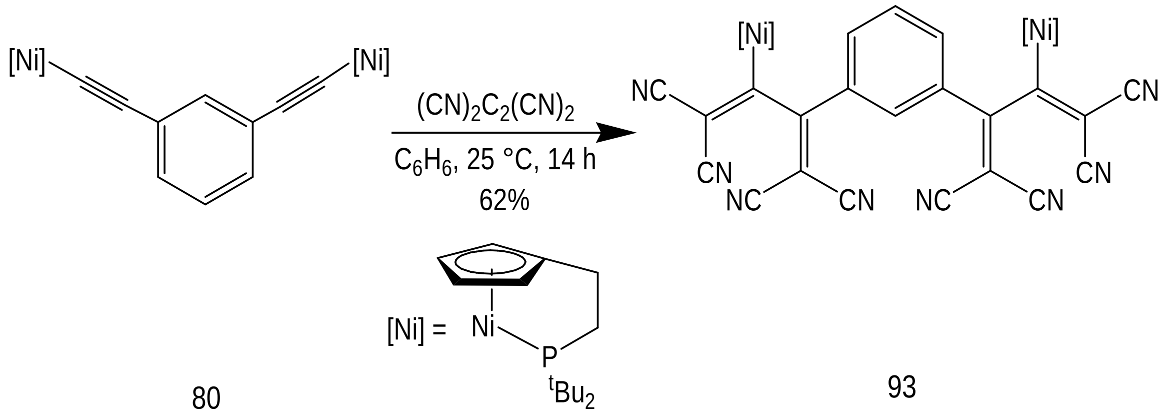
91: R = H (80%)
92: R = CH_3 (79%)

The complexes **91** and **92** have been observed as stable compounds for 1 to 2 h and can be handled in air. However, after 2 h decomposition starts. It is observed that the butadienyl complexes **91** and **92** are soluble in all common organic solvents (THF, diethyl ether, ethyl acetate chloroform, benzene and dichloromethane). The butadienyl complexes **91** and **92** are fully characterized by IR, ^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectroscopy, and LREIMS and HREIMS spectrometry. The IR absorption bands for $\tilde{\nu}$ (C≡N) and $\tilde{\nu}$ (C=C) at ca. 2220 and 1530 cm^{-1} provided clear evidence for the ring-opened formulation. The ^{1}H NMR spectra of complexes **91** and **92**, each shows two sets of signals as two doublets at δ = 1.39 and δ = 1.46 ppm for 18 protons of two $C(CH_3)_3$ groups. The ethylene bridge protons also show four sets of broad signals δ = 1.71, δ = 1.80, δ = 2.00 and δ = 2.24 ppm. Four sets of broad signals were found at ca. δ = 3.32, δ = 4.71, δ = 4.96 and δ = 6.11 ppm for four protons of Cp ring. Similarly the ^{13}C NMR spectra of complexes **91** and **92** show two sets of signals for two $C(CH_3)_3$ groups at ca. δ = 29.4 and 29.9 ppm and two sets of signals at δ = 34.5 and 35.7 ppm for two quaternary carbon atoms next to phosphorous atom. Four sets of absorption signals were found for C-2, C-3, C-4 and C-5. The four different signals have been observed at ca. δ = 110.5, δ = 112.8, δ = 115.2 and δ = 117.0 ppm for (4 × CN) groups. The ^{13}C NMR spectra of **91** and **92** provide a strong evidence for the ring-opened butadienyl system showing signals at ca. δ = 213.1, δ = 180.3, δ = 75.4 and δ = 94.3 ppm, respectively for C-12, C-13, C-14 and C-15. The simple ^{1}H NMR and ^{13}C NMR spectra were well assigned which gave the information about two conformations of each complex **91** and **92**.

The ^{31}P NMR spectroscopy has a significant role in the structure elucidation of the nickel chelate complexes. The complexes **91** and **92** show one singlet at δ = 96.1 and δ = 95.8 ppm indicating that phosphane ligand is coordinated to the nickel center. The MS (ESI acetonitrile) mass spectra of complexes **91** and **92** show the molecular ion peaks $[M^+ + H]$ at m/z = 525 (28%) and m/z = 539 (29%). The HRMS (ESI acetonitrile) mass spectra have also been measured and are in close agreement with the respective molecular masses of the complexes **91** and **92**. All the analytical data confirm the constitutions of **91** and **92** except the conformation analysis. The H, H-COSYGCMF and ROESY experiments of complex **92** were performed to get the conformational analysis study which is discussed in the section 2.4.3 of this chapter.

2.4.2 [2+2] Cycloaddition Reaction of Tetracyanoethylene to the Triple Bond of σ-Acetylide Nickel Chelate Complex 80

The complex **93** was prepared by treatment of alkynyl nickel chelate complex **80** with an excess of tetracyanoethylene $(CN)_2C_2(CN)_2$ at 25 °C. The colour of the benzene solution immediately had changed from brown to dark red. After stirring for 14 h, the reaction mixture was chromatographed over silica gel (SiO_2) using petroleum ether and ethyl acetate (10:1) as eluent to obtain the product in 62% yield identified spectroscopically as a butadienyl nickel complex **93** as a dark brown solid.

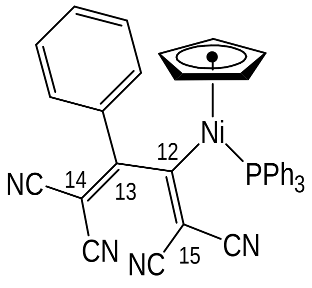


The complex **93** is an air stable compound for 1 h. However, it starts to decompose after 1 h period of time. It is soluble in most of the organic solvents (THF, diethyl ether, ethyl acetate chloroform, benzene and dichloromethane). The butadienyl complex **93** is characterized by IR, ^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectroscopy, and LREIMS spectrometry. The IR absorption bands for $\tilde{\nu}$(C≡N) and $\tilde{\nu}$(C=C) at 2223 and 1530 cm^{-1} shows an evidence for the ring-opened butadienyl system. The two sets of signals were found at δ = 1.39 and δ = 1.47 ppm for 36 protons of two $C(CH_3)_3$ groups in the ^1H NMR spectrum of complex **93.** The ethylene bridge protons show four sets of broad signals δ = 1.72, δ = 1.82, δ = 2.00 and δ = 2.25 ppm. Four sets of broad signals have been found at δ = 3.42, δ = 4.77, δ = 5.01 and δ = 6.12 ppm for four protons of Cp ring. The ^{13}C NMR spectrum of complex **93** shows two sets of signals for two $C(CH_3)_3$ groups at δ = 29.4 and 29.9 ppm and two sets of signals at δ = 34.6 and 35.7 ppm for two quaternary carbon atoms next to phosphorous atom. Four sets of signals have been observed for C-2(2′), C-3(3′), C-4(4′) and C-5(5′). In the ^{13}C NMR spectrum of **93**, signals at δ = 212.4, δ = 178.9, δ = 76.0 and δ = 94.8 ppm were observed which presumably correspond to C-12, C-13, C-14 and C-15, respectively indicating the ring-opened butadienyl formulation. The four signals have been observed at δ = 110.5, δ = 112.6, δ = 115.3 δ = 116.9 ppm for (8 × CN) groups. Like complexes **91** and **92** the ^1H NMR and ^{13}C NMR spectra gave the information for two different conformations of complex **93.**

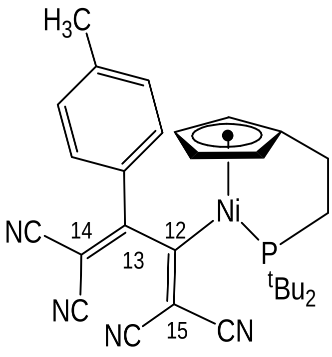
The ^{31}P NMR spectrum of **93** has a significant singlet at δ = 96.3 ppm indicating that phosphorous atom is coordinated to the nickel center. The MS (ESI acetonitrile) mass spectrum of complex **93** shows the fragment peak $[C_{15}H_{26}NiP + CH_3CN]^+$ at *m/z* = 336 (31%), obtained by the cleavage of butadienyl ligand from nickel followed by the reaction of resulting fragment with acetonitrile. The structure of complex **93** is highly hindered which facilitates the fragmentation and the molecular ion peak could not be observed in the mass spectrum. All the analytical data are in complete accord with the assigned constitution of **93**.

2.4.3 Conformational Analysis of Butadienyl Complexes Bearing Di-*tert*-butylphosphanylalkyl Chain as a Pendant Ligand

The ^1H and ^{13}C NMR spectra of butadienyl complexes **91-93** showed two sets of signals for two $C(CH_3)_3$ and four sets of signals for C-2, C-3, C-4 and C-5. Presumably these observations gave some information for the existence of conformers resulting from the rotation of C12─C13 bond and C12─Ni bond in the complexes **91-93**. Bruce et al.[93] noted that within the butadienyl ligand in the complex **61c**, the mutual dispositions of the four groups in the two dicyanomethylene fragments are such as to prevent the cisoid diene from achieving planarity. He reported the X-ray structure analysis of **61c** showing the torsion angle C15-C12-C13-C14 [67.2°]. This results in the presence of localized single bond C12─C13 [1.483(6) Å] and double bond C12=C13 [1.338(8) Å] and C13=C14 [1.356(6) Å] in the complex **61c**. This shows that the degree of twisting about the central C12─C13 bond of the diene is independent of the size of the ligand coordinating to the metal and is a reflection of the interaction between the overlapping CN groups in the complex **61c**.



61c

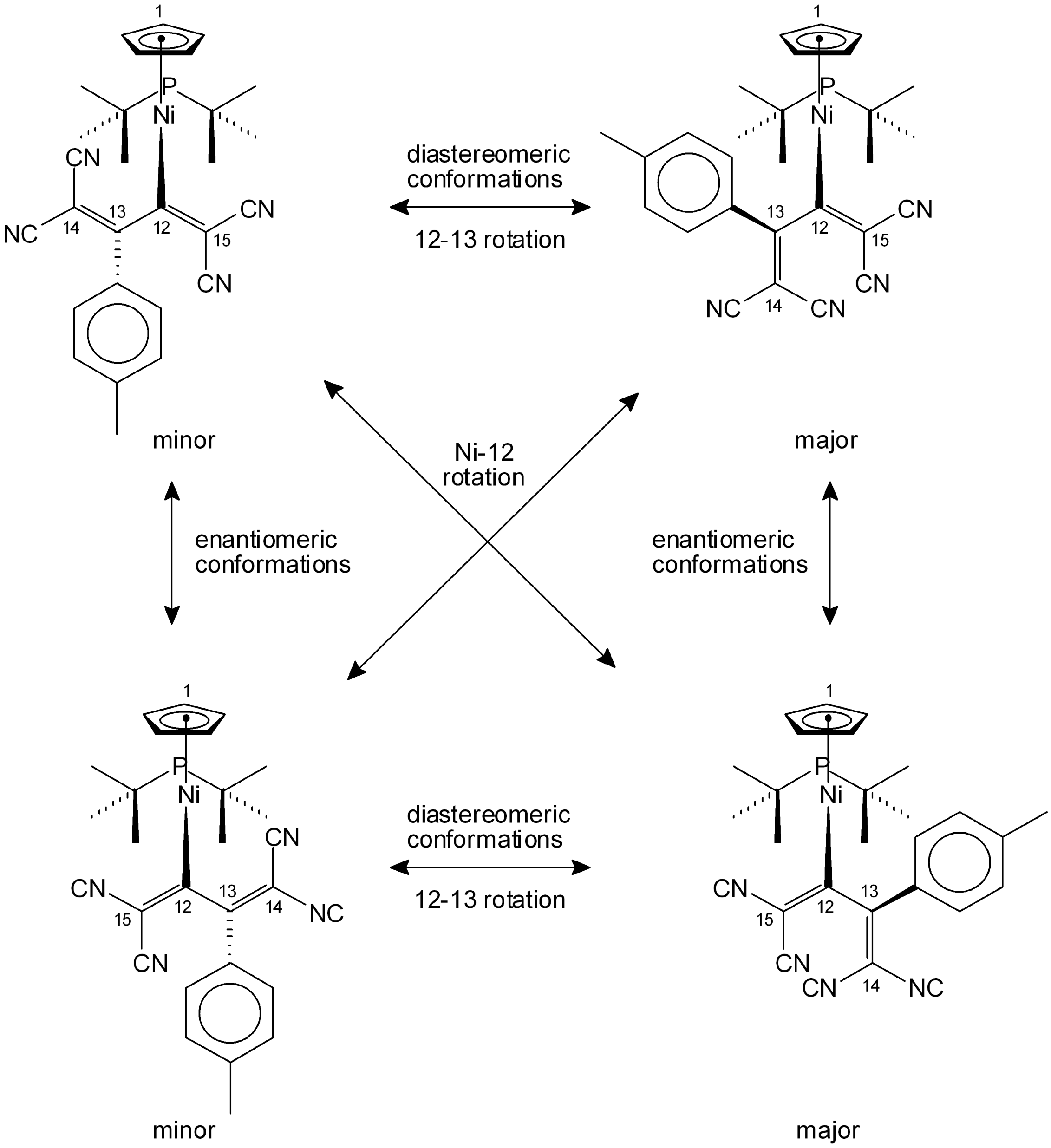


92

In complex **61c** C12─C13 bond and Ni─C12 bond independently can rotate. However, in nickel chelate complexes like **92**, the bulky di-*tert*-butylphosphane ligand connected to the Cp ring by an ethylene bridge. The staggered conformation of an ethylene bridge provides too much stability to the chelate complexes and the Ni─P bond is fixed. Due to chelate formation the rotation of Cp ring in **92** is also locked up. This shows much more influence of the two bulky *tert*-butyl groups on the geometry of complexes **91**-**93** which causes a barrier for the rotation of C12─C13 bond and Ni─C12 bond and results the different conformations of **91**-**93**.

The H, H-COSYGCMF and ROESY NMR experiments of complex **92** were performed to get the conformational analysis study which led to the following observations. As described earlier, the NMR spectra show two sets of signals with 4 Cp proton signals in a 1:1:1:1 ratio each. Each set of signals shows two $C(CH_3)_3$ proton signals. The two sets of signals have an approximate integrated ratio of 6.6:1. The two $C(CH_3)_3$ proton signals of the minor component show a much larger chemical shift difference than those of the major component. The four Cp protons of the major component show a much larger chemical shift difference than those of the minor component. The energy barrier of the exchange between the major and the minor component is rather low, thus observable on the NMR time scale at 25 °C.

From these observations it has been concluded that the 1:1:1:1 ratio of the Cp proton signals of each of the components indicates that there are four conformers present, which are two pairs of enantiomers, so that only two sets of signals are observed. The conformers show four different Cp protons each. This indicates that either one of the conformers lacks a plane of symmetry through Ni-P-C1. Obviously a rotation around the Ni─C12 bond causes a dihedral angle C15─C12─Ni─• to significantly deviate from 180°. (Scheme 4) • is the center of the Cp ring. In summary, the following four conformations are in accord with the experimental NMR data (Scheme 4).

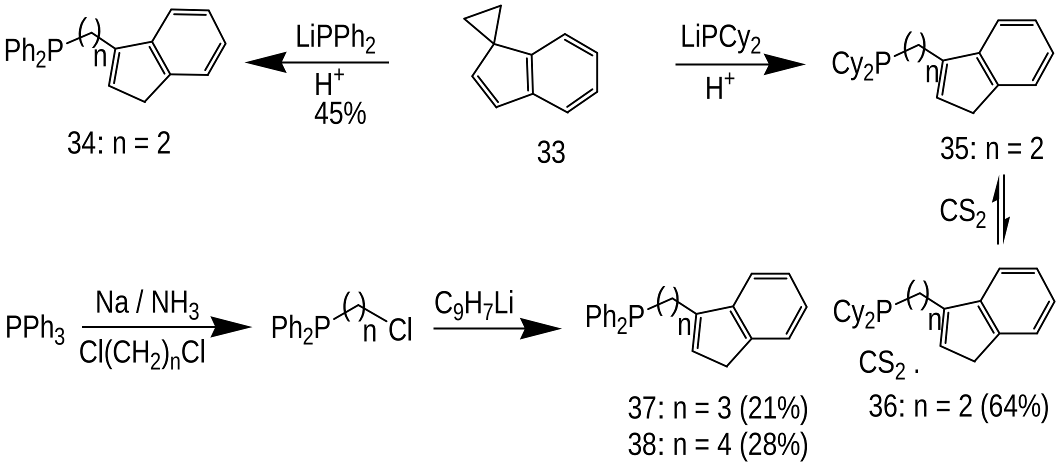


Scheme 4

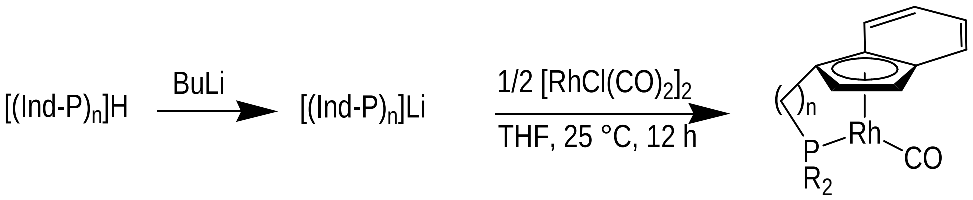
The relatively large difference in proton chemical shift of the *tert*-butyl substituents in the minor conformer and of the Cp protons in the major conformer are a result of magnetic anisotropy and indicate some proximity of the phenyl substituent to one of the *tert*-butyl substituents in the minor and to some of the Cp protons in the major conformer. This presumably is a result of a rotation around the C12─C13 bond. A rotation around Ni─C12 and around C12─C13 gives an enantiomeric conformation. These enantiomeric conformations cannot be differentiated by NMR. Rotation only around C12─C13 gives diastereomeric conformations, which can be differentiated by NMR. Rotation only around Ni─C12 gives also diastereomeric conformations, but the other enantiomer. If either one of the two rotations takes place on the NMR time scale, exchange between all signals would have to occur. This is not the case, only one exchange is observed. Therefore, only one of the rotations takes place on the NMR time scale. One cannot determine by NMR, if this is the Ni─C12 bond rotation or the C12─C13 bond rotation.

2.5 Synthesis of [1-(Di-*tert*-butylphosphanylethyl)indenyl]chloronickel(II) (63)

The development of chiral transition metal catalysts for asymmetric transformations has been one of the most significant advances in synthetic organic chemistry over the past decade.[63] The chemistry using the metal centered chirality is much less developed than using chiral auxiliaries or ligands.[63] One of the most common ligands in transition metal chemistry is the cyclopentadienyl ligand (and related substituted and indenyl versions), and there have been many attempts to develop effective chiral versions, with limited success.[118] For efficient transfer chirality from a metal complex to a substrate the source of chirality needs to be very near to the metal center. The best prospect for this with Cp complexes is when the cyclopentadiene is nonsymmetrically substituted, thus generating planar chirality on coordination to the metal. The cyclopentadienyl metal complexes bearing phosphanylalkyl chain have been reviewed.[10] Examples of cyclopentadienylphosphanylalkyl ligands with chiral centers in the connecting chain are also known.[10,57,119,120] Tani[57-59] prepared several types of achiral [Cp′-P]H ligands starting from [4,5]-benzospiro[2.4]hepta-4,6-diene (**33**).[60] Treatment of **33** with $LiPPh_2$ or with $LiPCy_2$ gave ligands **34** in 45% yield and **35** which was stored as its CS_2 adduct **36** in 64% yield. Homologues **37** and **38** were also reported by Tani[61] obtained by nucleophilic substitution of 1-chloro-3-(diphosphanyl)propane or 1-chloro-4-(diphenylphosphanyl)butane with indenyllithium in 21% and 28% yield, respectively.



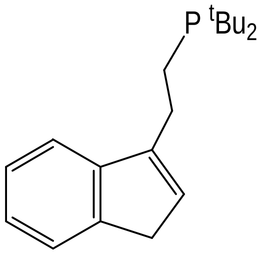
The only use of linked indenyl-phosphane achiral ligands have been reported for some rhodium complexes by Tani.[57,61] The indenyl-based planer chirality was induced in the achiral ligands [(Ind-P)$_n$]H, **34**, **35**, **37** and **38** on coordination to a metal center. The mononuclear Rh(I) complex **43** was obtained in 80% isolated yield as an air stable yellow powder. The complexes **44** (50%), **45** (71%) and **46** (64%) were also prepared by similar procedures.



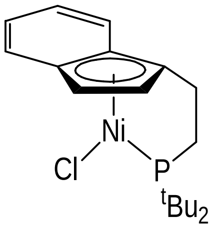
43: R = Ph, n = 2; 44: R = Ph, n = 3
45: R = Ph, n = 4; 46: R = Cy, n = 2

In order to accomplish asymmetric reactions using metal centered chirality easy and convenient methods for the preparation of optically active complexes which are configurationally stable at the metal center should be supplied. (Di-*tert*-butylphosphanylethyl)cyclopentadiene has been proven successfully to obtain cobalt[10,16-25] and nickel complexes in excellent yield, the latter one being discussed in the preceding section 2.1. The achiral analogue indenylphosphane ligand with *tert*-butyl substituent at the phosphorous atom as a pendent phosphane ligand has not been reported so far. Herein we firstly report the synthesis of the achiral di-*tert*-butyl-2-(1′-indenylethyl)phosphane ligand (**94**) and secondly, we have induced the indenyl-based planer chirality on coordination of indenylphosphane ligand **94** to the nickel center to get [1-(di-*tert*-

butylphosphanylethyl)indenyl]chloronickel(II) (**63**) which is the first planar chiral representative of nickel chelate complexes bearing a pendant phosphane ligand connected by an appropriate spacer.



94



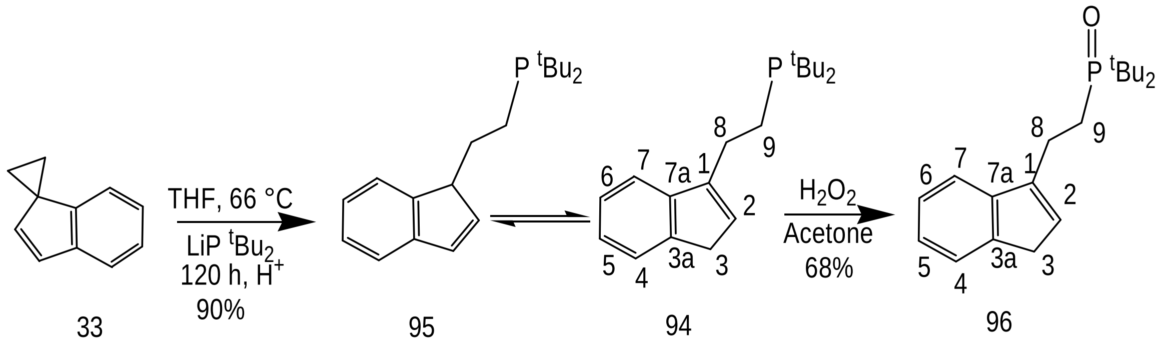
63

2.5.1 Synthesis of Di-*tert*-butyl-2-(1′-indenylethyl)phosphane (94) and its Analogue Phosphanoxide 96

At 0 °C, a solution of di-*tert*-butylphosphane in THF was treated with butyl lithium to get a yellow solution of lithium di-*tert*-butylphosphide. The reaction mixture was heated and [4,5]benzospiro[2.4]hepta-4,6-diene (**33**)[60] was added to the boiling solution. The solution was heated at reflux for 120 h. The colour of the reaction mixture had changed from yellow to red. After hydrolysis the product was extracted by pentane to get di-*tert*-butyl-2-(1′-indenylethyl)phosphane (**94**) in 90% yield as a light yellow dense oil.

Kauffmann reported the ring cleavage of [4,5]benzospiro[2.4]hepta-4,6-diene[60] (**33**) by the nucleophilic attack of lithium diphenylphosphide by heating the reaction mixture in THF for 3 h. However due to the steric bulk of di-*tert*-butylphosphide, the cyclopropane ring opening of **33** requires longer heating time. The achiral indenyl phosphane ligand **94** is obtained as a stable compound and can be stored at low temperature under protective gas but is oxidised in a very short period of time to its analogue phosphanoxide **96**.

For the oxidation of **94**, indenylethylphosphane **94** in acetone was treated with hydrogenperoxide. The reaction mixture was stirred at 25 °C for 30 min. After removal of the solvent, water was added to the residue. The product was extracted by chloroform to get the di-*tert*-butyl-2-(1′-indenyl)ethylphosphanoxide (**96**) in 68% yield as an off white solid.



The di-*tert*-butyl-2-(1′-indenylethyl)phosphane (**94**) is the first example of achiral indenyl ligand contaning the di-*tert*-butylphosphane part connected to the indenyl moiety by an appropriate spacer which is highly sensitive to air and can be oxidised in a very short period of time if exposed to air. However it has been observed that **94** is stable and can be stored under protective gas at low temperature for two or three weeks. The achiral ligand **94** is soluble in all common organic solvents (THF, diethyl ether, chloroform, ethyl acetate and petroleum ether). The indenylethylphosphanoxide **96** is an air stable compound and soluble in polar solvents. The di-*tert*-butyl-2-(1′-indenylethyl)phosphane (**94**) and its analogue phosphanoxide **96** are fully characterized by IR, ^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectroscopy, and LREIMS (ESI acetonitrile) and HREIMS (ESI acetonitrile) spectrometry. The characteristic absorption in the IR spectrum of **96** is the absorption of P=O group which is observed at 1260 cm^{-1}, however, the absorption band at 1260 cm^{-1} has also been observed in the IR spectrum of **94**, which is obtained due to the oxidation of the sample during recording the IR spectrum.

The significant absorption signals in the ^{1}H NMR spectra of **94** and **96** are the two multiplet signals for 8-H and 9-H which are observed at δ = 1.73-1.78 ppm and δ = 2.75-2.81 ppm, respectively, in the ^{1}H NMR spectrum of **94**, while the ^{1}H NMR spectrum of **96** shows the respective multiplets for 8-H and 9-H at δ = 2.07 ppm and δ = 2.93 ppm. Another characteristic absorption obtained in the ^{1}H NMR spectra of **94** and its phosphanoxide **96** is the signals at δ = 3.35 and δ = 3.34 ppm, respectively, for two methylene protons 3-H. The regeoisomer **95** is not stable and **94** is obtained which is confirmed by ^{1}H NMR spectrum. The ^{1}H NMR spectrum of **94** exhibits one dublet at δ = 1.21 ($^{3}J_{\mathrm{PH}}$ = 11.0 Hz) ppm which corresponds to 18 protons of the two $C(CH_3)_3$ groups. In the ^{1}H NMR spectrum of **96**, the two $C(CH_3)_3$ groups absorb at δ = 1.31 ($^{3}J_{\mathrm{PH}}$ = 13.1 Hz) ppm. The ^{13}C NMR spectrum of **94** shows characteristic absorptions at δ = 29.4 ($^{1}J_{\mathrm{CP}}$ = 29.1 Hz) ppm, which corresponds to carbon atom C-9 and the respective carbon atom C-9 in the spectrum of **96** absorbs at δ = 27.2 ($^{1}J_{\mathrm{CP}}$ = 70.9 Hz) ppm. Another noticeable absorption in the ^{13}C NMR spectrum of **94** is at δ = 31.5 ($^{1}J_{\mathrm{CP}}$ =

19.8 Hz), which corresponds to the quaternary carbon atoms next to phosphorous. The respective absorption signal for these quaternary carbon atoms in the ^{13}C NMR spectrum of **96** is obtained at δ = 36.3 ($^{1}J_{CP}$ = 58.7 Hz) ppm. The spectra of **94** and **96** show absorptions for carbon atom C-3 at δ = 37.7 and δ = 37.8 ppm, respectively, indicating that the regioisomer **94** is stable and **96** can not be obtained. The ^{1}H NMR and ^{13}C NMR spectra of **94** and **96** are well assigned and all the other absorption signals are in expected range.

In the structure elucidation of **94** and **96** the significant role is the absorption of phosphorous atom. The ^{31}P NMR spectrum of **94** shows one singlet at δ = 32.2 ppm which is within the typical absorption range of a P^{III} compound[121] like the achiral ligand **94**. The respective absorption in the ^{31}P NMR spectrum of the phosphanoxide **96** is obtained as a singlet at δ = 60.2 ppm also falling in the typical range of phosphanoxide[122,123] which confirms that **96** is a P^{V} compound.

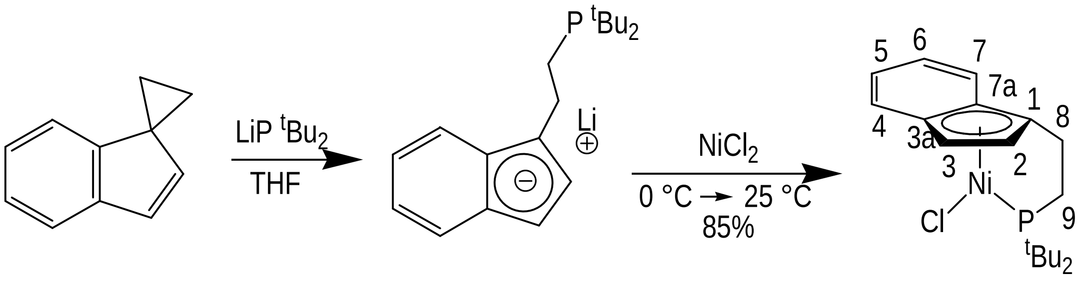
The LRMS (ESI acetonitrile) mass spectrum of **94** shows the molecular ion peak [M^{+} + H] at m/z = 289 (54%). The LRMS (ESI acetonitrile) mass spectrum of **96** exhibits the molecular ion peak [M^{+} + H] at m/z = 305 (55%). The HRMS (ESI acetonitrile) mass spectra were also measured which are in close agreement to all the analytical data. All measurements are in complete accord to the assigned constitutions of **94** and **96**.

2.5.2 Microwave-Assisted Cyclopropane Ring Cleavage of [4,5]-Benzospiro[2.4]-hepta-4,6-diene (33)

Microwave (MW) heating has emerged as a powerful technique by which reactions can be brought to completion in minutes rather than hour or days.[124] Butyllithium was added dropwise at 25 ^{o}C into the THF solution of di-*tert*-butylphosphane. After stirring for 2 h at 25 °C, spiroindene was added. To avoide the extended reaction time of 5 days for the cyclopropane ring cleavage of **33**, the solution was heated under microwave irradiations (Power = 200 W, Temperature = 150 °C, Ramp time = 3 min, Hold time = 40 min). The colour of the reaction mixture had changed to dark red. The solution was cooled to 25 °C. The normal workup of the reaction mixture yielded a light yellow dense oil in 91% yield identified as di-*tert*-butyl-2-(1′-indenylethyl)phosphane (**94**). Although the ring cleavage of spiroindene with conventional heating gave 90% yield of **94**. The microwave technique was more successful because of the significantly reduced reaction time.

2.5.3 Synthesis of [1-(Di-*tert*-butylphosphanylethyl)indenyl]chloronickel(II) (63)

The synthesis of indenyl nickel chelate complex **63** bearing a pendant phosphane ligand separated by an ethylene bridge can be accomplished by the application of the method introduced by Kölle.[47] The anion **97** was prepared by the cyclopropane ring cleavage of [4,5]benzospiro[2.4]hepta-4,6-diene[60] (**33**) by the nucleophilic attack of di-*tert*-butylphosphide. The lithium di-*tert*-butylphosphide was easily accessible at 0°C by the treatment of di-*tert*-butylphosphane with butyllithium in THF. The light yellow THF solution of lithium di-*tert*-butylphosphide was heated and spiroindene **33** was added. The reaction mixture was heated at reflux for 120 h till the colour of the solution had changed from light yellow to red. After removal of solvent and unconsumed phosphane, the residue was dissolved in THF. Anhydrous $NiCl_2$ was added to the solution at 0 °C. The colour changed from red to dark purple. After 14 h stirring at 0 °C the solvent was removed and the product was crystallized from diethyl ether at −20 °C to obtain pure [1-(di-*tert*-butylphosphanylethyl)indenyl]chloronickel(II) (**63**) in 85% yield as a deep purple solid.



33 97 63

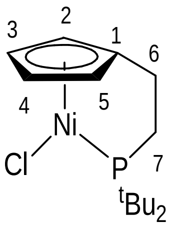
Complex **63** in hand is the first indenyl-based planar chiral nickel chelate complex with a hemilabile phosphanylalkyl chain. The complex **63** seems to be more stable than **62** if exposed to air. **63** can be handled in air for 1 h. Recently, one publication appeared in which it has been reported that all attempts at preparing the indenyl nickel chelate complex bearing a pendant phosphanylalkyl ligand, an analogue of **63**, were unsuccessful.[125] Fortunately the indenyl-based planar chiral nickel chelate complex **63** was prepared successfully in good yield. Here one point to be noted during course of the reaction is that complete exclusion of air is necessary for the complexation. The achiral indenyl phosphane **94** itself is highly air sensitive and anionic intermediate **97**, which can be obtained from the deprotonation of **94**, is much more reactive to air. Complex **63** is soluble in all common organic solvents (THF, diethyl ether, dichloromethane, chloroform, hexane and toluene). The indenyl-based planar chiral nickel chelate complex **63** is fully characterized by IR, ^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectroscopy, and LREIMS (ESI acetonitrile) and HREIMS (ESI acetonitrile) spectrometry including elemental analysis.

The ^{1}H NMR spectrum of **63** shows two signals for the two diastereotopic *tert*-butyl groups on phosphorous atom showing two doublets at δ = 1.31 and δ = 1.45 ppm. Diastereotopically an ABCDX spin system is observed showing two multiplet peaks at δ =1.87-1.94 and δ=2.4-2.6 ppm for the two sets of methylene protons of the bridge 8-H and 9-H respectively. The spectrum shows one doublet of doublet signal at δ = 5.42 ppm which corresponds to one proton 3-H of the indenyl unit. While 2-H absorbs at δ = 6.76 ppm. The four protons 4, 5, 6, 7-H show an ABCD spin system in the ^{1}H NMR spectrum.

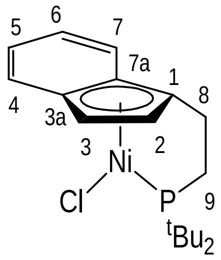
The ^{13}C NMR spectrum shows the absorptions of the two carbon atoms of ethylene bridge at δ = 25.8 and δ = 34.5 ppm for C-8 and C-9, respectively. The spectrum shows two different peaks at δ = 28.8 and δ = 29.4 ppm for the methyl carbon atoms of the two diastereotopic *tert*-butyl groups at the phosphorous atom. Similarly two different signals are observed for two quaternary carbon atoms next to the phosphorous atom which absorb at δ = 34.7 and δ = 35.9 ppm. The two carbon atoms C-2 and C-3 absorb at δ = 105.7 and δ = 81.2 ppm respectively while the carbon atom C-1 shows a signal at δ = 89.8 ppm. The ^{1}H NMR and ^{13}C NMR spectra of **63** have been well assigned, and all the signal absorptions observed are within typical range. The significant feature observed in the structure elucidation of complex **63** is the absorption of phosphorus atom in ^{31}P NMR spectrum which is observed as one singlet at δ = 84.2 ppm indicating that phosphorous side arm of the pendant phosphane ligand is coordinated to nickel center.

The LREIMS mass spectrum exhibits the molecular ion peak [M^{+}] at *m/z* = 380 (61%), which shows that **63** is not a dimeric complex. A fragment peak [M^{+} – NiCl +1] is observed at *m/z* = 288 (66%). All other signals obtained in the mass spectrum are in complete accord to the fragmentation pattern of the desired constitution of **63**. The HRMS mass spectrum was also measured and is in close agreement with all the analytical data. A correct elemental analysis data was also obtained. All these measurements confirm the assigned constitution of complex **63**.

The indenyl-based planar chirality can be explained by the NMR spectroscopic comparative study of **62** and **63**. The ^{1}H NMR spectrum of **62** exhibits one triplet at δ = 1.46 and one dublet of dublet at δ = 2.18 ppm for the 6-H and 7-H while the respective ^{1}H NMR spectrum of **63** shows an ABCDX spind system for 8-H and 9-H as two multiplets at δ = 1.87-1.94 and δ = 2.4-2.6 ppm, respectively. Similarly the six methyl groups in the ^{1}H NMR spectrum of **62** show one dublet at δ = 1.54 ppm. The ^{1}H NMR spectrum of **63** shows two doublets at δ =1.31 and δ = 1.45 ppm for the corresponding two diastereotopic *tert*-butyl groups. The ^{13}C NMR spectrum of complex **63** also shows two different signals for the six methyl carbon atoms of the two *tert*-butyl groups as two doublets at δ = 28.8 and δ = 29.4 ppm indicating diastereotpicity caused by the planar chirality induced by the indenyl ring on the coordination to the nickel center. The ^{13}C NMR spectrum of **62** shows only one doublet at δ = 30.3 ppm for the six methyl carbon atoms of both *tert*-butyl groups. Two quaternary carbon atoms next to phosphorous in the ^{13}C NMR spectrum of **62** show one signal at δ = 34.8 ppm and the ^{13}C NMR spectrum of **63** shows two different doublets at δ = 34.7 and δ = 35.9 ppm for the two diastereotopic quaternary carbon atoms.



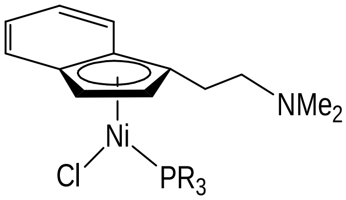
62



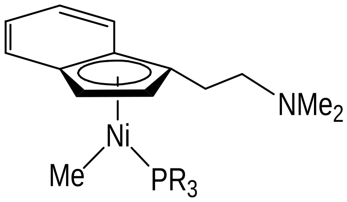
63

2.6 Synthesis of [1-(Di-*tert*-butylphosphanylethyl)indenyl]methyl- and –σ-alkynyl nickel(II)

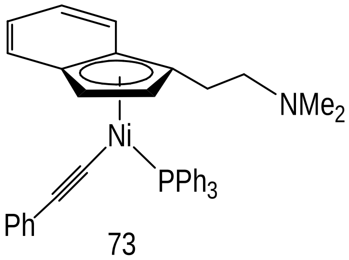
In the connection with section 2.3 reports have shown that the indenyl alkynyl and alkyl complexes **72-74** bearing a dimethylaminoethyl moiety as hemilabile ligand catalyze a number of important reactions.[114] Zargarian prepared the indenyl chloro complexes **69-71** and the alkynyl and alkyl complexes **72-74**. He reported that these indenyl complexes can catalyze the polymerization of styrene and hydrosilylation of styrene and 1-hexene with $PhSiH_3$ and Ph_2SiH_2.[114]



69: R = Ph
70: R = Me
71: R = Cy

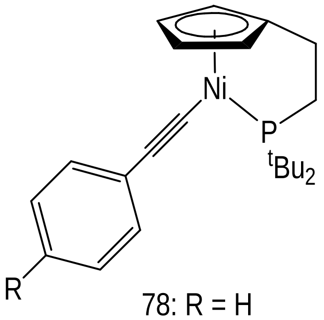


72: R = Ph
74: R = Me

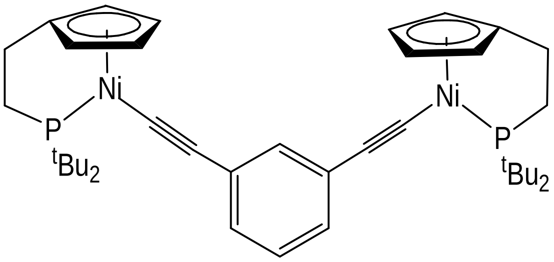


73

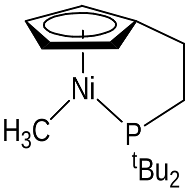
The syntheses of alkynyl nickel complexes **78-80** and alkyl chelate complex **81** bearing a pendant di-*tert*-butylphosphane ligand connected by an ethylene bridge and also having the indenyl-based planar chiral nickel chelate complex **63** in hand encouraged us to explore ligand exchange reactions of **63**.



78: R = H
79: R = CH$_3$



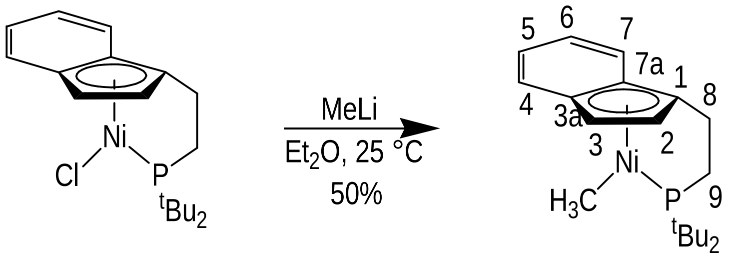
80



81

2.6.1 Synthesis of [1-(Di-*tert*-butylphosphanylethyl)indenyl]methylnickel(II) (98)

The preparation of [1-(di-*tert*-butylphosphanylethyl)indenyl]methylnickel(II) (**98**) was accomplished via a metathetic reaction of complex **63** and MeLi. Treatment of complex **63** with MeLi in diethyl ether at 25 °C changed the colour of solution from dark purple to dark brown. After 1 h stirring the solution was filtered through celite. After solvent removal the product was recrystallized from the saturated solution in hexane at −20 °C to yield the desired complex **98** in 50% as a green crystalline solid.



63 98

Alkyl chelate complex **98** is soluble in all common organic solvents (THF, diethyl ether, hexane, dichloromethane and chloroform). It has been observed that complex **98,** obtained by the replacement of Cl ligand by weakly electron donating methyl group, is less stable than **63**. However, **98** can be handled in air for 2 h. In solution methyl nickel chelate **98** immediately decomposes. Due to the solution phase instability ^{1}H NMR and ^{13}C NMR spectra could be obtained, however, all the signals were broad indicating the decomposition of the complex **98**. The proposed complex **98** is characterized by IR, ^{31}P NMR spectroscopy, LREIMS and HRMS spectrometry and X-ray structure diffraction study.

The ^{31}P NMR spectrum of **98** could be achieved which shows one singlet at δ = 85.1 ppm indicating that di-tert-butylphosphanylethyl chain is coordinated to the nickel center. The spectrum also shows absorption peak at δ = 60.3 ppm which corresponds to P=O group obtained from the oxidation of the phosphane side arm. The LREIMS mass spectrum of alkyl nickel chelate **98** exhibits the molecular ion peak also as a base peak [M^{+}] at *m/z* = 360 (100%). A fragment peak [M^{+} – CH$_3$] at *m/z* = 345 (31%) is observed, which is obtained by the loss of methyl group. All other fragment peaks observed in the mass spectrum are in close agreement to the fragmentation pattern of the assigned constitution of **98**. The HRMS mass spectrum of **98** was obtained which is in complete accord to the desired molecular mass of the complex **98**. Finally the assigned constitution of the alkyl indenyl-based planar chiral nickel chelate complex **98** was confirmed by X-ray structure analysis data. Complex **98** was recrystallized from the saturated solution in hexane at −20 °C to get the green crystals suitable for X-ray structure analysis. The plot of the structure in the crystal is depicted in figure 8. Some selected bond lengths and bond angles for **98** are listed in tables 10 and 11.

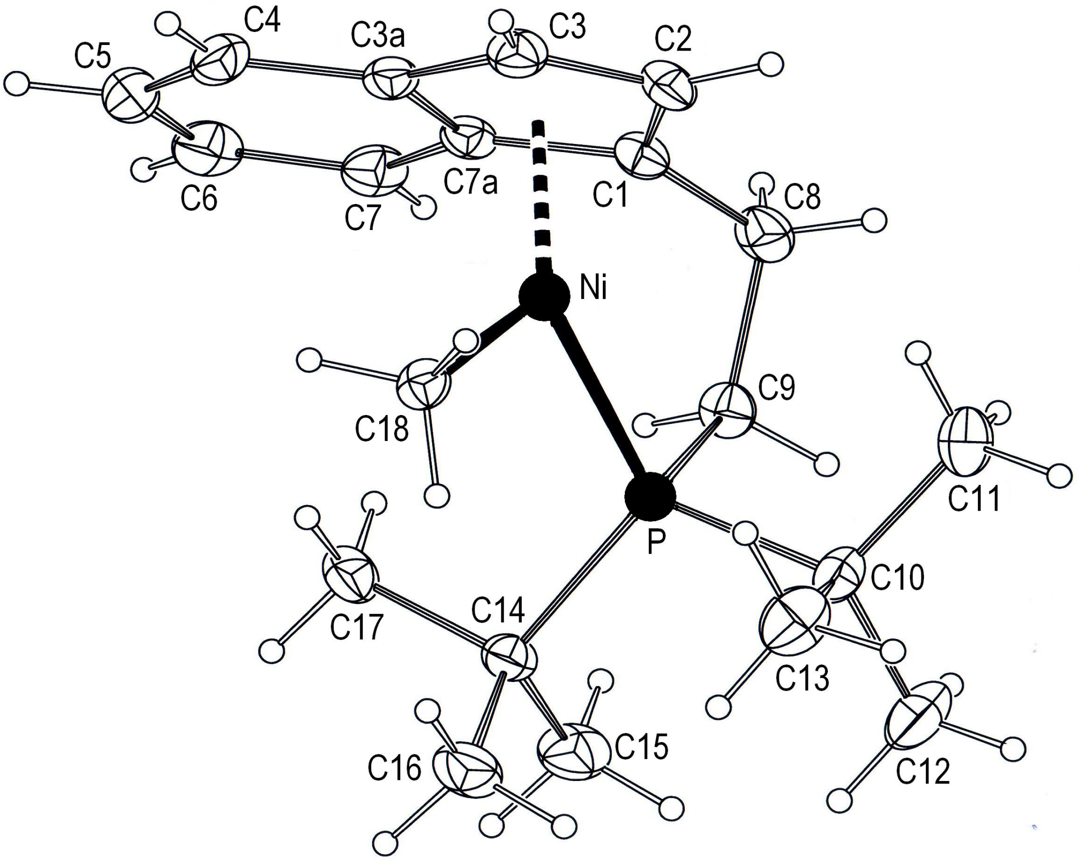


Fig. 8: structure of **98** in the crystal.

Table 10. Selected bond lengths for **98**.

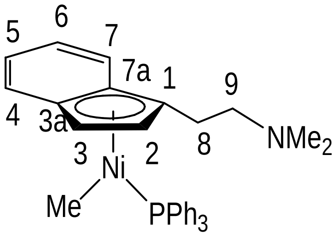
Bond	**Bond length in Å**	**Bond**	**Bond length in Å**
Ni-C1	2.071(2)	Ni-P	2.1532(9)
Ni-C2	2.050(3)	C2-C3	1.397(4)
Ni-C3	2.084(3)	C3-C3a	1.438(4)
Ni-C3a	2.315(3)	C3a-C7a	1.427(4)
Ni-C7a	2.334(3)	C1-C2	1.414(4)
Ni-C18	1.977(2)	C1-C7a	1.447(4)
C3a-C4	1.397(4)	C4-C5	1.368(4)
C5-C6	1.389(4)	C6-C7	1.374(4)
C7-C7a	1.392(4)	C1-C8	1.502(4)

Table 11. Selected bond angles for **98**.

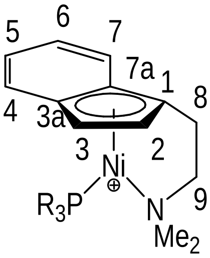
Bond angle	**[°]**	**Bond angle**	**[°]**
C18-Ni-C1	167.11(11)	C18-Ni-P	104.09(8)
C1-Ni-C3a	63.52(10)	C8-C1-Ni	115.9(2)
C3-Ni-C3a	37.68(10)	C1-Ni-P	88.37(8)
C1-C8-C9	111.3(2)	C9-P-Ni	102.10(9)

The structure of complex **98** shows some disorder due to the (di-*tert*-butylphosphanyl)ethyl moiety, as indicated by the large anistropic displacement parameters. This has also been observed for some nickel complexes[114] bearing the dimethylaminoethyl moeity as hemilabile ligand because of the staggered conformation of the ethylene bridge like in the complex **77**.[114] All the bond lengths and bond angles fall within the expected range of values. The Ni-C18 bond length [1.977(2) Å] is in typical range of σ-alkyl nickel complex indicating that the methyl group is strongly bonded to the nickel atom. The Ni-P bond length [2.1532(9) Å] also falls in the typical range showing the strong interaction of the pendant phosphane ligand to the nickel center. The Ni─C2 bond length [2.050(3) Å] is shorter than the other nickel carbon atoms bond lengths. C2 is the least affected by the benzene annellation presumably results some structure flexibility. This indicates that the coordination of the indenyl ring is off-center resulting the Ni atom closer to C2. The Ni─C1 bond length [2.071(2) Å] and the Ni─C3 bond length [2.084(3) Å] are shorter than the Ni-C3a bond length [2.315(3) Å] and Ni-C7a bond length [2.334(3) Å] which shows more interaction to the C1, C2 and C3 end of indenyl resulting the bending of this end more toward the nickel center. It has been also observed in the indenyl complexes **72** and **77**.[114] The bond angles C18-Ni-C1 [167.11(11)°], C18-Ni-P [104.09(8)°] and C1─Ni─P [88.37(8)°] indicate that phosphane region is sterically shielded and that the region around the methyl group is well accessible.

In the literature very few examples of X-ray structure analyses of indenyl nickel complexes with hemilabile ligands connected by an appropriate spacer exist.[114] The X-ray structure of complex **98** is the first one representative of indenyl-based planar chiral nickel chelate complexes bearing a pendant phosphanylalkyl ligands. Having the X-ray structure analysis of **98** at hand confirms the constitution of **98** and its parent chelate complex **63**. The comparative solid state structure analysis study of the alkyl nickel chelate **98** with the nickel complexes **72** and**77** gave interesting information about the structure. Some comparative bond lengths are listed in table 12.[114]



72



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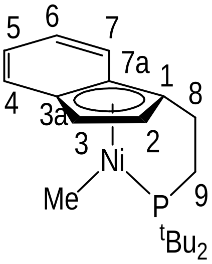


98

Table**:** 12. Selected bond lengths in Å for **72, 77** and **98**.

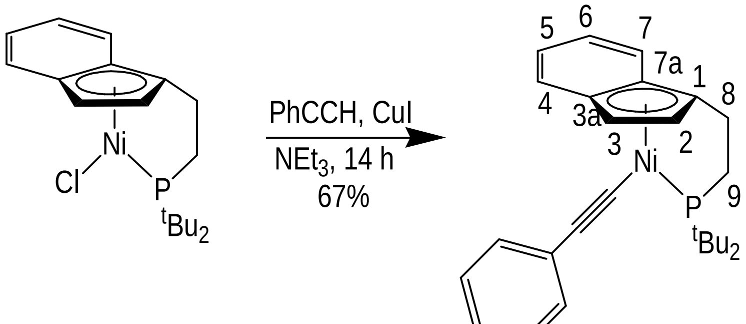
Bond	**72**[114]	**77**[114]	**98**
Ni-C1	2.0870(17)	2.0660(18)	2.071(2)
Ni-C2	2.0810(17)	2.0466(19)	2.050(3)
Ni-C3	2.1012(16)	2.096(2)	2.084(3)
Ni-C3a	2.2659(15)	2.4172(19)	2.315(3)
Ni-C7a	2.2811(16)	2.3932(19)	2.334(3)
Ni-Me	1.9508(17)	------	1.977(2)
Ni-P	2.1277(5)	2.2424(5)	2.1532(9)

All the bond lengths of the complex **98** fall within the range of expected values. However, there is significant bond lengths difference as shown in the table **12**. The Ni─methyl bond length [1.977(2) Å] in **98** is longer than the respective Ni─methyl bond length [1.9508(17) Å] in **72**[114], presumably because of the steric hindrance of the two *tert*-butyl groups on the phosphorous atom. The Ni─C2 bond length [2.050(3) Å] is shorter than the other carbon atoms to nickel in **98** indicating the coordination of the Ni atom off-center which results the slippage of cyclopentadiene ring from the plane of the benzene ring more toward the nickel. The same trend has been observed in the complexes **72** and **77.**[114] The chelate formation also has a pronounced effect on the disorder of the indenyl ring as shown the comparative bond lengths in table **12**. In complex **72** there is no interaction between hemilabile aminoethyl moiety and nickel center resulting no difference between the Ni─C1 bond length [2.0870(17) Å] and the Ni─C2 bond length [2.0810(17) Å]. The complex **98** shows the chelate formation which results that the Ni─C1 bond length [2.071(2) Å] is longer than the Ni─C2 bond length [2.050(3) Å]. The same effect of chelation has also been observed in complex **77.**[114] The Ni─P bond [2.1532(9) Å] in **98** is longer than the respective

Ni─P bond [2.1277(5) Å] in **72** presumeably due to hinderence of the bulky *tert*-butyl groups on the phosphorous atom in **98**. The staggered conformation of the ethylene bridge resulting from the chelate formation causes larger the C18-Ni-P bond angle [104.09(8)°] in **98** than the corresponding angle C18-Ni-P [93.23°(6)] in **72**.[114] It is concluded that the five membered ring in the indenyl unit loses its planarity from the benzene ring caused by the chelate formation.

2.6.2 {[1-(Di-*tert*-butylphosphanylethyl)indenyl](2-phenylethynyl)}nickel(II) (99)

For the preparation of novel alkynyl complex **99**, a mixture of **63** and catalytic amount of CuI was suspended at 25 °C in freshly distilled triethylamine. On the addition of phenyl ethyne, the colour of the suspension changed from dark purple to violet brown. After stirring the reaction mixture at 25 °C for 14 h the product was extracted with diethyl ether and chromatographed over silica gel by using petroleum ether / ethyl acetate (10 : 1) as eluent to obtain the alkynyl indenyl nickel chelate complex **99** in 67% yield as a deep brown solid.



63 99

The complex **99**, obtained by the replacement of the Cl ligand in **63** with more strongly donating alkynyl ligand, is more stable than **63**. Complex **99** can be handled in air for 2 to 3 h. The alkynyl complex **99** is soluble in all common organic solvents (THF, diethyl ether, dichloromethane, chloroform, hexane and toluene). The indenyl nickel chelate complex **99** is fully characterized by IR, ^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectroscopy, and LREIMS (ESI acetonitrile) and HREIMS (ESI acetonitrile) spectrometry.

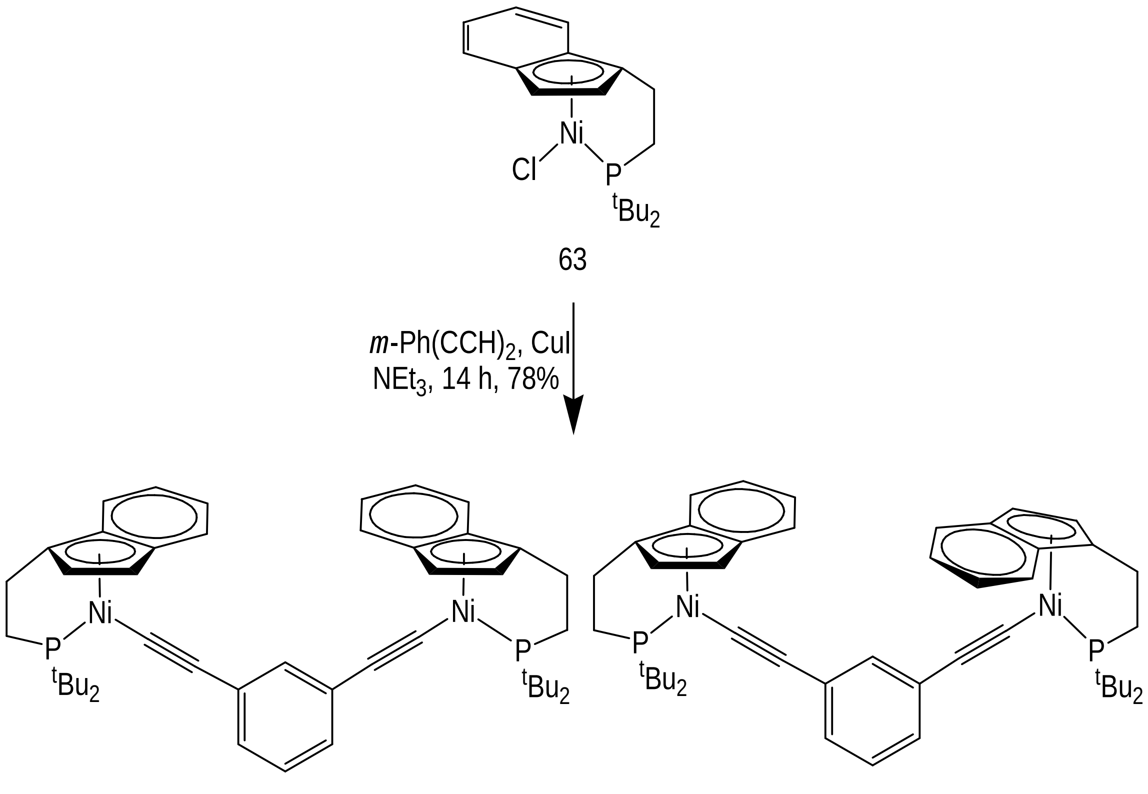
The IR spectrum of **99** exhibits noticeable absorption bands at 2168 and 2085 cm^{-1} $\tilde{\nu}$ (C≡C) streching. The absorption bands obtained in the IR spectrum of **99** at 3051, 2958, 2899 and 2869 cm^{-1} are for aromatic and aliphatic streching $\tilde{\nu}$ (C─H). The ^{1}H NMR spectrum of **99** shows the upfield shift of the two *tert*-butyl groups as two dublets at $\delta = 1.20$ and $\delta =$

1.40 ppm than the respective two dublets at $\delta = 1.31$ and $\delta = 1.45$ ppm in the spectrum of **63**. The four protons 8-H and 9-H of the ethylene bridge show absorption as a multiplet showing the diastereotopically ABCDX spin system at $\delta = 2.19$-2.47 ppm. The ^{13}C NMR spectrum of **99** shows significant absorptions for (C≡C) which are observed at $\delta = 97.6$ and $\delta = 117.4$ ppm for α and β carbon atoms to the nickel respectively. The ^{1}H NMR and ^{13}C NMR spectra of **99** are well assigned and all the absorption signals observed are within typical range. The noticeable point in the structure elucidation of alkynyl complex **99** is the absorption of phosphorus atom in ^{31}P NMR spectrum which is observed as one singlet at $\delta = 95.6$ ppm indicating that phosphorous side arm of the pendant phosphane ligand is coordinated to nickel center.

The LRMS (ESI acetonitrile) mass spectrum of **99** exhibits the molecular ion peak [M^+] at *m/z* = 447 (13%). The spectrum shows the base peak [M^+ – PhCC + CH_3CN] at *m/z* = 386 (100%) which is obtained by the cleavage of acetylide linkage from nickel center followed by the reaction of the resulting fragment with acetonitrile. The HRMS (ESI acetonitrile) spectrum was also obtained which is in close agreement to the expected molecular mass of complex **99**. All the analytical data are in complete accord to the assigned constitution of **99**.

2.6.3 Synthesis of 1,3-Bis{[1-(di-*tert*-butylphosphanylethyl)indenyl]nickel(II)-ethynyl}benzene (100)

For the synthesis of complex **100** a suspension of a planar chiral complex **63** and catalytic amount of CuI was treated with 1,3-diethynylbenzene at 25 °C in triethylamine. The colour of the suspension changed from deep purple to violet brown. After stirring the reaction mixture for 14 h, the crude product was extracted with diethyl ether and chromatographed over silica gel by using petroleum ether / ethyl acetate (10:1) as eluent to obtain 1,3-bis{[1-(di-*tert*-butylphosphanylethyl)indenyl]nickel(II)ethynyl}benzene (**100**) in 78% yield as a deep brown solid, spectroscopically identified as a mixture of a *meso* and racemic material (ca. 100:9 or ca. 9:100). The bimetallic complex **100** is soluble in THF, diethyl ether, ethyl acetate, TBME, dichloromethane and chloroform. Complex **100** seems to be more stable than **63** and can be handled in air for 2 to 3 h.



63

meso 100 *rac*

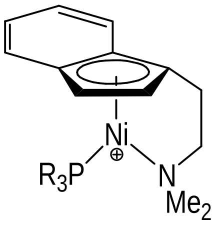
The indenyl nickel chelate complex **100** is fully characterized by IR, ^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectroscopy, and LREIMS (ESI acetonitrile) and HREIMS (ESI acetonitrile) spectrometry. The IR spectrum of **100** shows characteristic absorption bands at 2160 and 2083 cm^{-1} for $\tilde{\nu}$ (C≡C) streching. The ^{1}H NMR spectrum of **100** shows one set of signals as two doublets at δ = 1.21 and δ = 1.40 ppm while the second set of signals found are two doublets at δ = 1.26 and δ = 1.32 ppm for the two diasteriotopic *tert*-butyl groups. Similarly the ^{13}C NMR spectrum of **100** also shows two doublets at δ = 28.9 and δ = 29.5 ppm as one set of signals and other set of signals were observed at δ = 29.1 and δ = 29.9 ppm for the two diastereotopic $C(CH_3)_3$ groups. The ^{13}C NMR spectrum also shows two sets of signals for two diastereotopic quaternary carbon atoms next to the phosphorous atom. Two doublets at δ = 34.9 and δ = 36.0 ppm and other set of signals as two doublets at δ = 35.1 and δ = 35.7 ppm, were observed for the minor and major configurations, respectively. The significant absorptions for (C≡C) were observed at δ = 97.6 and δ = 117.4 ppm for α and β carbon atoms, respectively. In the structure elucidation of alkynyl complex **100**, ^{31}P NMR spectrum gave the key information about the assigned constitution of **100**. The ^{31}P NMR spectrum of **100** shows absorption of phosphorus atom as two singlets at δ = 96.0 and δ = 86.8 ppm showing the two diastereomers. The ^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra led us to the conclusion that two sets of signals were observed for a mixture of meso and racemic mixture in a ratio ca. 100:9. However, the assignment of the signals which is meso and which is recemate could not be made by ^1H NMR and ^{13}C NMR spectroscopy. The signals might be assigned by ^{31}P NMR spectroscopy using shift reagent.

The LRMS (ESI acetonitrile) mass spectrum of **100** shows the molecular ion peak $[M^+ + H]$ at *m/z* = 815 (1%). The spectrum shows the base peak $[C_{19}H_{28}NiP + CH_3CN]$ at *m/z* = 386 (100%) which is obtained by the cleavage of alkynyl linkage from the nickel center followed by the reaction of the resulting fragment with acetonitrile. The HRMS (ESI acetonitrile) spectrum was also obtained which is in close agreement with the assigned molecular mass of complex **100**. All the analytical data are in complete accord with the proposed constitution of **100**.

A comparison of the ^{31}P NMR chemical shift of the alkynyl substituted chelates **99** and **100** (δ = 95.6 and δ = 96.0 ppm, respectively) with that of the chloro substituted chelate **63** (δ = 84.2 ppm) reveals that electron withdrawing ligands cause an upfield shift where as electron donating ones cause a downfield shift.

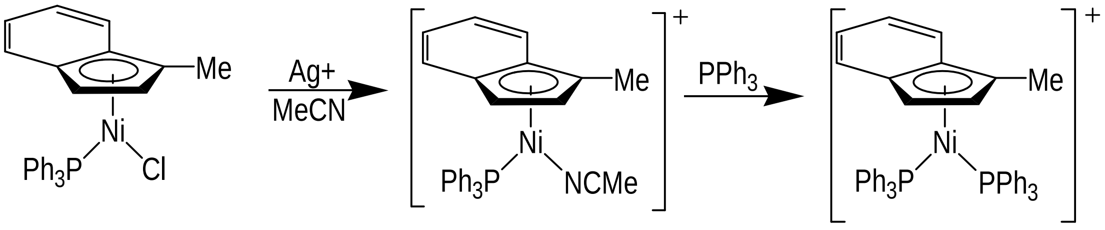
2.7 Synthesis of [(Di-*tert*-butylphosphanylethyl)cyclopentadienyl](acetonitrile)-nickel(II) Complexes

The importance of transition metal based cationic species in catalysis has been amply demonstrated in numerous studies.[126] In connection with section 2.3 reports have shown that metal centred cationic species catalyze polymerization of olefins and acetylenes and hydrosilylation of olefins acetylene and ketones[114, 127,128] and can promote a variety of others, such as C─H bond activation,[129] substitution and insertion.[130] In the search for direct access to obtain cationic species, a strategy based on a system has been explored in which one coordination site at nickel is temporarily occupied by a hemilabile ligand. This has been demonstrated with complexes such as $[(IndCH_2CH_2NMe_2)Ni(PPh_3)]^+$ **75**, which catalyze the polymerization of styrene promoted by the hemilabile coordination of the tethered amine moiety.[114,131] Zargarian et al.[131] reported that complex **75** is not reactive toward styrene at room temperature, but heating at 80 °C initiated the polymerization reaction. The complexes **76** and **77** also promote polymerization of styrene at room temperature but high level of catalytic activity and large molecular weights are obtained only at higher temperatures. The level of catalytic activity in these reactions seems to be affected mainly by steric effects.[114]



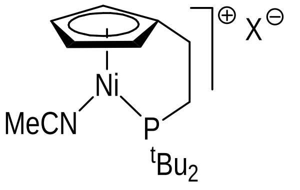
75: R = Ph
76: R = Me
77: R = Cy

As described in the previous section 2.3 the cationic complexes **75-77** were also reported as single component precatalysts in the olefin hydrosilylation reactions.[114] The most active precatalyst is the one bearing the most strongly donating phosphane ligand PMe_3 and is suggested that the hydrosilylation reaction does not involve phosphane ligand dissociation. It is believed that the catalysis involves the dissociation of the chelating amine moiety. Zargarian[132] reported the reaction of **101** with $AgBF_4$ in MeCN. The reaction product was identified as $[(1\text{-Me-Ind})Ni(PPh3)(MeCN)]^+$ **102**. The coordinated MeCN in **102** can be displaced readily by stronger ligands such as PPh_3 to get cationic complex **103**. It is also reported that complex **102** is relatively unstable in solution and decomposes over several minutes.

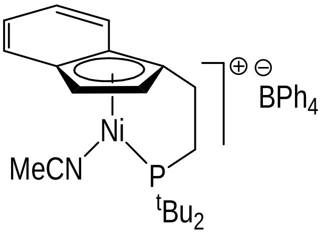


101 102 103

The efficiency of cationic nickel chelate complexes **75-77** to polymerization reactions of olefins and hydrosilylation reactions of olefins and ketones encouraged us to prepare cationic complexes **104-107**. Although the cationic indenyl nickel complexes with phosphane ligand[132] and a hemilabile tethered amine moiety[114,131] are known. The cationic Cp and indenyl nickel complexes with hemilabile phosphane ligand have not been reported so far. The present study is mainly focussed on the creation and characterization of cationic Cp and indenyl nickel species with a pendant di-*tert*-butylphosphane moiety. The strategy introduced by Zargarian[132] for the synthesis of **102** can be utilized for the syntheses of $\{[CpCH_2CH_2P^tBu_2]Ni(MeCN)\}^+$ **104-107** with different anionic counter parts. These cationic complexes **104-107** are expected to be the better candidates as single component catalysts in the polymerization reactions of olefins and acetylenes, and hydrosilylation reactions of olefins, ketones and acetylenes because the di-*tert*-butylphosphane linked to the Cp ring by two carbon spacer has been proven successful as a good chelate stabilizing agent in the field of cobalt complexes.[10,16-25] The synthesis of indenyl nickel cationic complex $\{[IndCHCHP^tBu_2]Ni(MeCN)\}^+$ **108** has been attempted, which is also expected as an efficient single component catalyst for the formation of chiral products.



104: X = SbF_6 (71%)
105: X = BF_4 (88%)
106: X = PF_6 (90%)
107: X = BPh_4 (92%)

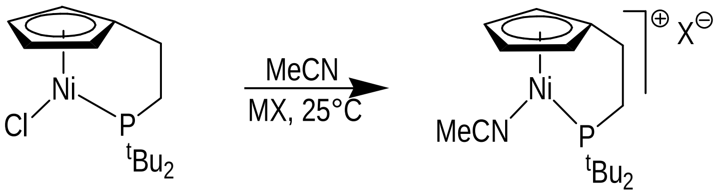


108 (92%)

2.7.1 Syntheses of [(Di-*tert*-butylphosphanylethyl)cyclopentadienyl](acetonitrile)-nickel(II) (104-107)

The cationic cyclopentadienyl nickel chelate complexes **104-107** bearing a di-*tert*-butylphosphane as a pendant ligand were prepared by treatment of complex **62** with an excess of MX ($AgSbF_6$, $AgBF_4$, $AgPF_6$ and $NaBPh_4$) In four different reaction flasks in MeCN. An immediate colour change from dark purple to yellow brown was observed which showed the abstraction of Cl ligand and coordination of MeCN to the vacant coordination site of nickel. After stirring the reaction mixtures for 1 or 2 h and removal of the acetonitrile, the residues were dissolved in dichloromethane. After filteration and removal of dichloromethane the residues were washed by diethyl ether to get the pure products as green solids in 71%, 88%, 90% and 92% yields identified as cationic complexes **104-107**, respectively.

The cationic nickel chelate complexes **104-107** are soluble only in polar solvents. It has been observed that coordination of acetonitrile to nickel causes the stability to the complexes **104-107**. These complexes can be handled in air for 2 to 3 h. However, solution phase decomposition starts after half hour. The solution phase decomposition of cationic complexes **104-107** may lead to use them as catalyst in polymerization and hydrosilylation of olefins and acetylenes and hydrosilylation of ketones.



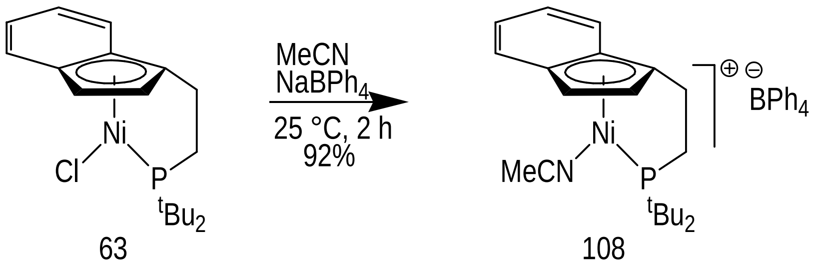
62

104: X = SbF_6 (71%)
105: X = BF_4 (88%)
106: X = PF_6 (90%)
107: X = BPh_4 (92%)

The cationic complexes **104-107** are fully characterized by IR, ^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectroscopy, and LREIMS (ESi acetonitrile) and HREIMS (ESI acetonitrile) spectrometry. The IR spectra of **104-107** show an increase in the value of $\tilde{\nu}$ (C≡N) vibration, in the range from 2262 to 2052 cm^{-1}, resulting the transfer of electron density from MeCN to the electrophilic Ni^{+} center. broad bands were observed. The ^{1}H NMR spectra of complexes **104-107** show characteristic signals at δ = 2.50, 2.49, 2.48 and 2.22 ppm, respectively, corresponding to CH_3CN. The ^{1}H NMR spectrum of **107** shows one dublet of dublet, two multiplets at δ = 6.79, δ = 6.92-6.96 and δ = 7.33-7.36 ppm, respectively *p*-H, *m*-H and *o*-H protons of each phenyl ring. The signals at δ = 3.7, 3.3, 3.3 and 3.5 ppm for the methyl carbon of CH_3CN are significant absorptions in the ^{13}C NMR spectra of **99-107**, respectively. The characteristic absorptions for C≡N in the ^{13}C NMR spectra of **104-107** were observed at δ = 131.9, 131.6, 131.6 and 131.8 ppm, respectively. The ^{13}C NMR spectrum of **107** shows signals at δ = 122.2 ($^{4}J_{B\text{-}C}$ = 0.6 Hz), δ = 125.9 ($^{3}J_{B\text{-}C}$ = 2.7 Hz) and δ = 136.9 ($^{2}J_{B\text{-}C}$ = 1.5 and 1.2 Hz) ppm for *p*-C *m*-C and *o*-C of each phenyl ring of BPh_4 counter part. The quaternary carbon atoms next to boron absorb at δ =164.6 ppm ($^{1}J_{B\text{-}C}$ = 49.2 Hz) as 4-line multiplet. The significant feature in the structure elucidation of the cationic complexes **104-107** is the absorption of the phosphorous atom in the ^{31}P NMR spectra. The ^{31}P NMR spectra of complexes **104-107** show absorption signals as singlets at δ = 106.0, 106.5, 106.0 and 106.0 ppm, respectively, indicating that even coordination of the strong acetonitrile ligand to nickel center, phosphane side arm is still coordinated to the metal for the formation of chelate providing sufficient stability to the complexes **104-107**. The positive ion MS (ESI acetonitrile) mass spectra of **104-107** exhibit fragment peaks at *m/z* = 336 (100%) corresponding to cationic counter part $[(CpCH_2CH_2P^tBu_2)Ni(MeCN)]^+$. The negative ion MS (ESI acetonitrile) mass spectra of **104-107** have also been measured to get the fragment peaks of the anionic counter parts. The HRMS (ESI acetonitrile) spectra of positive and negative ion counter parts of complexes **104-107** were also obtained which are in complete accord to the respective molecular masses of the complexes. On the basis of all the analytical data the assigned constitutions of complexes **104-107** are confirmed.

2.7.2 Synthesis of [1-(Di-*tert*-butylphosphanylethyl)indenyl](acetonitrile)nickel(II) Tetraphenylborate (108)

The indenyl based planar chiral nickel chelate cationic complex **108** bearing a di-*tert*-butylphosphane as a pendant ligand was prepared the treatment of complex **63** with an access of $NaBPh_4$ in MeCN at 25 °C. On the addition of acetonitrile to the mixture of **63** and $NaBPh_4$ the colour of the solution had changed from dark purple to yellow brown indicating the abstraction of the Cl ligand and coordination of MeCN to the vacant coordination site of nickel. After stirring the reaction mixtures for 2 h and removal of the acetonitrile, the residue was dissolved in dichloromethane. After filteration through the celite and removal of dichloromethane the residue was washed by diethyl ether to get the pure cationic species as a green solid in 92% yield identified as a cationic indenyl nickel chelate complex **108**.

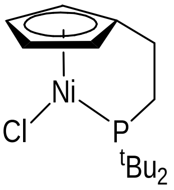


The indenyl based planar chiral nickel cationic complex **108** is the first representative of its own type bearing phosphanylalkyl chain as a pendant ligand. The desired cationic nickel chelate complex **108** is soluble only in polar solvents. It has been observed that coordination of acetonitrile to nickel causes more stability than **63**. Complex **108** can be handled in air also for hours; however, solution phase decomposition is observed after 30 min. The cationic complex **108** is fully characterized by IR, ^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectroscopy, and LREIMS (ESi) and HREIMS (ESI) spectrometry. The IR spectrum of **108** shows significant absorption bands at 2262 and 2157 cm^{-1} which correspond to the $\tilde{\nu}$ (C≡N) vibration.

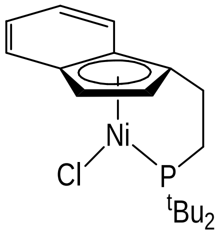
The ^{1}H NMR spectrum **108** shows a characteristic absorption signal at δ = 2.24 ppm corresponding to CH_3CN. In the spectrum two multiplets and a broad signals at δ = 6.78-6.82, δ = 6.89-6.97 and δ = 7.35 ppm were observed for *p*-H, *m*-H and *o*-H protons of phenyl rings. The ^{13}C NMR spectrum of **108** shows noticeable absorption signal at δ = 4.0 ppm for the methyl carbon of MeCN. The characteristic absorptions for C≡N group was observed at δ = 130.9 ppm. The ^{13}C NMR spectrum of **108** shows the absorption signals at δ = 122.9 (d, $^4J_{B\text{-}C}$ = 0.5 Hz), δ = 126.6 (dd, $^3J_{B\text{-}C}$ = 2.7 Hz), δ = 137.7 (dd, $^2J_{B\text{-}C}$ = 1.5 and 1.2 Hz) and δ = 165.8 (4-line multiplet, $^1J_{B\text{-}C}$ = 49.1 Hz) ppm, respectively, for *p*-C, *m*-C, *o*-C and quatarnary carbon atom of BPh_4 counterpart. The ^{1}H NMR and ^{13}C NMR spectra of **108** are well assigned and all the signals observed are in complete accord to the assigned constitution **108**. Here an interesting feature is the absorption of phosphorous atom in the ^{31}P NMR spectrum of **108** which is observed at δ = 47.5 ppm indicating that the interaction of phosphane side arm to nickel is weak due to the coordination of the strong acetonitrile ligand to nickel center. The ^{31}P NMR spectrum shows some unidentified peaks which are presumably obtained due to the decomposition of the complex **108**. The positive ion MS (ESI acetonitrile) mass spectrum of **108** shows fragment peak at *m/z* = 386 (100%) corresponding to cationic counterpart $[(IndCH_2CH_2P^tBu_2)Ni(MeCN)]^+$. The negative ion MS (ESI acetonitrile) mass spectrum of **108** has also been obtained to get the fragment peak of anionic counterpart (BPh_4) at *m/z* = 319 (100%). The positive and negative ion HRMS (ESI acetonitrile) spectra of complex **108** were measured which confirm the respective masses, cationic and anioin counterparts of the complex **108**. On the basis of all the analytical data the assigned constitution of complex **108** is confirmed.

3 Summary and Future Plan

The aim of this project was to investigate the methodology for the synthesis of [(di-*tert*-butylphosphanylethyl)cyclopentadienyl]chloronickel(II) (**62**) and planar chiral [1-(di-*tert*-butylphosphanylethyl)indenyl]chloronickel(II) (**63**) as well as their ligand exchange chemistry to get different analogues. Cyclopentadienyl nickel and phosphane nickel complexes, particularly in catalytic reactions,[11-15] have earlier been investigated, but still no cyclopentadienyl nickel chelate complexes bearing a pendant phosphane ligands have been reported.

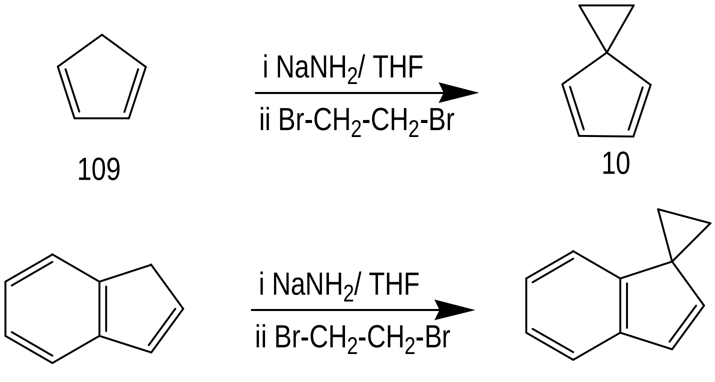


62



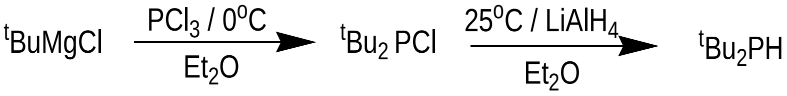
63

1,3-Cyclopentadiene (**109**) and indene (**110**) were treated with sodium amide in THF followed by the addition of 1,2-dibromoethane to get spiro[2.4]hepta-4,6-diene (**10**)[39] in 47% yield and [4,5]benzospiro[2.4]hepta-4,6-diene (**33**)[60] in 50% yield.



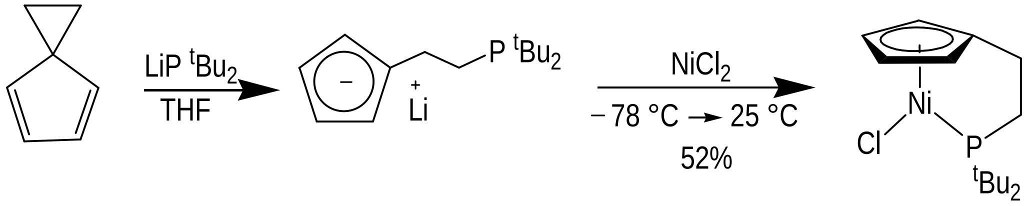
109 10 110 33

tert-Butylmagnesium chloride was treated with PCl_3 at 0 °C in diethyl ether to obtain di-*tert*-butylchlorophosphane (**112**) in 57% yield which was reduced with lithium aluminium hydride at 25 °C in diethyl ether to yield 73% of di-*tert*-butylphosphane (**113**).[134,135]



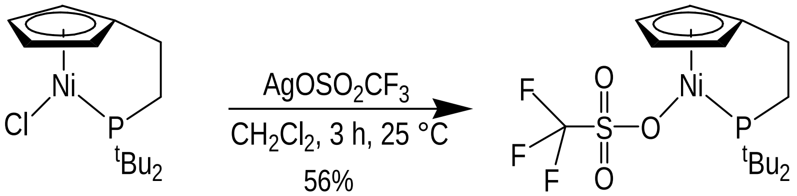
111 112 113

At 0 ^{o}C di-*ter*-butylphosphane (**113**) was treated with butyllithium in anhydrous THF to get deep yellow solution of lithium di-*tert*-butylphosphide. The cyclopropane ring of spiro[2.4]hepta-4,6-diene (**10**) was cleaved by the nucleophilic attack of di-*tert*-butylphosphide to get the anionic ligand **13**.[24] At –78 ^{o}C anhydrous nickel chloride was added to obtain the first nickel chelate complex **62** with a pendant phosphanylalkyl chain connected to the Cp ring by an appropriate spacer in 52% yield.



10 13 62

For the ligand exchange, complex **62** was treated with an excess of silver triflate in dichloromethane to get the complex **68** in 56% yield as a reddish brown solid. The complex **68** would be used as precursor to highly reactive cationic intermediates. The complex **68** was recrystallized from a mixture of dichloromethane and hexane at –20 °C to get the fine crystals suitable for X-ray structure analysis. The X-ray plot is depicted in figure 9, as the representative of first nickel chelate complexes bearing a pendant phosphanylalky chain connected to the Cp ring by a linker.



62 68

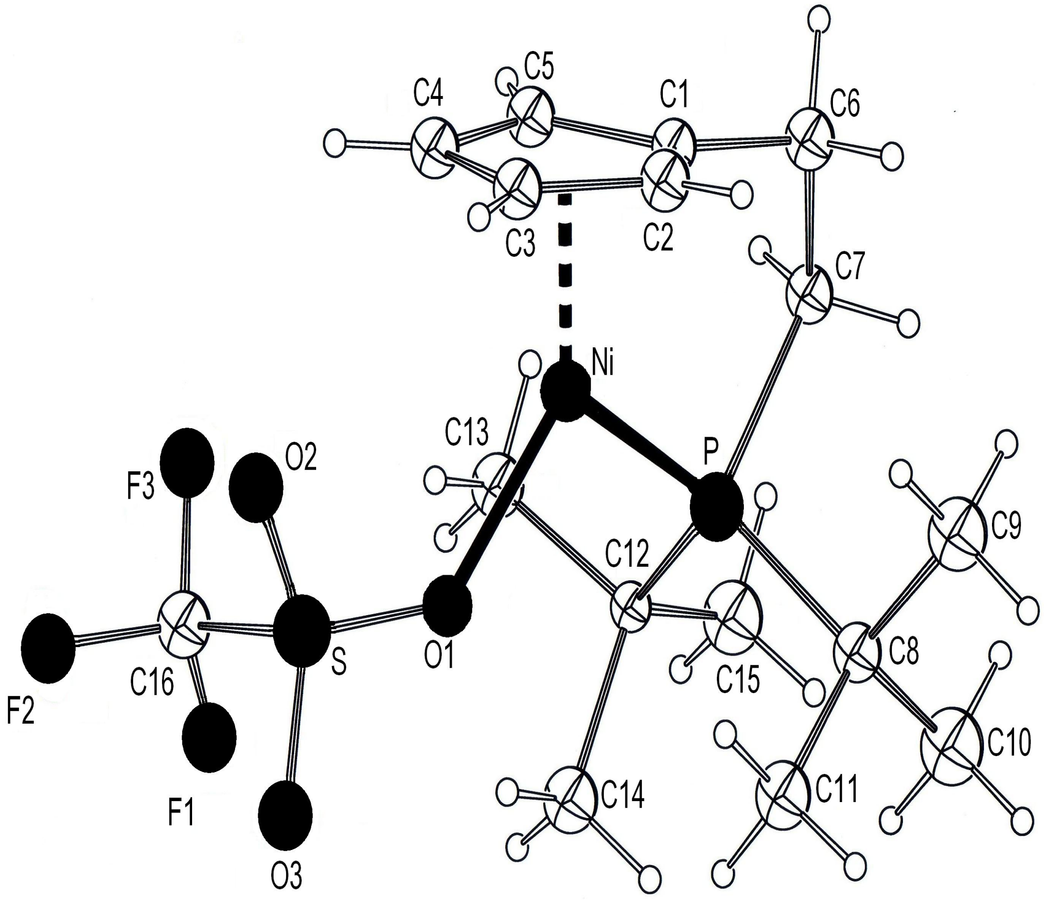
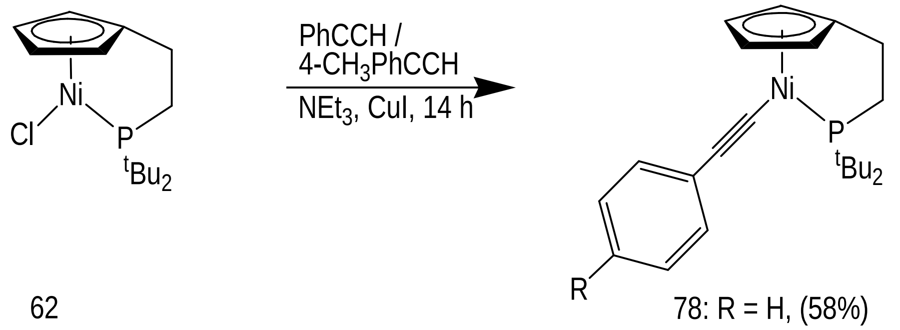


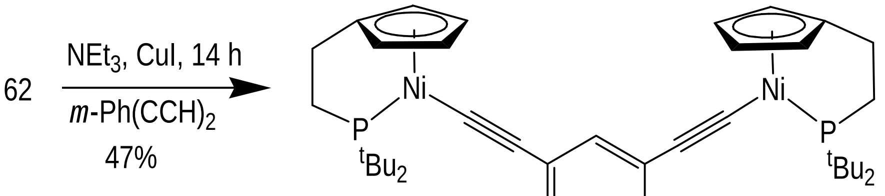
Fig. 9: Structure of **68** in the crystal.

The Cl ligand in complex **62** was replaced by the more strongly electron donating alkynyl ligands to obtain alkynyl complexes **78-80**. In three separate reactions the complex **62** and CuI were suspended in triethylamine followed by the addition of respective acetylenes to obtain alkynyl nickel chelate complexes **78-80** in 58%, 91% and 47% yield, respectively. A part of the complex **79** was recrystallized from hexane at −20 °C to get fine crystals for crystallographic measurement. The picture of complex **79** is shown in figure 10.



62

78: R = H, (58%)
79: R = CH_3, (91%)



80

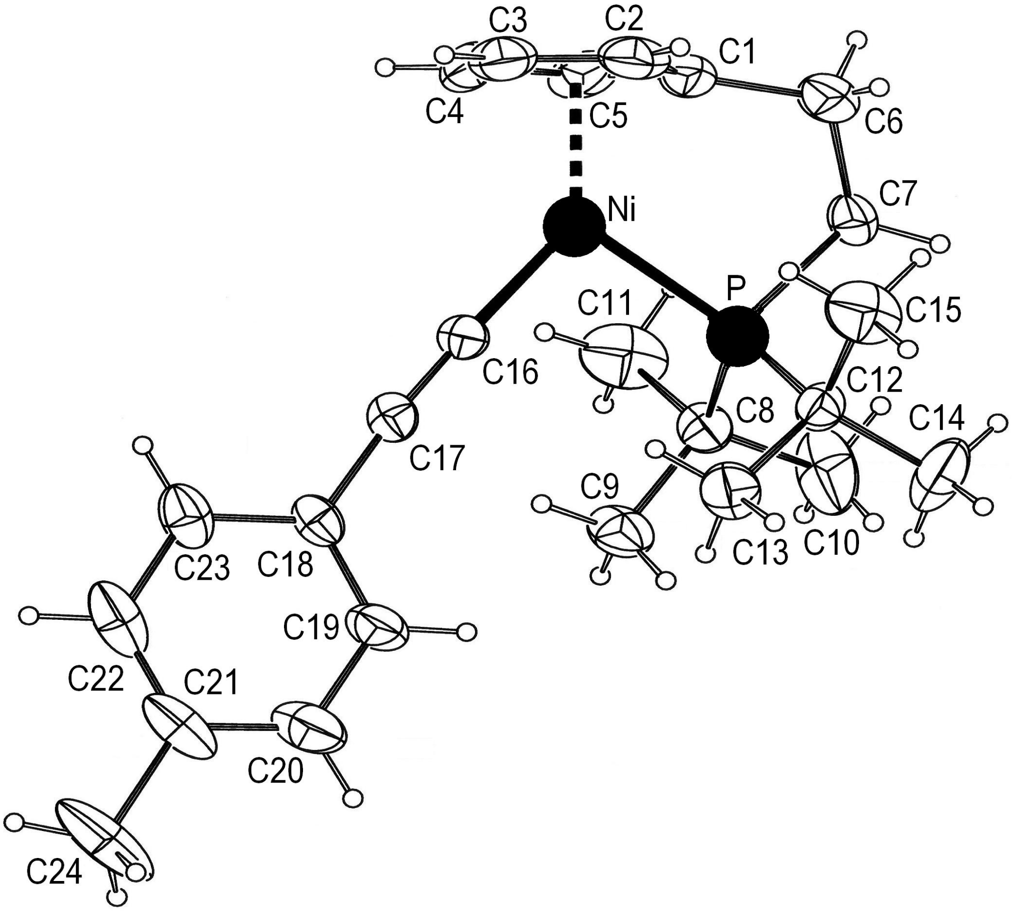
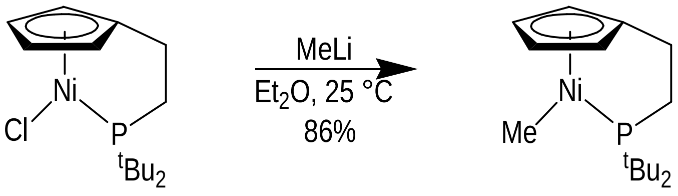


Fig. 10**:** Structure of **79** in crystal.

Treatment of complex **62** with MeLi at 25 °C in diethyl ether yielded methyl nickel chelate in 86% yield. Recrystallization from hexane at −20 °C gave crystals suitable for X-ray structure determination. The structure of **81** in crystal is depicted in figure 11. The complexes **79** and **81** were tested as active catalysts in the hydrosilylation of styrene which showed that the neutral complexes bearing di-*tert*-butylphosphane as a pendant ligand can catalyze the hydrosilylation reactions of olefin. The cyclovoltammetry results of complexes **62** and **78-81** were obtained showing the oxidation potential (V) in the range from −1.7 to 0.4 V.



62 81

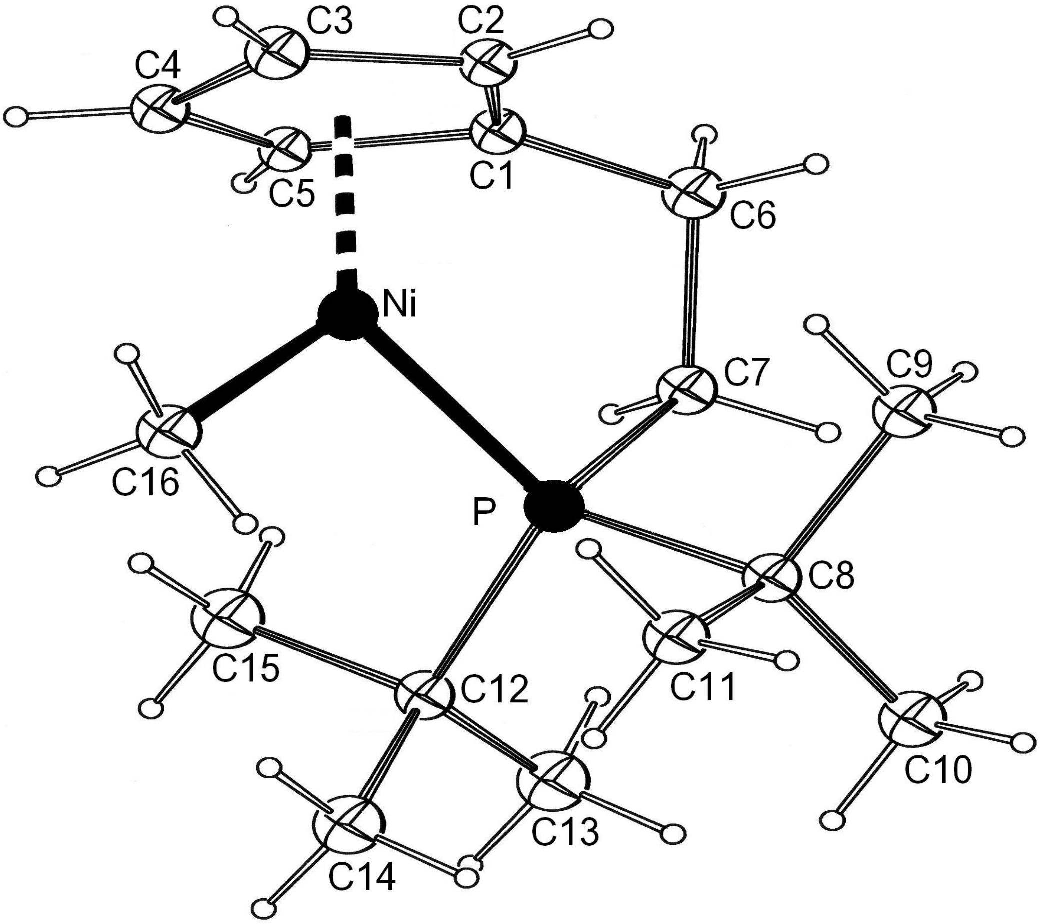
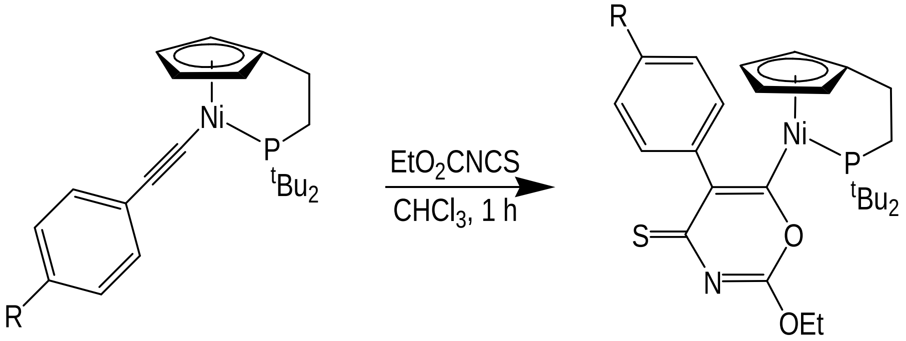


Fig. 11: Structure of **81** in the crystal.

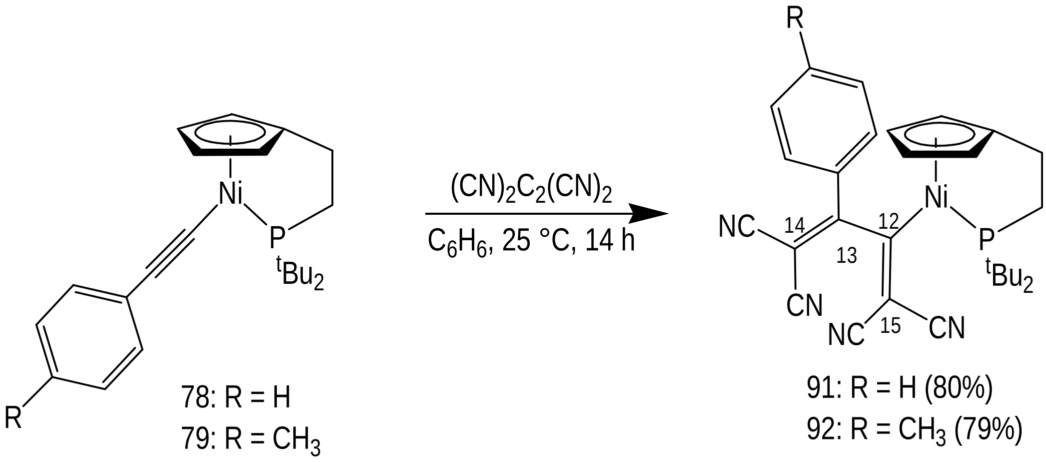
Cycloaddition reactions of several nickel σ-alkynyl complexes[82] with isocyanates have been reported. Complexes **78** and **79** were treated with EtO_2CNCS to check the efficiency of the activated C≡C bonds in such reactions. The respective cycloaddition products **89** and **90** with a six membered 2-imino-1,3-thiazine-4-thione ligand in 85% and 90% yields, respectively, were obtained. The reactions were completed within 1 h indicating the nickel alkynyl sytem is much more active toward [4+2] cycloaddition reactions than that of the reported ruthenium alkynyl complexes.[91]

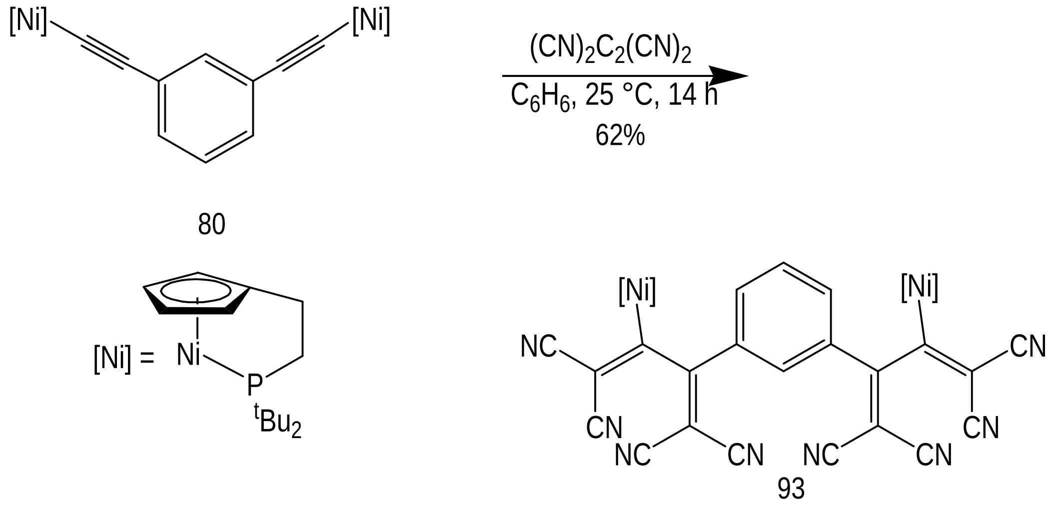


78: R = H
79: R = CH_3

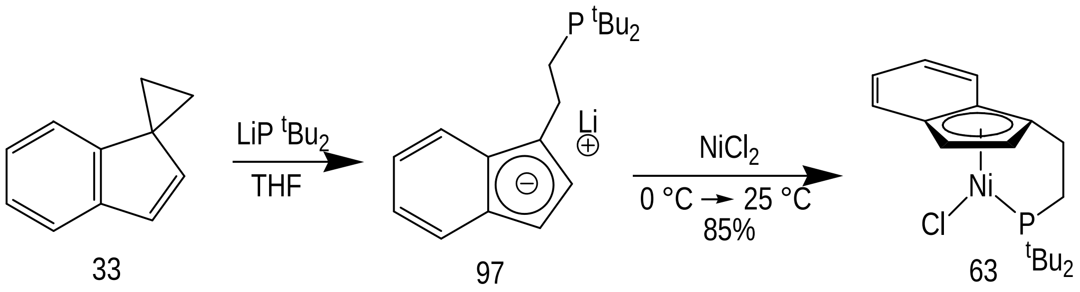
89: R = H, 85%
90: R = CH_3, 90%

The [2+2] cycloaddition of tetracyanoethylene, $C_2(CN)_4$ to σ-acetylide complexes **78-80** gave the ring-opened butadienyl complexes **91-93** in 80%, 79% and 62% yields**,** respectively, as dark brown solids. Due to the steric bulk of di-*tert*-butyl groups at the phosphorus atom and the staggered conformation resulted from the chelation, the rotation of Cp ring around Cp-Ni bond was locked and it was possible to get a mixture of two major and two minor conformations of complexes **91-93**.

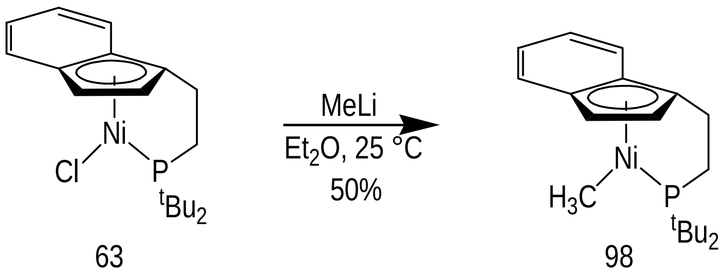




Tani[57,61] reported the only use of linked indenyl-phosphane achiral ligands in the synthesis some rhodium complexes. For the synthesis of inedenyl-based planar chiral nickel complex **63**, [4,5]benzospiro[2.4]hepta-4,6-diene (**33**)[60] was added to the boiling solution of lithium di-*tert*-butylphosphide. The solution was heated at reflux for 5 days to yield the anion **97** obtained by the cyclopropane ring cleavage. To reduce the extended heating time the cyclopropane ring opening was also achieved under microwave (MW) irradiation in only 40 min reaction time. This reaction nicely works with the efficiency of microwave heating. This ring cleavage is the first example of its own kind. Anhydrous $NiCl_2$ was added to the solution at 0 °C to obtain a planar chiral [1-(di-*tert*-butylphosphanylethyl)indenyl]chloronickel(II) (**63**) from **33** in 85% yield as a deep purple solid.



The preparation of [1-(di-*tert*-butylphosphanylethyl)indenyl]methylnickel(II) (**98**) was accomplished via a metathetic reaction of complex **63** and MeLi in 50% yield. The complex **98** is stable in air for 2 h; however in solution it decomposes immediately in connection of air. Complex **98** was recrystallized from the saturated solution in hexane at −20 °C to get the crystals suitable for X-ray structure analysis. The structure of **98** in crystal is depicted in the figure 12.



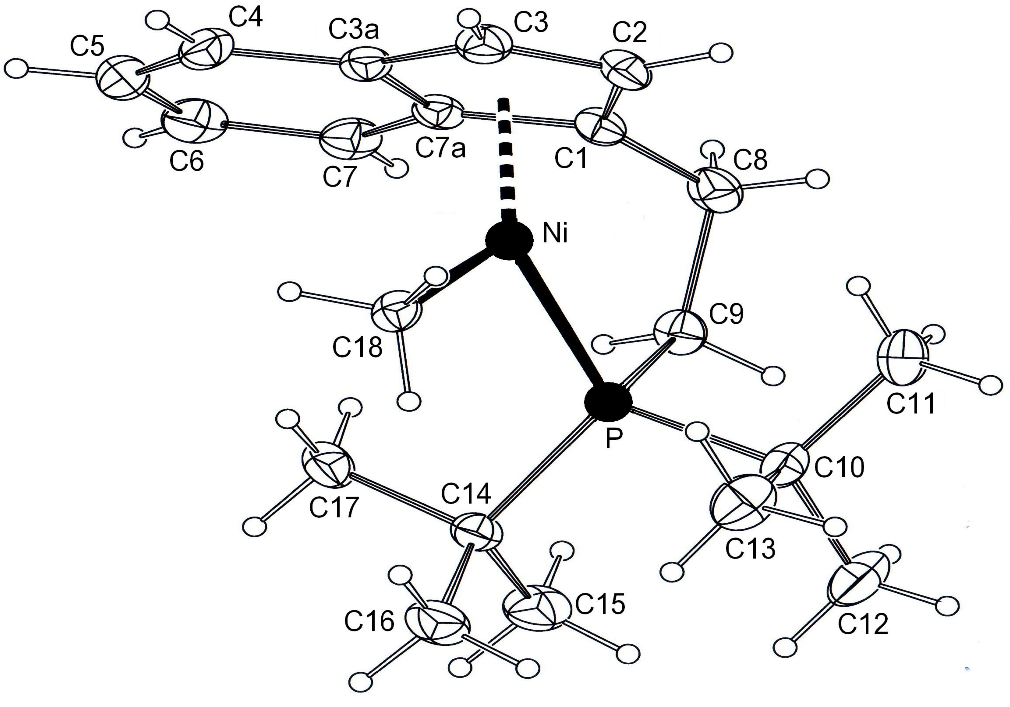
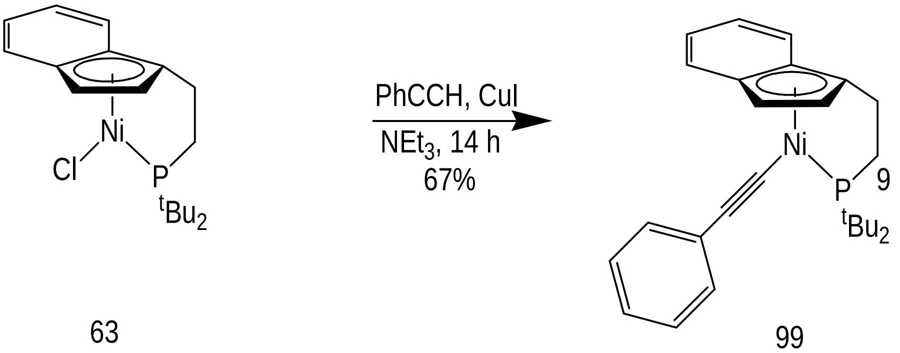
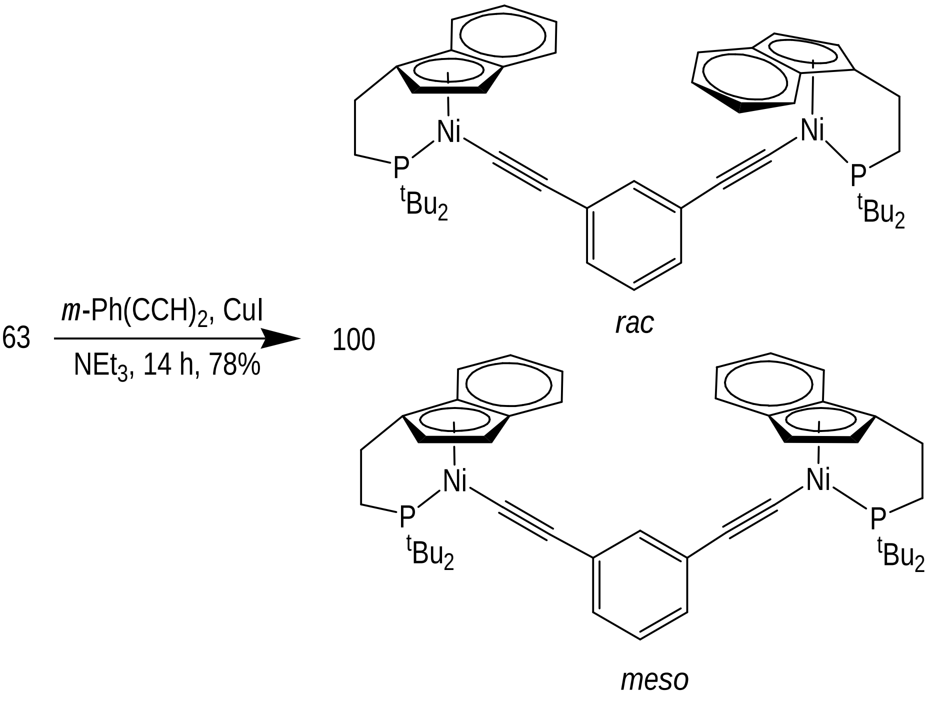


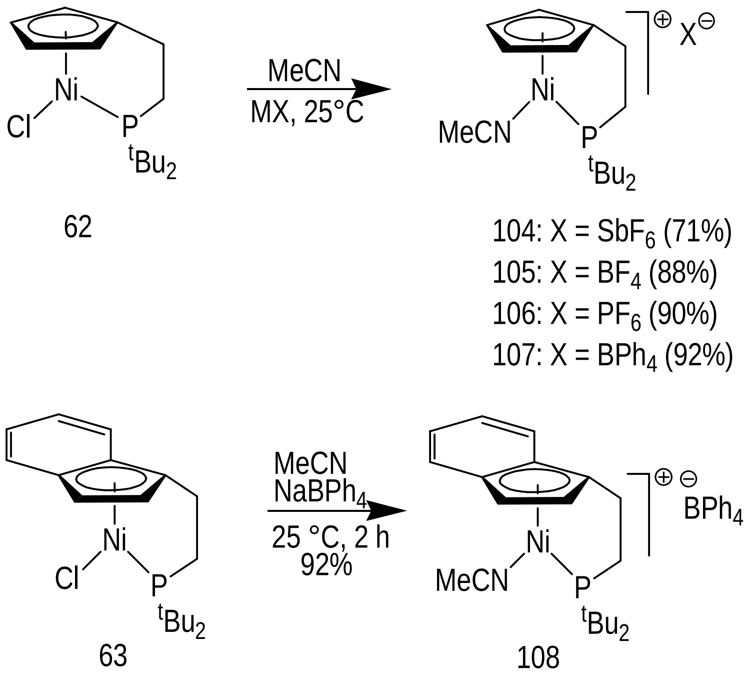
Fig. 12: structure of **98** in the crystal.

The Cl ligand in **63** was also replaced with more strongly electron donating alkynyl ligand to get the novel planar chiral alkynyl nickel complexes **99** and **100**. A suspension of complex **63** and CuI in triethyl amine was treated with the respective alkynes to obtain complexes **99** and **100** in 67% and 78% yield, respectively. The ^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra of complex **100** show two sets of signals in a ratio ca. 100: 9 indicating a mixture of meso and racemic material.





The cationic indenyl nickel complexes with the phosphane ligand[131] and a hemilabile tethered amine moiety[114,130] are known, however the cationic Cp and indenyl nickel complexes with hemilabile phosphane ligand have not been reported so far. The cationic cyclopentadienyl nickel chelate complexes bearing a di-*tert*-butylphosphane as a pendant ligand were prepared by treating the complex **62** with an excess of MX ($AgSbF_6$, $AgBF_4$, $AgPF_6$ and $NaBPh_4$) in MeCN to obtain the complexes **104-107** in 71%, 88%, 90% and 92% yield, respectively, identified as cationic complexes. An immediate colour change from dark purple to yellow brown shows the abstraction of Cl ligand and coordination of MeCN to the vacant coordination site of nickel. This provides more stability to the complexes, however, in solution phase the decomposition was observed presumably due to the decoordination of acetonitrile ligand. The cationic chelate complexes might be an active catalyst in the hydrosilylation of olefins, alkynes and ketones, and polymerization of olefins and acetylenes. Similarly the complex **63** was also treated with sodium tetraphenylborate to create a chiral cationic species **108** in 92% yield, which is expected as an efficient single component catalyst for the formation of chiral products.



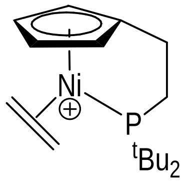
62

104: X = SbF_6 (71%)
105: X = BF_4 (88%)
106: X = PF_6 (90%)
107: X = BPh_4 (92%)

63

108

The complexes **62** and **63** obey the 18 electron rule and therefore have been observed to be reasonably stable. Reaction of chelate complexes **62** and **63** with $AgBF_4$ or $AgBF_6$ followed by electroneutral ligands such as alkenes or alkynes possibly can result in the formation of cationic complexes like **114-117** and may be the basis for a variety of coupling reactions. The striking point of complex **63** as compared to **62** is the planer chirality which should allow for enantioselectivity in catalytic reactions. For such asymmetrically catalyzed reactions **63** has to be enantiomerically pure or at least enriched, which might be achieved by chiral HPLC.



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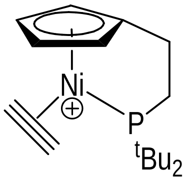

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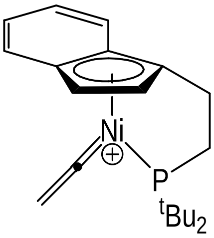

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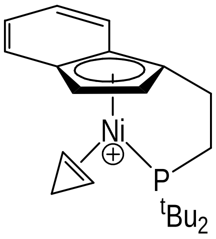


117

Overall, the first cyclopentadienyl and indenyl nickel chelate complexes with a pendant phosphane tether have been prepared and their chemistry has been investigated. The work presented here are a basis for future investigations directed to the synthesis of new complexes and their catalytic affiliations in organic chemistry.

4 EXPERIMENTAL SECTION

4.1 General

All manipulations were performed in flame-dried reaction vessels in a nitrogen atmosphere using vacuum line and standard schlenk techniques. Diethyl ether, dibutyl ether and THF were distilled from sodium benzophenone ketyl. Hexane, pentane, dichloromethane and chloroform were dried with calcium hydride and freshly distilled before use. Petroleum ether and tert-butylmethyl ether were dried with calcium chloride. All the solvents were degassed with nitrogen before use.

Preparative column chromatography was carried out by flash chromatography.[133] Silica gel used was from the J. T. Baker with particle size 40 µm. The silica gel was degassed by heating it with a flame at reduced pressure followed by setting it at normal pressure with nitrogen. All the solvents used for column chromatography were first distilled over drying agents e.g. calcium chloride and then degassed for about 20 min by passing constant nitrogen stream.

Thin layer chromatography (TLC) was performed using aluminium TLC plate coated with the silica gel $60F_{254}$ (Merck) combined with the polygram® Alox N/UV_{254} from Macherey-Nagel. The spots were visualised with the help of UV-lamp ($\lambda = 254$ nm) and developed in $KMnO_4$ reagent.

Microwave experiments were carried out using a CEM Discover Labmate™ microwave apparatus (300 W with ChemDriver™ software).

4.2 Analytical Methods

IR-Spectra were obtained using the instrument FT-IR spectrometer 580 and 1170 of Bruker as golden gate ATR. The following abbreviations were used to indicate the intensity of the absorption bands: s = strong, m = middle, w = weak, br = broad.

Mass Spectrometry: Mass spectra (EI) were obtained at 70 eV with a type of VG autospec apparatus (Micromass). Some of the spectra were measured using Finnegan mass spectrometers MAT 112 and MAT 312 at 70 eV.

HRMS (ESI) Spectra were performed using micromass LCT with lock spray ion source combined with water alliances 2695 HPLC unit. Some measurements were recorded using a VG autospec spectrometer with the peak-matching method (PEK) and the NBA-Matrix was used.

GC Analyses were conducted using a HPGC series 6890 Series Hewlett Packard equipped with an SE-54 capillary column (25 m, Macherey-Nagel) and an FID detector 19231 D/E.

GC-MS Analyses were performed by using the instrument Shimadzu QP-5000 Spectrometer and GC-17A.

^{1}H NMR Spectra were measured using the instrument Bruker AVS 200 (200.1 MHz), AVS 400 (400.1 MHz) and AVS 500 (500.1 MHz). In the case where no tetramethylsilane (TMS, δ = 0.00) was used as a reference, a solvent peak was used as a reference (δ = 7.27 for $CHCl_3$ and δ = 2.05 for acetone-d_5). The multiplicity of the peaks were abbreviated as s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad.

^{13}C NMR Spectra were measured using the instrument Bruker AVS 200 (50.3 MHz) and AVS 400 (100.6). In the case where no tetramethylsilane (TMS, δ = 0.0) was used as a reference, a solvent peak was used as a reference (δ = 77.0 for $CDCl_3$ and δ = 29.8 for acetone-d_6). The multiplicity of the signals was determined with ATP and DEPT techniques. Signals (peaks) with negative phase for CH and CH_3 were labelled with "–", and those with positive phase for C and CH_2 were labelled with "+".
Air sensitive samples were prepared under nitrogen using the Schlenk technique. The deuterated solvents were stored under nitrogen.

^{31}P NMR Spectra were measured using the instrument Bruker AVS 400 (161.978). In the case where no tetramethylsilane (TMS, δ = 0.0) was used as a reference.

Cyclovoltammetry Results were obtained by using Potentiostat Heka PG 285, reference electrode Ag/AgCl (Alfa), counter electrode Pt wire.

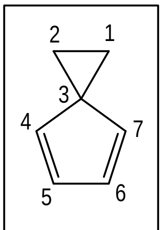
Melting points were measured by using Electrothermal IA9000 Series Digital Melting Point Apparatus.

Elemental analyses were carried out for CHN with Elementar Vario EL instrument.

General Remarks: The atom numbering of the molecule is arbitrary; however, the naming of the molecule is according to the IUPAC system. The lithium sand used contains 2% of sodium. Commercially available reagents were used as received.

4.3 Syntheses of Ligands

4.3.1 Synthesis of Spiro[2.4]hepta-4,6-diene (10)[39]

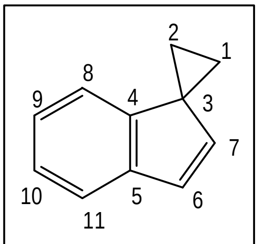


10

Sodium amide (12.0 g, 0.30 mol) was slowly added to anhydrous THF (200 mL). Then the freshly distilled 1,3-cyclopentadiene (10.0 g, 0.15 mol.) was added dropwise over 30 min. The reaction mixture was heated at reflux for one hour. After cooling the reaction mixture to 25 °C, 1,2-dibromoethane (28.2 g, 0.15 mol.) was added dropwise over 3 h. The colour of the reaction mixture was dark brown. The reaction mixture was stirred for 15 h at 25 ^{o}C. The organic layer was decanted off. The residue was dissolved in water (100 mL) and extracted with PE (3 × 100 mL). The combined organic layers were washed with water (2 ×100 mL) then with dilute hydrochloric acid solution (100 mL) and finally with water (2 × 100 mL). After drying over magnesium sulphate and solvent removal at reduced pressure, the product was distilled off at 111-115 ^{o}C to yield 6.5 g (0.07 mol, 47%) of **10**.

10: ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 1.66 [s, 4 H, 1(2)-H], 6.14, 6.53 [AA′BB′ line system, 4 H, 4(7), 5(6)-H] ppm. - ^{13}C NMR ($CDCl_3$, 100 MHz, BB): δ = 12.6 [s, C-1(2)], 37.8 (s, C-3), 129.1 [s, C-4(7)], 139.3 [s, C-5(6)] ppm.

4.3.2 Synthesis of [4,5]Benzospiro[2.4]hepta-4,6-diene (33)[60]

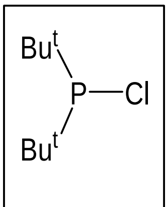


33

Sodium amide (15.6 g, 0.40 mol) was slowly added to anhydrous THF (160 mL) into a 500 (mL) round bottomed flask. After the dropwise addition of indene (25.6 g, 0.2 mol) in THF (40 mL) to the reaction flask, the colour of the reaction mixture was dark brown. The reaction mixture was heated at reflux for 2 h. 1,2-Dibromoethane (17.3 mL, 0.2 mol.) was added at a rate that the reaction mixture boiled without external heating. The reaction mixture was heated at reflux for 2 h and then stirred for 15 h at 25 °C. The organic layer was decanted off and the residue was dissolved in water (200 mL) and extracted with TBME (3 × 100 mL). The combined organic layers were washed with water (3 × 100 mL) and then with dilute hydrochloric acid (200 mL) and finally with water (3 × 100 mL). After drying over magnesium sulphate and solvent removal at reduced pressure, the product was distilled off at 5 mbar / 75-80°C to yield 14.2 g (0.1 mol, 50%) of **33**.

33: ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 1.70 (m, 2 H, 1-H), 1.78 (m, 2 H, 2-H), 6.34 (d, ^3J = 5.4 Hz, 1 H, 7-H), 7.01 (d, ^3J = 5.1 Hz, 1 H, 6-H), 7.09 (d, ABCD system, 1 H, 8-H,), 7.28, [dd, ABCD system, 1 H, 9-H], 7.37 [dd, ABCD system, 1 H, 10-H], 7.55 (d, ABCD, 1 H, 11-H) ppm. - ^{13}C NMR (CDCl$_3$, 100 MHz, BB): δ = 14.6 [s, C-1(2)], 33.1 (s, C-3), 117.3 (s, C-7), 121.3 (s, C-6), 124.1 (s, C-8), 125.3 (s, C-9), 128.2 (s, C-10), 140.7 (s, C-11), 143.4 (s, C-5), 147.8 (s, C-4) ppm. - MS (70 eV): *m/z* (%) = 143 (13) [M$^+$ + 1], 142 (100) [M$^+$], 141 (81) [M$^+$ –H], 128 (8) [M$^+$ – CH$_2$], 115 (77) [M$^+$ – C$_2$H$_3$], 89 (10) [M$^+$ – C$_4$H$_5$], 77 (9) [M$^+$ – C$_5$H$_5$].

4.3.3 Synthesis of Di-*tert*-butylchlorophosphane (112) [134,135]

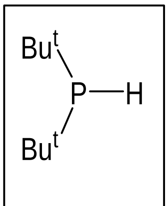


112

Phosphorous trichloride (52.5 g, 0.38 mol) and anhydrous diethyl ether (250 mL) were placed into a 1000 (mL) round bottomed flask. *tert*-Butylmagnesium chloride in diethyl ether (0.84 mol, 250 mL) was slowly added over 5 h at 0°C. The reaction mixture was stirred for 15 h followed by the addition of diethyl ether (100 mL). The mixture was heated at reflux for 2 h. Then the reaction mixture was cooled to 25°C and filtered. The residue was washed with diethyl ether (2 × 100 mL). After the solvent removal at reduced pressure, the product was distilled out at 5 mbar / 41-45°C to yield 38.6 g (0.21 mol, 57%) of **112**.

112: ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.23 (d, ^3J = 12.2 Hz, 6 x CH_3) ppm. - ^{13}C NMR ($CDCl_3$, 100 MHz, BB): δ = 23.4 (d, $^2J_{CP}$ = 20.9 Hz, 6 x CH_3), 35.6 [d, $^1J_{CP}$ = 40.2 Hz, $C(CH_3)_3$] ppm. - ^{31}P NMR ($CDCl_3$, 161 MHz): δ = 147.6 (s) ppm.

4.3.4 Synthesis of Di-*tert*-butylphosphane (113)[135]



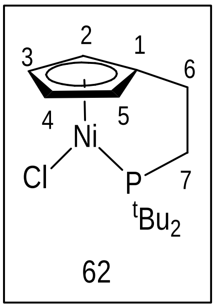
113

To lithium aluminium hydride (4.5 g) in anhydrous diethyl ether (300 mL), di-*tert*-butylchlorophosphane (21.5 g, 0.12 mol) was added dropwise over 2 h. After stirring the solution for 14 h, the reaction was quenched by the addition of saturated solution of ammonium chloride in methanol (20 mL). Then the reaction mixture was stirred for 2 h. The dilute solution of hydrochloric acid (70 mL) was added to adjust the pH = 4. After stirring the reaction mixture for 1 h, the organic layer was decanted off. The aqueous layer was extracted with diethyl ether (3 × 100 mL). The combined organic layers were dried over magnesium sulphate and filtered. After the solvent removal at reduced pressure and low temperature, the product was distilled out at 5 mbar / 38-43°C to give 12.5 g (0.09 mol, 73%) of **113**.

113: ^{1}H NMR (CDCl3, 200 MHz): $\delta = 1.22$ (d, $^3J = 11.5$ Hz, 18 H, 6 x CH_3), 2.95 (br, 1 H, P-H) ppm. - ^{13}C NMR ($CDCl_3$, 100 MHz, BB): $\delta = 29.7$ [d, $^1J_{CP} = 15.2$ Hz, $C(CH_3)_3$], 31.5 (d, $^2J_{CP} = 12.6$ Hz, 6 x CH_3) ppm. - ^{31}P NMR ($CDCl_3$, 161 MHz): $\delta = 21.2$ (s) ppm.

4.4 Synthesis of [(Di-*tert*-butylphosphanylethyl)cyclopentadienyl]chloronickel(II) and Triflate Derivative.

4.4.1 [(Di-*tert*-butylphosphanylethyl)cyclopentadienyl]chloronickel(II) (62)

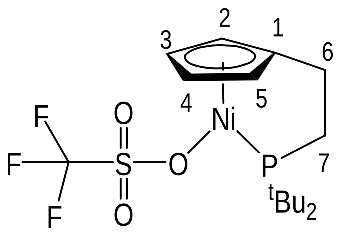


62

At 0 °C a solution of butyllithium (5.5 mL, 13.8 mmol, 2.5 M in hexane) was slowly added to di-*tert*-butylphosphane (2.0 g, 13.6 mmol) in anhydrous THF (50 mL). After the addition the colour of the reaction mixture was deep yellow. The reaction mixture was warmed slowly to 25 °C and stirred for 14 h. Spiro[2.4]hepta-4,6-diene (**10**) (1.25 g, 13.6 mmol) was slowly added to the reaction mixture. The colour of the reaction mixture became light yellow. The reaction mixture was heated at reflux for 3 h. The colour of the reaction mixture became orange red. At – 78 °C anhydrous $NiCl_2$ (5.2 g, 40.8 mmol) was added. The dry ice bath was taken away after 25 min. The colour of the reaction mixture had changed to purple red. After stirring for 12 h THF was removed at reduced pressure and residue was dissolved in diethyl ether. After filtration through celite, the product was crystallized from diethyl ether to yield 2.3 g (6.9 mmol, 52%) of **62** as deep purple red solid (m.p. 189 °C decomp.).

62: IR (ATR): $\tilde{\nu}$ = 3077 cm^{-1} (w), 2946 (s), 2897 (s), 1645 (w), 1473 (m), 1439 (w), 1389 (m), 1366 (m), 1358 (s), 1302 (w), 1180 (m), 1167 (s), 1064 (w), 1048 (m), 1018 (s), 932 (m), 895 (w), 864 (w), 830 (s), 810 (s), 780 (s), 678 (m), 622 (w). - ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.46 (t, $^3J_{HH}$ = 7.5 Hz, 2 H, 6-H), 1.54 (d, $^3J_{PH}$ = 13.4 Hz, 18 H, 6 × CH_3), 2.18 (dd, $^2J_{PH}$ = 8.2, $^3J_{HH}$ = 7.5, 2 H, 7-H), 5.87, 5.43 [AA′BB′ line system, 4 H, 2(5), 3(4)-H] ppm. - ^{13}C NMR ($CDCl_3$, 100 MHz, BB): δ = 25.5 (d, $^2J_{CP}$ = 3.9 Hz, C-6). 30.3 (d, $^2J_{CP}$ = 3.3 Hz, 6 × CH_3), 34.5 (d, $^1J_{CP}$ = 21.8 Hz, C-7), 34.8 [d, $^1J_{CP}$ = 14.2 Hz, $C(CH_3)_3$], 96.7 (d, J = 8.1 Hz, C-1), 97.5 [d, J = 1.3 Hz, C-2(5)], 98.5 [d, J = 5.9 Hz, C-3(4)] ppm. - ^{31}P NMR ($CDCl_3$, 161 MHz): δ = 92.9 (s) ppm. - MS (70 eV): *m/z* (%) = 330 (76) [M^+], 295 (3) [$M^+ - Cl$], 274 (3) [$M^+ - C_4H_8$], 239 (78) [$M^+ - C_4H_8Cl$], 238 (25) [$M^+ - C_4H_8 - HCl$], 182 (100) {$M^+ - [2C_4H_8] - HCl$}, 136 (29). - $C_{15}H_{26}PNiCl$ (330.0814): Calcd. C 54.35, H 7.91; found C 54.86, H 7.95.

4.4.2 Synthesis of [(Di-*tert*-butylphosphanylethyl)cyclopentadienyl]nickel(II) Triflate (68)



68

At 25 °C a solution of **62** (0.16 g, 0.5 mmol) in dichloromethane (25 mL) was added to the suspension of silver triflate (0.19 g, 0.75 mmol) in dichloromethane (15 mL). After stirring for 3 h, the reaction mixture was filtered through the celite. The solvent was removed at reduced pressure and the residue was dissolved in dichloromethane (5 mL). The hexane was layered to crystallize the product at –20 °C to yield 0.12 g (0.28 mmol, 56%) of **68** as reddish brown solid (m.p. 240 °C decomp.).

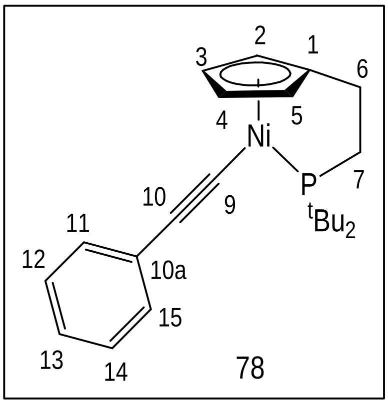
68: IR (ATR): $\tilde{\nu}$ = 2965 cm^{-1} (w), 2888 (w), 1470 (w), 1396 (w), 1373 (w), 1260 (s), 1160 (w), 1092 (w), 1022 (s), 936 (w), 867 (w), 795 (s), 687 (w), 663 (m), 636 (s).- MS (70 eV): *m/z* (%) = 444 (20) [M^+], 295 (9) [$M^+ - CF_3SO_3$], 281 (6) [$M^+ - C_2H_2F_3SO_3$], 238 (75) [$M^+ - C_5H_9F_3SO_3$], 182 (100) [$M^+ - C_9H_{17}F_3SO_3$], 149 (8) [C_7H_8Ni]$^+$, 136 (23). - HRMS: Calcd. for $C_{16}H_{26}O_3F_3PSNi$ [M^+]: 444.064587; found 444.064484.

4.4.3 Crystal Structure Analysis Data of 68

Empirical formula $C_{16}H_{26}F_3NiO_3PS$, Formula weight 445.11, Crystal system, Monoclinic, space group P 21/c, Unit cell dimensions a = 9.431(2), b = 13.919(4), c = 15.115(3) Å α = 90°, β = 101.63° (3), γ = 90°, V = 1943.4(8) A^3, Z = 4, $d_{Calc.}$ = 1.521 Mg/m^3, F(000) =928, μ = 1.228 mm^{-1}, Crystal size 0.12 x 0.07 x 0.03 mm, Diffractometer Stoe IPDS area detector diffractometer T = 300(2) K, MO_{ka} = 0.71073 Å, θ_{min} = 2.01°, θ_{max} = 26.24°, -11<=h<=11, -17<=k<=17, -18<=l<=18, Absorption correction None, Extinction correction None, Reflections collected 15553, unique 3858, [R(int) = 0.5061], Completeness to theta = 26.2, 100 %, Refinement method Full-matrix least-squares on F^2, Data 3858, restraints 0, parameters 146, Goodness-of-fit on F^2, 0.451, Final R indices [I>2sigma(I)], R1 = 0.0435, wR2 = 0.0787, Rindices (all data), R1 = 0.3263, wR2 = 0.1903,Largest diff. peak and hole 0.241 and -0.365 eA^{-3}.

4.5 Synthesis of [(Di-*tert*-butylphosphanylethyl)cyclopentadienyl]alkyl- and –σ-alkynyl nickel(II)

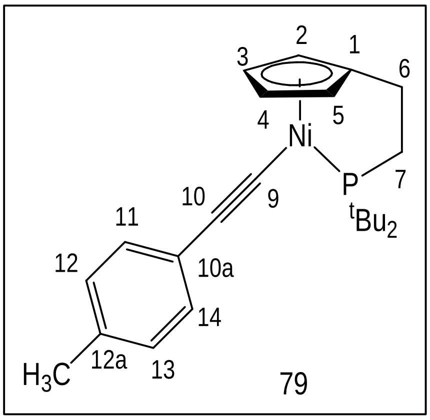
4.5.1 Synthesis of {[(Di-*tert*-butylphosphanylethyl)cyclopentadienyl](2-phenylethynyl)} nickel(II) (78)



To a suspension of **62** (0.33 g, 1.0 mmol) and CuI (5 mg) in freshly distilled triethylamin (20 mL) phenyl acetylene (0.17 g, 1.6 mmol) was added dropwise. The reaction mixture was stirred for 14 h at 25 °C. The solvent was removed at reduced pressure and the crude product **78** was extracted with diethyl ether (3 × 25 mL). The complex **78** was chromatographed (SiO_2, petroleum ether / ethyl acetate 10 : 1, 30 × 4 cm) to yield 0.23 g (0.6 mmol, 58%) of **78** as a deep brown solid (m.p. 218 °C decomp.).

78: IR (ATR): $\tilde{\nu}$ = 3083 cm^{-1} (w), 3068 (w), 2944 (s), 2895 (s), 2090 (m) 1652 (w), 1589 (m),1481 (m), 1438 (w), 1390 (m), 1371 (m), 1357 (s), 1306 (w), 1179 (m), 1064 (w), 1037 (m), 1024 (s), 927 (m), 900 (w), 861 (w), 812 (s), 790 (s), 690 (m), 676 (w). - ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 1.51 (d, $^3J_{\mathrm{PH}}$ = 13.5 Hz, 18 H, 6 × CH_3), 2.01 (dt, 2 H, $^3J_{\mathrm{HH}}$ = 7.5, 7.4 Hz, 6-H), 2.49 (dd, $^2J_{\mathrm{PH}}$ = 8.5 Hz, $^3J_{\mathrm{HH}}$ = 7.5, 2 H, 7-H), 5.52, 5.71 [AA′BB′ line system, 4 H, 2(5), 3(4)-H], 6.98 (dd, $^3J_{\mathrm{HH}}$ = 6.0, $^4J_{\mathrm{HH}}$ = 1.2 Hz, 1 H, 13-H), 7.1 [dd, $^3J_{\mathrm{HH}}$ = 7.8, $^3J_{\mathrm{HH}}$ = 7.4 Hz, 2 H, 12(14)-H], 7.2 [dd, $^3J_{\mathrm{HH}}$ = 7.0, $^4J_{\mathrm{HH}}$ = 1.3 Hz, 2 H, 11(15)-H] ppm. - ^{13}C NMR (CDCl$_3$, 100 MHz, BB): δ = 25.6 (d, $^2J_{\mathrm{CP}}$ = 3.6 Hz, C-6), 29.4 (d, $^2J_{\mathrm{CP}}$ = 3.4 Hz, 6 × CH_3), 35.1 [d, $^1J_{\mathrm{CP}}$ = 16.1 Hz, $C(\mathrm{CH_3})_3$], 39.0 (d, $^1J_{\mathrm{CP}}$ = 19.5 Hz, C-7), 90.3 (d, $^2J_{\mathrm{CP}}$ = 33.9 Hz, C-9), 91.9 [d, J = 5.6 Hz, C-2(5)], 94.7 [d, J = 1.7 Hz, C-3(4)], 108.1 (d, J = 8.2 Hz, C-1), 117.1 (d, $^3J_{\mathrm{CP}}$ = 1.7 Hz, C-10), 124.3 (s, 13-C), 127.5 (s, 12(14)-C), 128.6 (s, 10a-C), 131.0 [d, $^5J_{\mathrm{CP}}$ = 0.57 Hz 11(15)-C] ppm. - ^{31}P NMR (CDCl$_3$, 161 MHz): δ = 104.8 (s) ppm. - MS (70 eV): *m/z* (%) = 397 (100) [M$^+$ + 1], 340 (34) [M$^+$ – C_4H_8], 282 (28), 284 (47) [M$^+$ – 2(C_4H_8)], 238 (31), 206 (15), 180 (10), 182 (37), 160 (11), 136 (14). - HRMS (ESI): Calcd. for $C_{23}H_{31}PNi$ [M$^+$ + H]: 397.1595; found 397.1581.

4.5.2 Synthesis of {[(Di-*tert*-butylphosphanylethyl)cyclopentadienyl]-2-(4-methyl phenyl)ethynyl}nickel(II) (79)



79

To a suspension of **62** (0.20 g, 0.6 mmol) and CuI (5 mg) in freshly distilled triethylamin (10 mL), (4-methylphenyl)ethyne (0.14 g, 1.2 mmol) was added dropwise. The colour of the reaction mixture became violet brown. After stirring the mixture for 14 h, the solvent was removed till dryness. The crude product **79** was extracted with diethyl ether (3 × 25 mL) and was chromatographed (SiO$_2$, petroliumether / ethyl acetate 10 : 1, 30 × 4) to yield

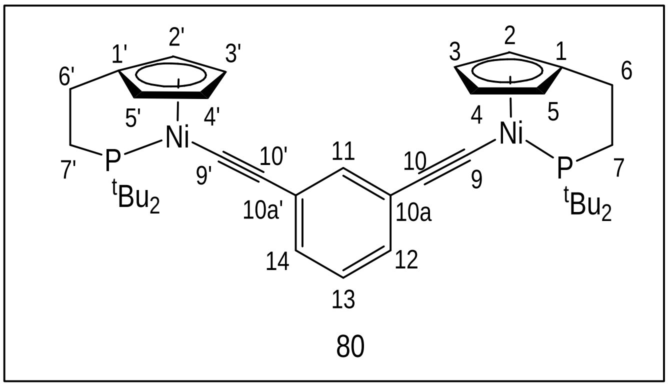
0.23 g (0.56 mmol, 91%) of **79** as a deep brown solid (m.p. 220 °C decomp.). A part of the complex **79** was recrystallized from hexane at −20 °C to get fine crystals for crystallographic measurement.

79: IR (ATR): $\tilde{\nu}$ = 2962 cm^{-1} (w), 2944 (s), 2895 (s), 2086 (m), 1605 (w), 1503 (m), 1455 (m), 1357 (m), 1259 (s), 1173 (m), 1017 (s), 865 (w), 782 (s), 674 (m). - ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.50 (d, $^{3}J_{PH}$ = 13.5 Hz, 18 H, 6 × CH_3), 2.02 (dt, $^{3}J_{HH}$ = 7.4 Hz, 2 H, 6-H), 2.25 (s, 3 H, CH_3-Ph), 2.48 (dd, $^{2}J_{PH}$ = 8.5 Hz, $^{3}J_{HH}$ = 7.5 Hz, 2 H, 7-H), 5.5, 2 5.70 [AA′BB′ line system, 2(5), 4 H, 3(4)-H], 6.92 [d, $^{3}J_{HH}$ = 7.9 Hz, 2 H, 12(13)-H], 7.10 [d, $^{3}J_{HH}$ = 8.0 Hz, 2 H, 11(14)-H] ppm. - ^{13}C NMR ($CDCl_3$, 100 MHz, BB): δ = 21.1 (s, CH_3-Ph), 25.6 (d, $^{2}J_{CP}$ = 3.7 Hz, C-6), 29.4 (d, $^{2}J_{CP}$ = 3.5, 6 × CH_3), 35.1 (d, $^{1}J_{CP}$ = 15.8 Hz, $C(CH_3)_3$], 39.0 (d, $^{1}J_{CP}$ = 19.3 Hz, C-7), 88.0 (d, $^{2}J_{CP}$ = 34.0 Hz, C-9), 91.9 [d, J = 5.7 Hz, C-2(5)], 94.7 [d, J = 1.8 Hz, C-3(4)], 107.9 (d, J = 8.2 Hz, C-1), 117.0 (s, C-10), 125.9 (s, C-10a), 128.2 [s, C-12(13)], 130.9 [d, $^{4}J_{CP}$ = 0.4 Hz, C-11(14)], 133.8 (s, C-12a) ppm. - ^{31}P NMR ($CDCl_3$, 161 MHz): δ = 104.5 (s) ppm. - MS (ESI acetonitrile): *m/z* (%) = 509 (8) [M^+ + K + H_2O +CH_3CN], 474 (6) [M^+ + Na + CH_3CN], 411 (12) [M^+ + H], 336 (100) [M^+ – C_9H_7 + CH_3CN], 294 (5) [M^+ – C_9H_6], 255 (4) [$C_{13}H_{10}NiP$]. - HRMS (ESI acetonitrile): Calcd. for $C_{24}H_{33}PNi$ [M^+ + H]: 411.1752; found 411.1767.

4.5.3 Craystal Structure Analysis Data of 79

Emperical formula $C_{24}H_{33}NiP$, Formula weight 411.18, Crystal system, Orthorhombic, space group, P c c n, a = 14.645(3), b = 17.867(4), c = 17.329(5) Å, α = 90°, β = 90°, γ = 90°, V = 4534(2) Å^3, Z = 8, d_{calcd} = 1.205 Mg/m^3, F(000) = 1760, μ = 0.931 mm^{-1}, Crystal size 0.67 x 0.63 x 0.52 mm, Stoe IPDS area detector diffractometer, T = 300(2) K, Mo_{ka} = 0.71073 Å, θ_{min} = 2.15°, θ_{max} = 24.15°, -16<=h<=16, -20<=k<=20, -19<=l<=19, no absorption correction, no extinction correction, 49417 collected, 3555 unique reflections, [R(int) = 0.0540], completeness to theta = 24.2, 99.1 %, refinement method Full-matrix least-squares on F^2, data = 3555, restraints = 0 parameters = 235, Goodness-of-fit on F^2 = 1.218, Final R indices [I>2sigma(I)] R1 = 0.0436 , wR2 = 0.0952, R indices (all data), R1 = 0.0624 , wR2 =0.0984Largest diff. peak and hole0.334 and -0.304 eÅ^3.

4.5.4 Synthesis of 1,3-Bis{[(di-*tert*-butylphosphanylethyl)cyclopentadienyl]nickel(II)-ethynyl}benzene (80)



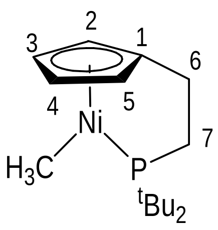
80

To a suspension of **62** (0.4 g, 1.2 mmol) and CuI (5 mg) in freshly distilled triethylamin (10 mL) 1,3-diethynylbenzene (0.08g, 0.6 mmol) was added dropwise. The colour of reaction mixture became violet brown. After stirring the mixture for 14 h the solvent was removed at reduced pressure till dryness. The crude product **80** was extracted with diethyl ether (3 × 25 mL) and was chromatographed (SiO_2, petroliumether / ethyl acetate 10 : 1, 30 × 4) to yield 0.4 g (0.56 mmol, 47%) of **80** as a deep brown solid (m.p. 302 ^{o}C decomp.).

80: IR (ATR): $\tilde{\nu}$ = 3081 cm^{-1} (w), 3070 (w), 2962 (s), 2870 (s), 2082 (m), 1584 (m),1471 (m), 1435 (w), 1390 (m), 1371 (m), 1357 (m), 1306 (w), 1259 (s), 1179 (m), 1064 (w), 1037 (m), 1016 (s), 911 (m), 900 (w), 865 (w), 798 (s), 733 (m), 687 (m), 675 (w). - ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.50 (d, $^3J_{PH}$ = 13.5 Hz, 36 H, 12 × *CH3*), 2.03 [dt, $^3J_{HH}$ = 7.5, 7.4 Hz, 4 H, 6(6′)-H], 2.47 [dd, $^2J_{PH}$ = 8.5 Hz, $^3J_{HH}$ = 7.5 Hz, 4 H, 7(7′)-H], 5.51, 5.70 [AA′BB′ line system, 2,2′ (5,5′), 3,3′ (4,4′)-H, 8 H], 7.05 (dd, $^3J_{HH}$ = 7.6 Hz, 1 H, 13-H), 7.18 [ddd, $^3J_{HH}$ = 7.6, 6.2 Hz, $^4J_{HH}$ = 1.4 Hz, 2 H, 12(14)-H], 7.3 (s, 11-H) ppm. - ^{13}C NMR ($CDCl_3$, 100 MHz, BB): δ = 25.8 [d, $^2J_{CP}$ = 3.6 Hz, C-6(6′)], 29.5 [d, $^2J_{CP}$ = 3.5, 12 × *CH3*], 35.3 [d, $^1J_{CP}$ = 16.2 Hz, *C*(CH_3)$_3$], 39.2 [d, $^1J_{CP}$ = 19.5 Hz, C-7(7′)], 92.1 [d, *J* = 5.7 Hz, C-2,2′(5,5′)], 93.5 [d, $^2J_{CP}$ = 33.8 Hz, C- 9(9′)], 94.9 [d, *J* = 1.9 Hz, C-3,3′ (4,4′)], 108.51 [d, *J* = 7.9 Hz, C-1(1′)], 116.3 [s, C-10(10′)], 121.3 [s, C-10a(10a′)], 127.6 [s, C-12(14)], 131.7 (s, C-13), 134.6 (s, C-11) ppm. - ^{31}P NMR ($CDCl_3$, 161 MHz): δ = 105.2 (s) ppm. - MS (ESI acetonitrile): *m/z* (%) = 778 (3) [M$^+$ + Na + CH_3CN], 715 (19) [M$^+$ + H], 539 (4) [M$^+$ – $C_{13}H_{19}$], 421 (9) [M$^+$ –

$C_{15}H_{24}NiP$], 336 (100) [M^+ – $C_{25}H_{30}NiP$ + CH_3CN], 318 (5) [M^+ – $C_{23}H_{31}NiP$], 255 (11) [$C_{13}H_{10}NiP$], 215 (11) [$C_{10}H_7NiP$], 102 (3) [C_8H_6]. - HRMS (ESI acetonitrile): Calcd. for $C_{40}H_{56}P_2Ni_2$ [M^+ + H]: 715.2642; found 715.2663.

4.5.5 Synthesis of [(Di-*tert*-butylphosphinoethyl)cyclopentadienyl]methylnickel(II) (81)



81

To a solution of **62** (0.20 g, 0.6 mmol) in diethyl ether (60 mL), methyllithium (0.5 mL, 0.7 mmol, 1.6 M in diethyl ether) was added dropwise at 25 °C. The colour of the reaction mixture became green. The solution was stirred for 1 h and filtered through celite. After solvent removal at reduced pressure the product was recrystallized from saturated hexane solution at −20 °C to yield 0.16 g (0.5 mmol, 86%) of **81** as a crystalline solid (m.p. 182 ^{o}C decomp.).

81: IR (ATR): $\tilde{\nu}$ = 2945 cm^{-1} (w), 2903 (w), 2858 (w), 1457 (w), 1388 (w), 1361 (w), 1304 (w), 1260 (m), 1179 (w), 1166 (w), 1127 (s), 1092 (w), 1088 (s), 1017 (s), 931 (w), 871 (w), 821 (m), 808 (m), 778 (s), 668 (m), 650 (w), 620 (m). - ^{1}H NMR ($CDCl_3$, 200 MHz): δ = – 1.07 (d, ^3J = 3.2 Hz, 3 H, CH_3-Ni), 1.36 (d, $^3J_{PH}$ = 12.7 Hz, 18 H, 6 × CH_3), 1.93 (dt, $^3J_{HH}$ = 7.5, 6.9 Hz, 2 H, 6-H), 2.36 (dd, $^2J_{PH}$ = 7.6 Hz, $^3J_{HH}$ = 7.5 Hz, 2 H, 7-H), 5.13 [s, 2 H, 2(5)-H], 5.70 [s, 2 H, 3(4)-H] ppm. - ^{13}C NMR ($CDCl_3$, 100 MHz, BB): δ = – 43.5 (d, $^2J_{CP}$ = 20.3 Hz, CH_3-Ni), 24.9 (s, C-6), 29.4 (s, 6 × CH_3), 34.6 (d, J_{CP} = 18 Hz, C-7), 40.3 [s, $C(CH_3)_3$], 88.7 [s, C-2(5)], 93.9 [s, C-3(4)], 97.4 (s, C-1) ppm. - ^{31}P NMR ($CDCl_3$, 161 MHz): δ = 90.0 (s) ppm. - MS (70 eV): *m/z* (%) = 310 (40) [M^+], 295 (32) [M^+ – CH_3], 268 (32) [M^+ – C_3H_6], 254 (21) [M^+ – C_4H_8], 239 (29) [M^+ – C_5H_{11}], 226 (25) [M^+ – C_6H_{12}], 198 (20){M^+ – [2C_4H_8], 183 (42) {M^+ – 2[C_4H_8] – CH_3}, 162 (62), 138 (32). - HRMS: Calcd. for $C_{16}H_{29}PNi$ [M^+]: 310.1360; found 310.1345.

4.5.6 Crystal Structure Analysis Data of 81

Emerical formula $C_{16}H_{29}NiP$, Formula weight 311.07, Crystal system Hexagonal, space group, P 61, a = 8.967(1) Å, b = 8.967(1) Å, c = 36.131(4) Å, α = 90°, β = 90°, γ = 120°, V = 2516.0(5)$Å^3$, Z = 6, $d_{calcd.}$ = 1.232 Mg/m^3, F(000) = 1008, μ = 1.236 mm^{-1}, Crystal size 0.25 x 0.07 x 0.04 mm, Stoe IPDS area detector diffractometer, T = 300(2) K, $Mo_{K\alpha}$ = 0.71073 Å, θ_{min} = 2.62 θ_{max} = 20.95°, -8<=h<=8, -8<=k<=8, -35<=l<=35, 99 % Absorption correction, Completeness to theta = 20.95, no extinction correction, 18505 collected, 1745 unique, 1745 observed reflections [$I>2\sigma(I)$], restraints / parameters, / 1 / 83, [R(int) = 0.1887], no refinement method, refinement by full-matrix least-squares method (F^2), goodness-of-fit on F^2, 0.852, final R-indices: [$I>2\sigma(I)$] R_1 = 0.0474 , wR_2 = 0.0707, R-indices (alldata), R_1 = 0.1196, wR_2 = 0.0806, Absolute structure parameter 0.06(4) largest diff. peak and hole 0.340 and -0.707 $eÅ^3$.

4.5.7 Cyclic Volatammetry of 62, 79, 80 and 81

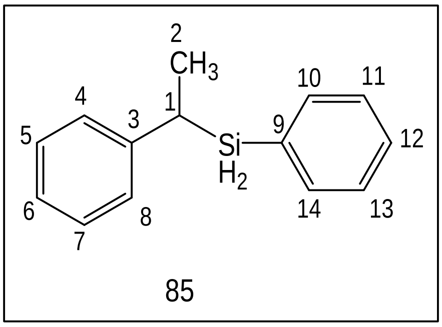
The electrochemical measurements were performed by using Potentiostat Heka PG 285, reference electrode Ag/AgCl (Alfa), counter electrode Pt wire 0.001 M solutions of complexes **62**, **79**, **80** and **81** in a 0.2 M CH_2Cl_2 solution of n-Bu_4NPF_6. the cyclic voltammogram were obtained in a standard, one –compartment electrochemical cell using a graphite-disk electrode as working electrode, a platinium wire as the counter electrode and Ag/AgCl reference electrode. The experiments were performed in the potential range of −1.0 to 1.5 V using scan rate (0.05, 0.1, 0.2, and 0.5 V/s) and normalized to ferrocene/ferrocenium ion (E_0 = 4.9 V vs Ag/AgCl).

4.5.8 Dehydropolymerization of phenylsilane

Addition of $PhSiH_3$ (3.0 mmol, 0.4 ml) to the solid samples of **79** and **81** (0.015 mmol) led to the evolution of gas (presumably H_2). The colour of the reaction mixtures had changed from dirty green to dark red. Stirring the reaction mixture for one day for reaction with **81** and two days for reaction with **79** gave thick oils consisting of various mixtures of cyclic and linear polysilane. The ^{1}H NMR spectra showed absorption peaks for Si─H at δ = 5.17-5.19 ppm for cyclic oligomers and at δ = 4.40-4.56 ppm for linear oligomers. The cyclic to linear oligomer ratio was determined for each case by integration of these peaks (ca. 80:20 for reaction with **81** and ca. 60:40 for reaction with **79**), while the monomer conversion was determined relative to the $PhSiH_3$ signal at δ = 4.19 ppm (ca. 94% for the reaction of **80** and ca. 85% for reaction of **79**).

^1H NMR ($CDCl_3$, 200 MHz): δ = 4.40-4.56 [m, Si-H (linear)], 5.17-5.19 [m, Si-H(cyclic)], 7.41-7.62 (m, arom.-H) ppm.

4.5.9 Hydrosilylation of Styrene



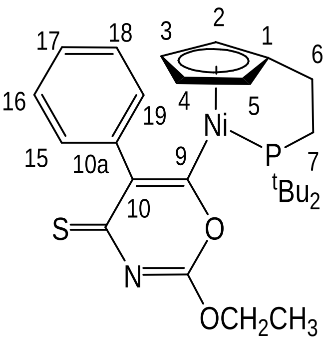
85

In two separate reactions Styrene **82** (150 μL, 1.3 mmol, 100 equiv) was added to the solution of **79** (7.3 mg, 0.013 mmol) and **81** (5.3 mg, 0.013 mmol) in CD_2Cl_2 (ca. 0.75 mL) at 25 °C. On the addition of $PhSiH_3$ (164 μL, 1.3 mmol, 100 equiv) into the CD_2Cl_2 solutions the colour of the reaction mixtures had started to change slowly from dark green to orange red. After stirring the solution for 24 h for the reaction with **81**, the ^1H NMR spectrum showed the completion of the reaction and in case of reaction with **79** after 48 h stirring the ^1H NMR spectrum showed 50% conversion of phenylsilane into polysilane. The solutions were filtered through silica gel and dried to get hydrosilylation product **83** in 90% yield for reaction with **81** and 49% yield with **79**.

^1H NMR ($CDCl_3$, 400 MHz): δ = 1.46 (d, $^3J_{HH}$ = 7.1 Hz, 3 H, *CH_3*), 2.60-2.66 (m, 1 H, *CH*), 4.33 (d, $^3J_{HH}$ = 3.0 Hz, 2 H, Si-H), 7.09-7.13 (m, 2 H, 6-H, 12-H), 7.24-7.33 [m, 4 H, 4(8)-H, 10(14)-H], 7.40-7.42 [m, 5(7)-H, 11(13)-H] ppm. - ^{13}C NMR ($CDCl_3$, 100 MHz, BB): δ = 16.5 (s, *CH_3*), 31.0 (s, *CH*), 125.1 (s, C-6), 127.2 [s, C-4(8)], 127.9 [s, C-11(13)], 128.5 [s, C-5(7)], 129.9 (s, C-12), 131.5 (s, C-9), 135.7 [s, C-10(14)], 144.7 (s, C-3) ppm. - GCMS *m/z* = 212 [M^+].

4.6 [4+2] Cycloaddition Reactions of EtO_2CNCS to σ-Alkynyl Complexes 78 and 79

4.6.1 Synthesis of $CH_3PhC\{=C[OC(OC_2H_5)=N]CS\}Ni$ (η-$C_5H_4C_2H_4P\ {}^tBu_2$) (89)

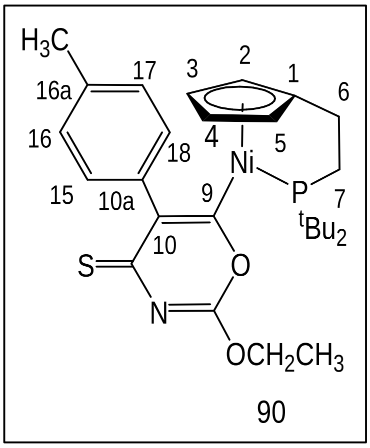


89

To a solution of **78** (0.20 g, 0.5 mmol) in chloroform (10 mL), ethoxcarbonyl-isothiocayanate (80 mg, 0.6 mmol, 70 µL) was added and stirred at 25 °C for 2 h. The volume of the solution was reduced to (1 mL) and pentane (30 mL) was added. Then the solution was filtered through celite. After solvent removal at reduced pressure, the residue was dried and dissolved in diethyl ether (5 mL). Hexane (5 mL) was layered over the diethyl ether solution to crystallize the product at −20 °C to yield 0.27 g (0.5 mmol, 85%) as an orange solid of **89** (m.p. 154 ^oC decomp.).

89: IR (ATR): $\tilde{\nu}$ = 2958 cm^{-1} (w), 2903 (w), 2861 (w), 2155 (w), 2087 (w), 1670 (w), 1606 (w), 1523 (w),1507 (w), 1308 (w), 1259 (s), 1210 (w), 1088 (s), 1016 (s), 865 (w), 791 (w), 694 (w), 673 (w). - ^1H NMR ($CDCl_3$, 400 MHz): δ = 1.34 (d, $^3J_{PH}$ = 13.8 Hz, 18 H, 6 × CH_3), 1.35 (t, $^3J_{HH}$ = 7.0 Hz, 3 H, CH_3-CH_2), 2.08 (dt, $^3J_{HH}$ = 7.4, 7.2 Hz, 2 H, 6-H), 2.52 (dd, $^2J_{PH}$ = 8.4 Hz, $^3J_{HH}$ = 7.5 Hz, 2 H, 7-H), 4.23 (q, $^3J_{HH}$ = 7.1 Hz, 2 H, CH_2-CH_3), 5.33, 5.70 [AA′BB′ line system, 4 H, 2(5), 3(4)-H], 7.13 (dd, $^3J_{HH}$ = 7.4 Hz, 1 H, 17-H), 7.28 [dd, $^3J_{HH}$ = 7.5, 7.8 Hz, 2 H, 16(18)-H], 8.21 [d, $^3J_{HH}$ = 7.1, $^4J_{HH}$ = 1.1 Hz, 2 H, 15(19)-H] ppm. - ^{13}C NMR ($CDCl_3$, 100 MHz, BB): δ = 14.4 (s, CH_3-CH_2), 25.5 (d, $^2J_{CP}$ = 3.1 Hz, C-6), 29.3 (d, $^2J_{CP}$ = 4.1 Hz, 6 × CH_3), 34.9 [d, $^1J_{CP}$ = 16.1 Hz, $C(CH_3)_3$], 39.9 (d, $^1J_{CP}$ = 20.5 Hz, C-7), 62.5 (s, CH_2-CH_3), 91.6 [d, J = 4.8 Hz, C-2(5)], 95.9 [d, J = 1.4 Hz, C-3(4)], 113.0 (d, J = 8.5 Hz, C-1), 124.4 [s, C-16(18)], 125.1 (s, C-17), 127.6 [s, C-15(19)], 134.8 (d, $^4J_{CP}$ = 0.7 Hz, C-10a), 150.3 (d, ${}^3J_{CP}$ = 0.9 Hz, C-10), 160.6 (s, C=N), 165.4 (d, ${}^2J_{CP}$ = 1.7 Hz, C-9), 211.7 (d, ${}^4J_{CP}$ = 20.5 Hz, C=S) ppm. - ^{31}P NMR ($CDCl_3$, 161 MHz): δ = 101.2 (s) ppm. - MS (ESI acetonitrile): *m/z* (%) = 583 (84) [$M^+ - H + H_2O + K$], 528 (100) [$M + H]^+$, 336 (38) [$M^+ - C_{12}H_{10}NO_2S + CH_3CN$]. - HRMS (ESI acetonitrile): Calcd. for $C_{27}H_{36}NO_2PSNi$ [$M^+ + H$]: 528.1636; found 528.1649.

4.6.2 Synthesis of $CH_3PhC\{=C[OC(OC_2H_5)=N]CS\}Ni(\eta\text{-}C_5H_4C_2H_4P\,{}^tBu_2)$ (90)



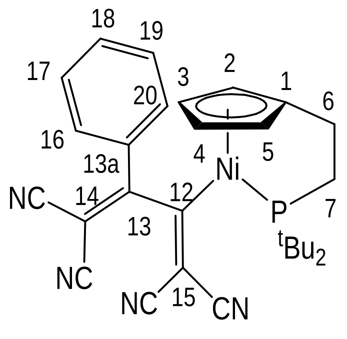
90

To a solution of complex **79** (0.10 g, 0.25 mmol) in chloroform (10 mL), ethoxcarbonylisothiocayanate (34 mg, 0.3 mmol, 30 µL) was added and stirred for 2 h at 25 °C. The volume of the solution was reduced to (1 mL) and pentane (30 mL) was added. Then the solution was filtered through celite. After solvent removal at reduced pressure, the residue was dried and dissolved in diethyl ether (5 mL). Hexane (5 mL) was layered over diethyl ether solution to crystallize the product to obtain 0.12 g (0.2 mmol, 90%) as an orange solid of **90** (m.p. 160 °C decomp.).

90: IR (ATR): $\tilde{\nu}$ = 2962 cm^{-1} (w), 2903 (w), 2859 (w), 2153 (w), 2086 (w), 1669 (w), 1609 (w), 1521 (w), 1505 (w), 1309 (w), 1259 (s), 1209 (w), 1087 (s), 1016 (s), 864 (w), 790 (w), 695 (w), 674 (w). - ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.31 (d, ${}^3J_{PH}$ = 13.8 Hz, 18 H, 6 × CH_3), 1.33 (t, ${}^3J_{HH}$ = 7.1 Hz, 3 H, CH_3-CH_2), 2.10 (dt, ${}^3J_{PH}$ = 7.4, 7.2 Hz, 2 H, 6-H), 2.32 (s, 3 H, CH_3-Ph), 2.54 (dd, ${}^2J_{PH}$ = 8.4 Hz, ${}^3J_{HH}$ = 7.5 Hz, 2 H, 7-H), 4.23 (q, ${}^3J_{HH}$ = 7.1 Hz, 2 H, CH_2-CH_3), 5.34, 5.72 [AA′BB′ line system, 4 H, 2(5), 3(4)-H], 7.10 [d, AA′BB′ line system, 2 H, 16(17)-H], 8.10 [d, AA′BB′ line system, 2 H, 15(18)-H] ppm. - ^{13}C NMR ($CDCl_3$, 100 MHz, BB): δ = 14.3 (s, *CH_3*-CH_2), 21.2 (s, *CH_3*-Ph), 25.5 (d, $^2J_{CP}$ = 3.4 Hz, C-6), 29.3 (d, $^2J_{CP}$ = 3.9 Hz, 6 × *CH_3*), 34.9 [d, $^1J_{CP}$ = 15.9 Hz, *C*(CH_3)$_3$], 39.9 (d, $^1J_{CP}$ = 20.5 Hz, C-7), 62.4 (s, *CH_2*-CH_3), 91.6 [d, *J* = 4.8 Hz, C-2(5)], 95.9 [d, *J* = 1.5 Hz, C-3(4)], 112.9 (d, *J* = 8.3 Hz, C-1), 124.3 [s, C-16(17)], 128.2 [s, C-15(18)], 132.1 (s, C-16a), 134.6 (s, C-10a), 150.5 (s, C-10), 160.6 (s, C=N), 165.2 (s, C-9), 209.1 (d, $^4J_{CP}$ = 20.5 Hz, C=S). - ^{31}P NMR ($CDCl_3$, 161 MHz): δ = 101.0 (s) ppm. - MS (ESI acetonitrile): *m/z* (%) = 597 (16) [M^+ – H + H_2O + K], 542 (100) [M^+ + H], 336 (71) [M^+ – $C_{13}H_{12}NO_2S$ + CH_3CN]. - HRMS (ESI acetonitrile): Calcd. for $C_{28}H_{38}NO_2PSNi$ [M^+ + H]: 542.1793; found 542.1813.

4.7 [2+2] Cycloaddition Reactions of Tetracyanoethylene to the Triple Bonds of σ-Alkynyl Complexes

4.7.1 Synthesis of {C[=C(CN)$_2$]CPh=C(CN)$_2$}Ni (η-$C_5H_4C_2H_4P$ ^{t}Bu$_2$) (91)

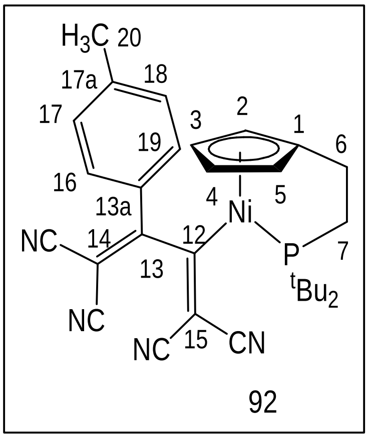


91

A solution of **78** (0.15 g, 0.4 mmol) and tetracyanoethylene (0.085 g, 0.7 mmol) in benzene (15 mL) was stirred for 14 h at 25 °C. After solvent removal at reduced pressure, the reaction mixture was chromatographed (SiO_2, petroleum ether / ethyl acetate 10 : 1, 30 × 4 cm) to yield 0.16 g (0.30 mmol, 80%) as dark brown solid, two major and two minor conformations of **91** (m.p. 180 °C).

91: IR (ATR): $\tilde{\nu}$ = 2962 cm^{-1} (w), 2944 (s), 2895 (s), 2219 (s), 1734 (w), 1602 (w), 1531 (m),1501 (w), 1473 (s), 1389 (m), 1365 (m), 1259 (s), 1177 (m), 1015 (s), 932 (w), 902 (w), 806 (s), 736 (w), 668 (m), 641 (w), 630 (w), 614 (m). - ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.39 (d, $^3J_{PH}$ = 14.5 Hz, 18 H, 6 × CH_3), 1.46 (d, $^3J_{PH}$ = 15.1 Hz, 18 H, 6 × CH_3), 1.71 (br, 1 H, 6-H), 1.80 (br, 1 H, 6-H), 2.00 (br, 1 H, 7-H), 2.24 (br, 1 H, 7-H), 3.32 (br, 1 H, 2(5)-H), 4.71 (br, 1 H, 2(5)-H), 4.96 (br, 1 H, 3(4)-H), 6.11 (br, 1 H, 3(4)-H), 7.28 [br, 2 H, 16(20)-H], 7.55 [br, 3 H, 17,18(19)-H] ppm. - ^{13}C NMR ($CDCl_3$, 100 MHz, BB): δ = 25.1 (s, C-6), 29.4 (s, 6 × CH_3), 29.9 (s, 6 × CH_3), 34.5 [d, $^1J_{CP}$ = 15.6 Hz, $C(CH_3)_3$], 35.7 [d, $^1J_{CP}$ = 14.3 Hz, $C(CH_3)_3$], 38.7 (d, $^1J_{CP}$ = 22.8 Hz, C-7), 75.4 (s, C-14), 91.7 [s, C-2(5)], 94.0 [s, C-2(5)], 94.3 (s, C-15), 96.9 [s, C-3(4)], 100.8 [s, C-3(4)], 110.5, 112.8, 115.2, 117.0 (4 × CN), 112.9 (s, C-1), 126.9 [s, C-17(19)], 129.0 [s, C-16(20)], 131.3 (s, C-13a), 134.6 (s, C-18), 180.3 (s, C-13), 213.1 (s, C-12) ppm. - ^{31}P NMR ($CDCl_3$, 161 MHz): δ = 96.1 (s) ppm. - MS (ESI acetonitrile): *m/z* (%) = 588 (38) [M^+ + Na + CH_3CN], 542 (100) [M^+ + H_2O], 525 (28) [M^+ + H], 336 (38) [M^+ – $C_{14}H_5N_4$ + CH_3CN]. - HRMS (ESI acetonitrile): Calcd. for $C_{29}H_{31}N_4PNi$ [M^+ + H]: 525.1718; found 525.1733.

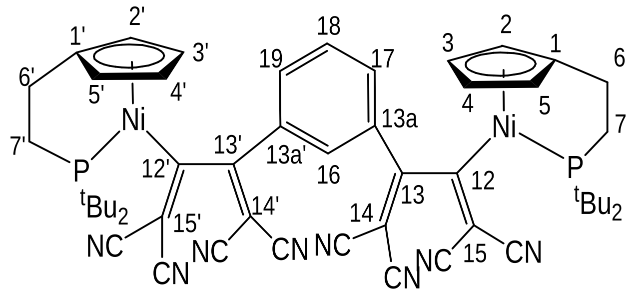
4.7.2 Synthesis of {C[=C(CN)$_2$]CCH$_3$Ph=C(CN)$_2$}Ni (η-C$_5$H$_4$C$_2$H$_4$P ^{t}Bu$_2$) (92)



A solution of **79** (0.19 g, 0.5 mmol) and tetracyanoethylene (0.10 g, 0.8 mmol) in benzene (20 mL) was stirred for 14 h at 25 °C. After solvent removal at reduced pressure the residue was chromatographed (SiO_2, petroleum ether / ethyl acetate 10 : 1, 30 × 4 cm) to yield 0.18 g (0.36 mmol, 79%) as dark brown solid, the two major and two minor conformations of **92** (m.p.183 °C).

92: IR (ATR): $\tilde{\nu}$ = 2960 cm^{-1} (w), 2940 (s), 2890 (s), 2220 (s), 1733 (w), 1606 (w), 1529 (m), 1504 (w), 1471 (s), 1391 (m), 1361 (m), 1258 (s), 1178 (m), 1014 (s), 934 (w), 904 (w), 806 (s), 739 (w), 667 (m), 642 (w), 630 (w), 614 (m). - ^1H NMR ($CDCl_3$, 400 MHz): δ = 1.38 (d, $^3J_{PH}$ = 14.2 Hz, 18 H, 6 × CH_3), 1.46 (d, $^3J_{PH}$ = 17.9 Hz, 18 H, 6 × CH_3), 1.71 (br, 1 H, 6-H), 1.80 (br, 1 H, 6-H), 2.00 (br, 1 H, 7-H), 2.25 (br, 1 H, 7-H), 2.45 (s, 3 H, CH_3-Ph), 3.41 [br, 1 H, 2(5)-H], 4.72 [br, 1 H, 2(5)-H], 4.96 [br, 1 H, 3(4)-H], 6.12 [br, 1 H, 3(4)-H], 7.17 [br, 2 H, 17(18)-H], 7.3 [d, $^3J_{HH}$ = 7.1 Hz, 2 H, 16(19)-H] ppm. - ^{13}C NMR ($CDCl_3$, 100 MHz, BB): δ = 21.5 (s, CH_3-Ph), 25.1 (s, C-6), 29.4 (s, 6 × CH_3), 29.9 (s, 6 × CH_3), 34.5 [d, $^1J_{CP}$ = 14.2 Hz, $C(CH_3)$], 35.7 [d, $^1J_{CP}$ = 15.1 Hz, $C(CH_3)$], 38.8 (d, $^1J_{CP}$ = 23.0 Hz, C-7), 75.0 (s, C-14), 91.6 [s, C-2(5)], 93.9 [s, C-2(5)], 94.2 (s, C-15), 97.2 [s, C-3(4)], 100.9 [s, C-3(4)], 110.5, 112.9, 115.1, 117.0 (4 × CN), 113.1 (s, C-1), 126.9 [s, C-17(18)], 129.6 [s, C-16(19)], 131.7 (s, C-13a), 141.9 (s, C-17a), 180.6 (s, C-13), 213.4 (s, C-12) ppm. - ^{31}P NMR ($CDCl_3$, 161 MHz): δ = 95.8 (s) ppm. - MS (ESI acetonitrile): m/z (%) = 602 (43) [M^+ + Na + CH_3CN], 556 (100) [M^+ + H_2O], 539 (29) [M^+ + H], 336 (29) [M^+ – $C_{15}H_7N_4$ + CH_3CN]. - HRMS (ESI acetonitrile): Calcd. for $C_{30}H_{33}N_4PNi$ [M^+ + H]: 539.1875; found 539.1884.

4.7.3 Synthesis of $\{\{C[=C(CN)_2]C=C(CN)_2\}Ni\ (\eta\text{-}C_5H_4C_2H_4P\ {}^tBu_2)\}_2Ph$ (93)



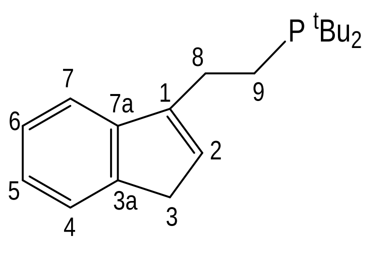
93

A solution of **80** (0.42 g, 0.6 mmol) and tetracyanoethylene (0.35 g, 2.4 mmol) in benzene (15 mL) was stirred at 25°C for 14 h. After solvent removal at reduced pressure, the residue was chromatographed (SiO_2, petroleum ether / ethyl acetate 10 : 1, 30 × 4 cm) to yield the two major and two minor conformations of complex **93**, 0.35 g (0.37 mmol, 62%) as a dark brown solid (m.p. 320 °C decomp.).

93: IR (ATR): $\tilde{\nu}$ = 2959 cm^{-1} (w), 2940 (s), 2895 (s), 2223 (s), 1729 (w), 1607 (w), 1530 (m),1504 (w), 1471 (s), 1393 (m), 1364 (m), 1257 (s), 1178 (m), 1015 (s), 935 (w), 903 (w), 806 (s), 739 (w), 667 (m), 645 (w), 632 (w), 612 (m). - ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.39 [d, $^3J_{PH}$ = 15.1 Hz, 36 H, 12 × CH_3], δ = 1.47 [d, $^3J_{PH}$ = 15.2 Hz, 36 H, 12 × CH_3], 1.72 [br, 2 H, 6(6′)-H], 1.82 [br, 2 H, 6(6′)-H], 2.00 [br, 2 H, 7(7′)-H], 2.48 [br, 2 H, 7(7′)-H], 3.41 {br, 2 H, [2(5)][2′(5′)]-H]}, 4.76 {br, 2 H, [2(5)][2′(5′)]-H]}, 5.00 {br, 2 H, [3(4)][3′(4′)]-H]}, 6.11 {br, 2 H, [3(4)][3′(4′)]-H]}, 7.32 (br, 1 H, 18-H), 7.53 [br, 2 H, 17(19)-H], 7.66 (d, $^3J_{HH}$ = 6.9 Hz, 1 H, 16-H) ppm. - ^{13}C NMR ($CDCl_3$, 100 MHz, BB): δ = 25.1 [s, C-6(6′)], 29.4 (s, 12 × CH_3), 29.9 (s, 12 × CH_3), 34.6 [d, $^1J_{CP}$ = 15.9 Hz, $C(CH_3)_3$], 35.7 [d, $^1J_{CP}$ = 15.1 Hz, $C(CH_3)_3$], 38.7 (d, $^1J_{CP}$ = 22.9 Hz, C-7(7′), 76.0 [s, C-14(14′)], 92.0 [s, C-[2(5)][2′(5′)], 94.2 [s, C-[2(5)][2′(5′)], 94.8 [s, C-15(15′)], 96.5 [s, C-[3(4)][3′(4′)], 100.9 [s, C-[3(4)][3′(4′)], 110.5, 112.6, 115.3, 116.9 (8 × CN), 115.4 (s, C-1(1′), 123.4 [s, C-13a(13a′)], 127.8 [s, C-17(19)], 130.2 (s, C-18), 135.9 (s, C-16), 178.9 [s, C-13(13′), 212.4 [s, C-12(12′)] ppm. - ^{31}P NMR ($CDCl_3$, 161 MHz): δ = 96.3 (s) ppm. - MS (ESI acetonitrile): *m/z* (%) = 653 (3) [$M^+ - C_{16}H_{22}NNiP$], 612 (38) [$M^+ - C_{18}H_{25}N_2NiP$], 566 (100) [$M^+ - C_{21}H_{25}N_4NiP + H_2O$], 549 (25) [$M^+ - C_{21}H_{24}N_4NiP$], 336 (31) [$M^+ - C_{37}H_{30}N_8NiP + CH_3CN$].

4.8 Synthesis of [1-(Di-*tert*-butylphosphanylethyl)indenyl]nickel(II)

4.8.1 Synthesis of Di-*tert*-butyl-2-(1′-indenylethyl)phosphane (94)



94

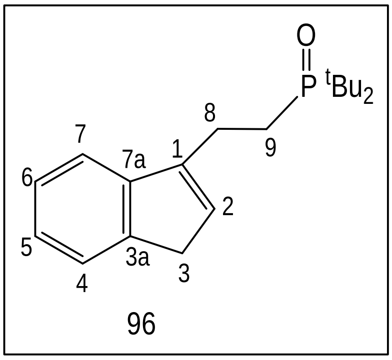
At 0 °C to a solution of di-*tert*-butylphosphane (2.92 g. 0.02 mol) in THF (400 mL), butyllithium (0.015 mol, 9.5 mL, 1.6 M in hexane) was addeddrop wise. After stirring for 2 h at 0°C, the reaction mixture was boiled and [4,5]benzospiro[2.4]hepta-4,6-diene (**33**) (2.84 g, 0.02 mol) was added. The solution was heated at reflux for 120 h. The colour of the reaction mixture had changed to red. Then the solution was cooled to 25 °C. After solvent removal at reduced pressure, the residue was washed with degassed pentane (3 × 30 mL). The reaction mixture was hydrolysed with water (50 mL). The product was extracted with pentane (3 × 100 mL). The combined organic layers were dried over sodium carbonate and filtered. Solvent removal at reduced pressure yielded 3.90 g (0.014 mol, 90%) of **94** as a light yellow oil.

94: IR (ATR): $\tilde{\nu}$ = 2953 cm^{-1} (w), 2903 (w), 2858 (w), 1462 (w), 1393 (w), 1366 (w), 1260 (w), 1155 (m), 1018 (w), 798 (s), 769 (s), 720 (m). - ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.21 (d, $^3J_{PH}$ = 11.0 Hz, 18 H, 6 × CH_3), 1.73 - 1.78 (m, 2 H, 8-H), 2.75 - 2.81 (m, 2 H, 9-H), 3.35 (d, $^3J_{HH}$ = 1.6, 2 H, 3-H), 6.29 (s, 1 H, 2-H), 7.21 (dd, ABCD line system, 1 H, 4-H), 7.26 (dd, ABCD line system, 1 H, 6-H), 7.39 (d, ABCD line system, 1 H, 5-H), 7.48 (d, ABCD line system, 1 H, 7-H) ppm.- ^{13}C NMR ($CDCl_3$, 100 MHz, BB): δ = 20.0 (d, $^1J_{CP}$ = 20.2 Hz, C-8), 29.4 (d, $^2J_{CP}$ = 29.1 Hz, C-9), 29.8 (d, $^2J_{CP}$ = 13.1 Hz, 6 × CH_3), 31.5 [d, $^1J_{CP}$ = 19.8 Hz, $C(CH_3)_3$], 37.7 (s, C-3), 119.0 (s, C-2), 123.9 (s, C-4), 124.6 (s, C-6), 126.1 (s, C-5), 127.6 (s, C-7), 144.6 (s, C-7a), 145.2 (s, C-3a), 145.8 (d, $^3J_{CP}$ = 15.4 Hz, C-1) ppm.- ^{31}P NMR ($CDCl_3$, 161 MHz): δ = 32.2 (s) ppm. - MS (ESI acetonitrile): *m/z* (%) = 368 (9) [$M^+ + CH_3CN + K$], 306 (22) [$M^+ + H_2O$], 305 (100) [$M^+ - H + H_2O$], 289 (54) [$M^+ + H$]. - HRMS (ESI acetonitrile): Calcd. for $C_{19}H_{29}P$ [$M + H$]$^+$: 289.2085; found 289.2090.

4.8.2 Microwave-Assisted Synthesis of Di-*tert*-butyl-2-(1′-indenylethyl)phosphane (94)

At 25 ^{o}C to a solution of di-*tert*-butylphosphane (0.10 g. 0.7 mmol) in THF (4 mL), butyllithium (0.6 mmol, 0.4 mL, 1.6 M in hexane) was added dropwise. After stirring the deep yellow solution for 2 h at 25 °C, [4,5]benzospiro[2.4]hepta-4,6-diene (**33**) (0.1 g, 0.7 mmol) was added. The solution was heated under microwave irradiations (Power = 200 W, Temperature = 150 °C, Ramp time = 3 min, Hold time = 40 min). The colour of the reaction mixture had changed from deep yellow to red. Then the solution was cooled to 25 °C. After solvent removal, the residue was washed with degassed pentane (3 x 5 mL). The reaction mixture was hydrolysed with water (10 mL). The product was extracted with pentane (3 x 10 mL). The combined organic layers were dried over sodium carbonate and filtered. The solvent removal at reduced pressure yielded 0.15 g (0.5 mmol, 91%) of **94** as a light yellow oil.

4.8.3 Synthesis of Di-*tert*-butyl-2-(1′-indenyl)ethylphosphanoxide (96)



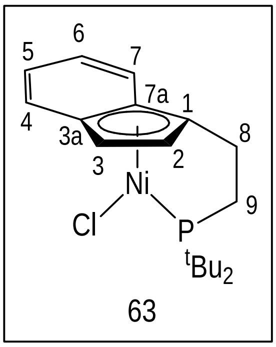
96

At 0 °C to a solution of di-*tert*-butylphosphane (2.92 g. 0.02 mol) in THF (400 mL), butyllithium (0.015 mol, 9.5 mL, 1.6 M in hexane) was addeddrop wise. After stirring for 2 h at 0°C, the reaction mixture was boiled and [4,5]benzospiro[2.4]hepta-4,6-diene (**33**) (2.84 g, 0.02 mol) was added. The solution was heated at reflux for 120 h. The colour of the reaction mixture had changed to red. Then the solution was cooled to 25 °C. After solvent removal at reduced pressure, the residue was washed with degassed pentane (3 × 30 mL). The reaction mixture was hydrolysed with water (50 mL). The product was extracted with pentane (3 × 100 mL). The combined organic layers were dried over sodium carbonate and filtered. After solvent removal the crude product was dissolved in 30 ml acetone and treated with hydrogenperoxide (5 mL, 30%). After stirring the reaction mixture for 30 min ferrous sulphate was added to destroy the excess of hydrogenperoxide. Solvent was removed and water (50 mL) was added to the reaction mixture. The product was extracted with chloroform (2 x 30 mL). After solvent removal and recrystallization of the crude product from a mixture of methanol and hexane yielded 3.1 g of phosphanoxide **95** (0.10 mol, 68%) as an off white solid (m.p. 108 °C).

95: IR (ATR): $\tilde{\nu}$ = 2967 cm^{-1} (w), 2926 (w), 2903 (w), 2868 (w), 1477 (w), 1388 (w), 1361 (w), 1304 (w), 1260 (m), 1099 (s), 1092 (w), 1014 (s), 946 (w), 815 (m), 797 (m), 761 (s), 727 (s), 720 (m), 650 (w), 620 (m). - ^{1}H NMR (CDCl$_3$, 400 MHz). δ 1.31 (d, $^3J_{PH}$ = 13.1 Hz, 18 H, 6 x *CH$_3$*), 2.07 (m, 2 H, 8-H), 2.93 (br, 2 H, 9-H), 3.34 (s, 2 H, 3-H), 6.25 (d, $^3J_{HH}$ = 7.4 Hz, 1 H, 2-H), 7.28-7.47 (m, 4 H, 4, 5, 6, 7-H) ppm. - ^{13}C NMR (CDCl$_3$, 100 MHz, BB): δ = 24.8 (s, C-8), 27.2 (d, $^1J_{CP}$ = 70.9 Hz, C-9), 31.5 (d, $^2J_{CP}$ = 19.5 Hz, 6 x *CH$_3$*), 36.3 [d, $^1J_{CP}$ = 58.7 Hz, *C*(CH$_3$)$_3$], 37.8 (s, C-3), 119.2 (s, C-2), 124.0 (s, C-4), 124.9 (s, C-6), 126.3 (s, C-5), 127.9 (s, C-7), 144.7 (s, C-7a), 144.9 (s, C-3a), 145.2 (s, C-1) ppm. - ^{31}P NMR (CDCl$_3$, 161 MHz): δ =

60.2 (s) ppm. - MS (ESI acetonitrile): *m/z* (%) = 402 (16) [$M^+ + H_2O + K + CH_3CN$], 368 (15) [$M^+ + CH_3CN + Na$], 361 (58) [$M^+ + H_2O + K$], 321 (100) [$M^+ - H + H_2O$], 305 (55) [$M^+ + H$]. - HRMS (ESI acetonitrile): Calcd. for $C_{19}H_{29}PO$ [M + H]$^+$: 305.2034; found 305.2028.

4.8.4 Synthesis of [1-(Di-*tert*-butylphosphanylethyl)indenyl]chloronickel(II) (63)



63

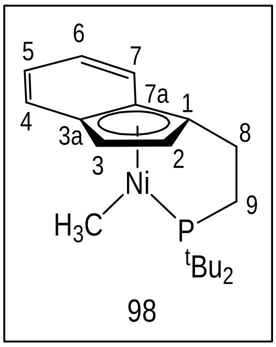
To a solution of di-*tert*-butylphosphane (4.3 g 0.03 mol) in THF (400 mL), butyllithium (0.022 mol, 15 mL, 1.6 M in hexane) was added dropwise at 0°C. The solution was stirred for 2 h at 0°C. After heating the solution to 65 °C and addition of spiroindene (4.12 g, 0.03 mol), the solution was heated at reflux for 120 h. Then the colour of the reaction mixture had changed to red. The solution was cooled to 25°C. After removal of the unconsumed di-*tert*-butylphosphane and solvent at reduced pressure at 100 °C, the residue was dissolved in THF (400 mL). After the addition of anhydrous $NiCl_2$ (12.9 g, 0.10 mol) at 0 °C, the reaction mixture was stirred for 14 h at the same temperature. The colour of the solution had changed to deep red. The reaction mixture was warmed slowly to 25°C. The solution was filtered through the 5 cm pad of celite. The solvent was removed at reduced pressure and residue was dissolved in diethyl ether (400 mL). The solution was filtered again through the celite. The product was crystallized from diethyl ether at –20°C to yield 7.1 g (0.018 mol, 85%) of **63** as a deep purple red solid (m.p. 91 °C decomp.).

63: IR (ATR): $\tilde{\nu}$ = 2964 cm^{-1} (w), 2903 (w), 2858 (w), 1459 (w), 1388 (w), 1259 (s), 1127 (s), 1016 (w), 796 (s), 749 (m), 684 (w).- ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.31 (d, $^3J_{PH}$ = 13.6 Hz, 9 H, 3 x *CH_3*), 1.45 (d, $^3J_{PH}$ = 13.1 Hz, 9 H, 3 x *CH_3*), 1.87-1.94 (m, 2 H, 8-H), 2.4-2.6 (m, 2 H, 9-H), 5.42 (dd, *J* = 3.3, 2.2 Hz, 1 H, 3-H), 6.76 (d, $^3J_{HH}$ = 3.4 Hz, 1 H, 2-H), 7.00

(dd, $^3J_{HH}$ = 7.5, 7.2, Hz, 1 H, 5-H), 7.09 (d, $^3J_{HH}$= 7.5 Hz, 1 H, 4-H), 7.16-7.13 (m, 2 H, 7,6-H) ppm. - ^{13}C NMR ($CDCl_3$, 100 MHz, BB): δ = 25.8 (d, $^2J_{CP}$ = 5.5 Hz, C-8), 28.8 (d, $^2J_{CP}$ = 3.6 Hz, 3 x CH_3), 29.4 (d, $^2J_{CP}$ = 4.0 Hz, 3 x CH_3), 34.5 (d, $^1J_{CP}$ = 20.5 Hz, C-9), 34.7 [d, $^1J_{CP}$ = 13.3 Hz, $C(CH_3)_3$], 35.9 [d, $^1J_{CP}$ = 13.1 Hz, $C(CH_3)_3$], 81.2 (d, J_{CP} = 13.9 Hz, C-3), 89.8 (d, J_{CP} = 7.2 Hz, C-1), 105.7 (d, J_{CP} = 2.4 Hz, C-2), 117.3 (s, C-7), 119.3 (s, C-6), 124.5 (s, C-5), 127.3 (s, C-4), 129.3 (s, C-3a), 131.2 (d, J_{CP} = 2.8 Hz, C-7a) ppm. - ^{31}P NMR ($CDCl_3$, 161 MHz): δ = 84.2 (s) ppm. - MS (70 eV): *m/z* (%) = 380 (61) [M^+], 318 (20) [$M^+ - C_2H_3Cl$], 304 (23) [$M^+ - C_6H_4$], 288 (66) [M^+ – NiCl +1], 232 (59) [$M^+ - C_8H_{17}Cl$], 186 (23) [$M^+ - C_9H_{20}ClP$], 173 (26) {$M^+ - C_8H_{18}ClNi$], 162 (55) 141 (76). - HRMS: Calcd. for $C_{19}H_{28}PClNi$ 380.097064; found 380.097107. - $C_{19}H_{28}PNiCl$ (380.0971): Calcd. C 59.81, H 7.40; found C 60.28, H 7.97.

4.9 Synthesis of [1-(Di-*tert*-butylphosphanylethyl)indenyl]methyl- and –ethynyl nickel(II)

4.9.1 Synthesis of [1-(Di-*tert*-butylphosphanylethyl)indenyl]methylnickel(II) (98)



98

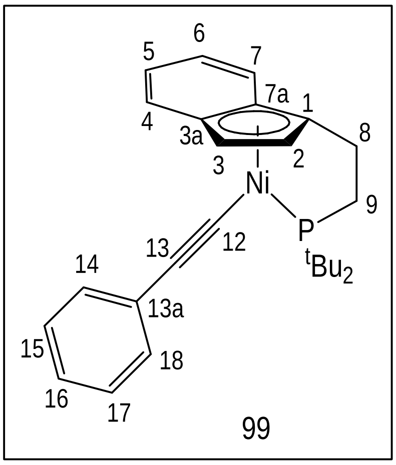
At 25 °C into a solution of **63** (0.12 g, 0.3 mmol) in diethyl ether (30 mL), methyllithium (0.2 mL, 0.3 mmol, 1.6 M in diethyl ether) was added dropwise. The colour of the reaction mixture had changed from deep purple to dark brown. The solution was stirred for 1 h and filtered through the celite. After solvent removal at reduced pressure, the product was recrystallized from the saturated hexane solution at −20 °C to yield 0.05 g (0.15 mmol, 50%) of **98** as a green crystalline solid (m.p. 268 °C). The immediate decomposition of complex **98** was observed in solution. The ^{1}H NMR and ^{13}C NMR spectra were obtained; however, all the signals were broad showed decomposition of the complex **98**.

98: IR (ATR): $\tilde{\nu}$ = 2948 cm^{-1} (w), 2903 (w), 2858 (w), 1599 (w), 1548 (w), 1530 (w), 1513 (w), 1468 (w), 1451 (w), 1367 (w), 1261 (w), 1118 (w), 1017 (w), 816 (w), 734 (s), 630 (m). - ^{31}P NMR ($CDCl_3$, 161 MHz): δ = 85.1 (s) ppm. - MS (70 eV): *m/z* (%) = 360 (100) [M^+], 345 (31) [$M^+ - CH_3$], 318 (10) [$M^+ - C_3H_6$], 304 (40) [$M^+ - C_4H_8$], 289 (21) [$M^+ - NiCH_3 +2$], 247 (39) [$M^+ - C_8H_{17}$], 233 (49) [$M^+ - C_9H_{19}$], 186 (51) [$M^+ - C_{10}H_{23}P$], 173 (10) {$M^+ - C_9H_{21}Ni$], 162 (35) 141 (62), 120 (47), 57 (64). - HRMS: Calcd. for $C_{20}H_{31}PNi$ 360.151687; found 360.151398.

4.9.2 Crystal Structure Analysis Data of 98

Emperical formula C20H31NiP, molecular weight 361.13, crystal system orthorhombic, space group P c a b, a = 11.668(3), b = 12.848(5), c = 25.332(3) Å, α = 90°, β = 90°, γ = 90°, V = 3798(2) $Å^3$, Z = 8, $d_{Calc.}$= 1.263 Mg/m^3, $F(000)$ = 1552, μ = 1.102 mm^{-1}, crystal size 0.41 x 0.37 x 0.37 mm, Stoe IPDS area detector diffractometer, T = 300(2) K, MO_{Ka} = 0.71073 Å, $\theta_{\min}$ = 2.26, $\theta_{\max}$ = 24.10°, -13<=h<=13, -14<=k<=14, -29<=l<=29, no absorption correction, no extinction correction, Reflections collected 37611, unique 3004 [R(int) = 0.0680], Completeness to theta = 24.1, 99.9 %, Refinement method Full-matrix least-squares on F^2, Data 3004, restraints 0, parameters 199, Goodness-of-fit on F^2 1.162, Final R indices [I>2sigma(I)] R1 = 0.0301 , wR2 = 0.0663, R indices (all data) R1 = 0.0498 , wR2 = 0.0693, largest diff. peak and hole 0.263 and -0.203 eA^{-3}.

4.9.3 Synthesis {[1-(Di-*tert*-butylphosphanylethyl)indenyl](2-phenylethynyl)}nickel(II) (99)



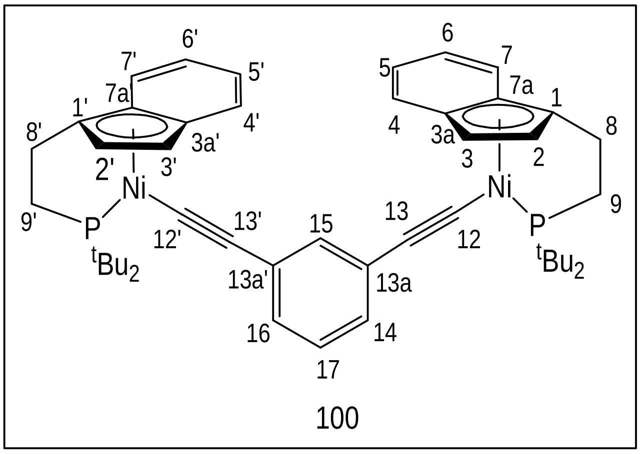
99

To a suspension of **63** (0.12 g, 0.3 mmol) and CuI (5 mg) in freshly distilled triethylamine (5 mL) phenylethyne (0.10 g, 1.0 mmol) was added dropwise. The colour of reaction mixture became violet brown. After stirring the mixture for 14 h the solvent was removed at reduced pressure till dryness. The crude complex **99** was extracted with diethyl ether (3 x 25 mL) and was chromatographed (SiO_2, petroliumether / ethyl acetate 10 : 1, 30 × 4 cm) to yield 0.09 g (0.2 mmol., 67%) of **99** as a deep brown solid (m.p. 109 ^oC decomp.).

99: IR (ATR): $\tilde{\nu}$ = 3051 cm^{-1} (w), 2958 (w), 2899 (w), 2869 (w), 2168 (w), 2085 (m), 1471 (m), 1429 (m), 1259 (s), 1124 (s), 1079 (s), 1014 (s), 845 (w), 790 (s), 750 (m), 730 (s), 697 (s). - ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.20 (d, $^3J_{PH}$ = 13.6 Hz, 9 H, 3 x CH_3), 1.40 (d, $^3J_{PH}$ = 13.1 Hz, 9 H, 3 x CH_3), 2.19-2.47 (m, 4 H, 8-H, 9-H), 5.63 (dd, $^3J_{HH}$ = 3.1, 1.2 Hz, 1H, 3-H), 6.44 (d, J_{HH} = 3.1 Hz, 1 H, 2-H), 6.95–7.02 (m, 2 H, 5-H, 16-H), 7.06–7.12 [m, 3 H, 4-H, 15(17)-H], 7.14–7.16 [m, 2 H, 6-H, 7-H), 7.23 [d, $^3J_{HH}$ = 7.6, 2 H, 14(18)-H] ppm. - ^{13}C NMR ($CDCl_3$, 100 MHz, BB): δ = 25.6 (d, $^2J_{CP}$ = 4.6 Hz, C-8), 29.2 (d, $^2J_{CP}$ = 3.4 Hz, 3 x CH_3), 29.7 (d, $^2J_{CP}$ = 3.6 Hz, 3 x CH_3), 35.4 (d, $^1J_{CP}$ = 14.4 Hz, $C(CH_3)_3$], 36.0 [d, $^1J_{CP}$ = 14.6 Hz, $C(CH_3)_3$], 38.9 (d, $^1J_{CP}$ = 18.1 Hz, C-9), 74.5 (d, $^2J_{CP}$ = 12.2 Hz, C-3), 97.6 (d, $^2J_{CP}$ = 26.9 Hz, C-12), 98.7 (d, J_{CP} = 7.2 Hz, C -1), 104.4 (d, J_{CP} = 2.2 Hz, C-2), 117.2 (s, C-7), 117.4 (s, C-13), 119.4 (s, C-6), 123.2 (s, C-5), 124.4 (s, C-16), 124.7 (s, C-3a), 125.8 (s, C-4), 125.9 (d, J_{CP} = 1.5 Hz, C-7a) 127.6 [s, 15(17)-C],128.8 (d, $^4J_{CP}$ = 1.0 Hz, 13a-C), 131.2 [d, $^5J_{CP}$ = 0.7 Hz, 14(18)-C] ppm. - ^{31}P NMR ($CDCl_3$, 161 MHz): δ = 95.6 (s) ppm. - MS (ESI acetonitrile):

m/z (%) = 716 (14) [$M^+ - C_4H_8 + C_{19}H_{28}P + K$], 460 (28) [$M^+ + H - C_2H_4 + CH_3CN$], 447 (13) [$M^+ + H$], 435 (4) [$M^+ - C_4H_4 + Na + H_2O$], 386 (100) [$M^+ - C_8H_5 + CH_3CN$], 372 (62) [$M^+ - C_8H_{17}$], 352 (12) [$M^+ - C_{12}H_{14} + CH_3CN + Na$], 336 (9) [$M^+ - C_{10}H_8 + H_2O$], 319 (6) [$M^+ - C_{14}H_{23} + CH_3CN + Na$], 303 (12) [$C_{19}H_{28}PO$]. - HRMS (ESI acetonitrile): Calcd. for $C_{27}H_{33}NiP$ [$M^+ + H$]: 447.1752; found 447.1751.

4.9.4 Synthesis of 1,3-Bis{[1-(di-*tert*-butylphosphanylethyl)indenyl]nickel(II)ethynyl}-benzene (100)



100

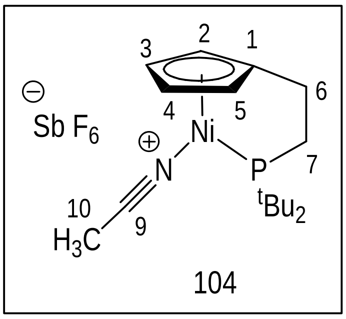
To a suspension of **63** (0.35 g, 0.9 mmol) and CuI (40 mg) in freshly distilled triethylamin (5 mL) 1,3-diethynylbenzene (0.05g, 0.4 mmol) was added dropwise. Colour of the reaction mixture had changed from deep purple to violet brown. After stirring the mixture for 14 h the solvent was removed at reduced pressure till dryness. The crude complex **100** was extracted with diethyl ether (3 x 25 mL) and was chromatographed (SiO_2, petroleum ether / TBME 1 : 1, 30 × 4 cm) to yield 0.25 g (0.3 mmol, 78%) of **100** as a deep brown solid (m.p. 170 °C decomp.).

100: IR (ATR): $\tilde{\nu}$ = 3043 cm^{-1} (w), 2961 (w), 2904 (w), 2869 (w), 2160 (w), 2083 (m), 1585 (m), 1471 (m), 1391 (s), 1368 (w), 1260 (s), 1226 (s), 1080 (m), 1015 (s), 792 (s), 734 (s), 699 (m), 685 (m). - ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.18 [d, $^3J_{PH}$ = 13.6 Hz, 18 H, 6 x CH_3], 1.26 [d, $^3J_{PH}$ = 12.6 Hz, 18 H, 6 x CH_3], 1.32 [d, $^3J_{PH}$ = 12.1 Hz, 18 H, 6 x CH_3], 1.40 [d, $^3J_{PH}$ = 13.1 Hz, 18 H, 6 x CH_3], 2.19-2.51 [m, 4 H, 8(8′)-H], 2.69-2.86 [m, 4 H, 9(9′)-H], 5.61 [br, 2

H, 3(3′)-H], 6.41 [br, 2 H, 2(2′)-H], 6.99 – 7.03 [m, 3 H, 5(5′)-H, 17-H], 7.11 [br, 3 H, 4(4′)-H, 15-H], 7.19 – 7.24 [m, 4 H, 6(6′)-H, 7(7′)-H], 7.45 [br, 2 H, 14(16)-H] ppm. - ^{13}C NMR ($CDCl_3$, 100 MHz, BB): δ = 25.4 [d, $^2J_{CP}$ = 4.5 Hz, C-8(8′)], 28.9 [d, $^2J_{CP}$ = 3.1 Hz, 6 x CH_3], 29.1 [d, $^2J_{CP}$ = 3.5 Hz, 6 x CH_3], 29.5 [d, $^2J_{CP}$ = 3.7 Hz, 6 x CH_3], 29.9 [d, $^2J_{CP}$ = 3.7 Hz, 6 x CH_3], 34.9 [d, $^1J_{CP}$ = 13.5 Hz, $C(CH_3)_3$], 35.4 [d, $^1J_{CP}$ = 14.5 Hz, $C(CH_3)_3$], 35.7 [d, $^1J_{CP}$ = 14.7 Hz, $C(CH_3)_3$], 36.0 [d, $^1J_{CP}$ = 13.7 Hz, $C(CH_3)_3$], 38.6 [d, $^1J_{CP}$ = 18.2 Hz, C-9(9′)], 74.3 [d, $^2J_{CP}$ = 11.7 Hz, C-3(3′)], 83.9 [s, C-13(13′)], 98.9 [d, J_{CP} = 8.3 Hz, C -1(1′)], 100.3 [d, $^2J_{CP}$ = 26.6 Hz, C-12(12′)], 104.1 [d, J_{CP} = 2.3 Hz, C-2(2′)], 117.2 [s, C-7(7′)], 119.2 [s, C-6(6′)], 121.1 [s, C-13a(13a′)], 123.1 [s, C-5(5′)], 124.4 [s, C-3a(3a′)], 126.1 [s, C-4(4′)], 125.5 [d, J_{CP} = 1.6 Hz, C-7a(7a′)], 127.6 [s, C-14(16)], 131.6 (s, C-17), 134.5 (s, C-15) ppm. – ^{31}P NMR ($CDCl_3$, 161 MHz): δ = 86.8 (s), 96.0 (s) ppm. – MS (ESI acetonitrile): *m/z* (%) = 815 (1) [M^+ + H], 716 (12) [$M^+ - C_7H_{14}$], 534 (6) [$M^+ - C_{20}H_{39}$], 471 (7) [$M^+ - C_{19}H_{26}NiP$], 445 (4) [$M^+ - C_{21}H_{28}NiP$], 435 (8) [$M^+ - C_{22}H_{26}NiP$], 386 (100) [$M^+ - C_{29}H_{32}NiP + CH_3CN$], 372 (28) [$M^+ - C_{27}H_{29}NiP$], 319 (6) [$M^+ - C_{31}H_{34}NiP$], 305 (16) [$C_{19}H_{28}P + H_2O$], 123 (8) [$C_{10}H_3$]. - HRMS (ESI acetonitrile): Calcd. for $C_{48}H_{60}Ni_2P_2$ [M^+ + H]: 815.2955; found 815.2983.

4.10 Synthesis of [(Di-*tert*-butylphosphanylethyl)cyclopentadienyl](acetonitrile)-nickel(II) Complexes

4.10.1 Synthesis of [(Di-*tert*-butylphosphanylethyl)cyclopentadienyl](acetonitrile)-nickel(II) Hexafluoroantimonate (104)



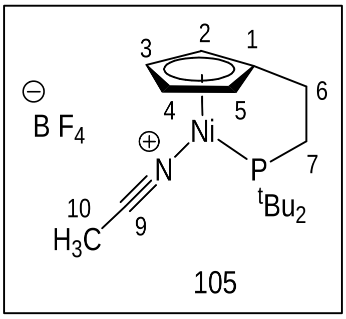
104

A solution of **62** (0.10 g, 0.30 mmol) and silver hexafluoroantimonate (0.13 g, 0.4 mmol) in acetonitrile (5 mL) was stirred for 1 h. After removal of the acetonitrile at reduced pressure, the residue was dissolved in dichloromethane (20 mL) and filtered through celite.

The dichloromethane was removed at reduced pressure and residue was washed with diethyl ether (2 x 30 mL) to yield 0.12 g (0.21 mmol, 71%) of **104** as a dark green solid (m.p. 237 °C decomp.).

104: IR (ATR): $\tilde{\nu}$ = 2965 cm^{-1} (w), 2888 (w), 2345 (w), 2207 (w), 2052 (w), 2039 (m), 1978 (w), 1478 (w), 1464 (w), 1393 (w), 1360 (w), 1261 (w), 1179 (w), 1093 (s), 1023 (w), 937 (w), 833 (m), 807 (s), 655 (m). - ^{1}H NMR (acetone-d$_6$, 400 MHz): δ = 1.52 (d, $^{3}J_{PH}$ = 13.9 Hz, 18 H, 6 x CH_3), 1.84 (m, 2 H, 6-H), 2.50 (d, $^{5}J_{PH}$ = 0.6 Hz, 3 H, 10-H), 2.67 (m, 2 H, 7-H), 5.71, 6.14 [AA′BB′ line system, 4 H, 2(5), 3(4)-H] ppm.- ^{13}C NMR (acetone-d$_6$, 100 MHz. BB): δ = 3.7 (s, C-10), 26.2 (d, $^{2}J_{CP}$ = 2.4 Hz, C-6), 29.2 (d, $^{2}J_{CP}$ = 3.6 Hz, 6 x CH_3), 35.3 (d, $^{1}J_{CP}$ = 25.2 Hz, C-7), 35.7 [d, $^{1}J_{CP}$ = 15.6 Hz, $C(CH_3)_3$], 97.9 [d, J_{CP} = 4.6 Hz, C-3(4)], 99.0 [d, J_{CP} = 1.9 Hz, C-2(5)], 106.8 (d, J_{CP} = 9.7 Hz, C-1), 131.9 (s, C-9) ppm.- ^{31}P NMR (acetone-d$_6$, 161 MHz): δ = 106.0 (s) ppm. - MS (ESI acetonitrile): *m/z* (%) = 462 (6) [M$^+$ – SbF$_6$ + Rb + CH$_3$CN], 385 (1) [M$^+$ – SbF$_6$ + H$_2$O + CH$_3$O$^-$], 336 (100) [M$^+$ – SbF$_6$], 296 (5) [M$^+$ + H – CH$_3$CNSbF$_6$], 294 (8) [M$^+$ – H – CH$_3$CNSbF$_6$], 234 (100) [SbF$_6$]$^-$. - HRMS (ESI acetonitrile): Calcd. for $C_{17}H_{29}NPNi$ [M$^+$]: 336.1391; found 336.1397, Calcd. for SbF$_6$ [M$^-$]: 234.8942; found 234.8946.

4.10.2 Synthesis of [(Di-*tert*-butylphosphanylethyl)cyclopentadienyl](acetonitrile)-nickel(II) Tetrafluoroborate (105)

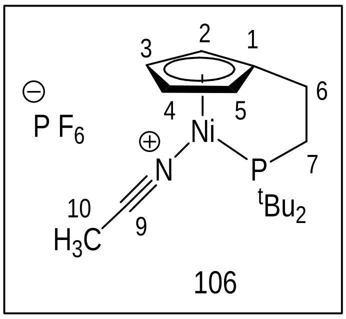


105

A solution of **62** (0.10 g, 0.3 mmol) and silver tetrafluoroborate (0.09 g, 0.50 mmol) in acetonitrile (5 mL) was stirred for 1 h. After removal of the acetonitrile at reduced pressure, the residue was dissolved in dichloromethane (20 mL) and filtered through celite. Dichloromethane was removed at reduced pressure and then the residue was washed with diethyl ether (2 x 30 mL) to yield 0.12 g (0.26 mmol, 88%) of **105** as a green solid (m.p.179 °C decomp.).

105: IR (ATR): $\tilde{\nu}$ = 2962 cm^{-1} (w), 2917 (w), 2360 (w), 2224 (w), 2193 (w), 2173 (s), 2145 (w), 2100 (w), 2090 (w), 2026 (w), 2011 (w), 1986 (w), 1964 (s), 1479 (s), 1262 (w), 1102 (w), 1085 (m), 1022 (m), 807 (s), 655 (s). - ^{1}H NMR (acetone-d$_6$, 400 MHz): δ = 1.52 (d, $^3J_{PH}$ = 14.0 Hz, 18 H, 6 x *CH$_3$*), 1.84 (m, 2 H, 6-H), 2.49 (s, 3 H, 10-H), 2.67 (m, 2 H, 7-H), 5.73, 6.15 [AA′BB′ line system, 4 H, 2(5), 3(4)-H] ppm.- ^{13}C NMR (acetone-d$_6$, 100 MHz): δ = 3.3 (s, C-10), 25.9 (d, $^2J_{CP}$ = 2.2 Hz, C-6), 28.8 (d, $^2J_{CP}$ = 3.6 Hz, *CH$_3$*), 34.9 (d, $^1J_{CP}$ = 25.1 Hz, C-7), 35.3 [d, $^1J_{CP}$ = 15.6 Hz, *C*(CH$_3$)$_3$], 97.5 [d, J_{CP} = 4.6 Hz, C-3(4)], 98.6 [d, J_{CP} = 1.9 Hz, C-2(5)], 106.5 (d, J_{CP} = 10.0 Hz, C-1), 131.6 (s, C-9) ppm.- ^{31}P NMR (acetone-d$_6$, 161 MHz): δ = 106.0, (s) ppm. - MS (70 eV): *m/z* (%) = 423 (2) [M$^+$], 422 (12) [M$^+$ – H], 295 (4) [M$^+$ – CH$_3$CNBF$_4$], 274 (3) [M$^+$ – C$_4$H$_8$], 238 (18) [M$^+$ – CH$_3$CNBF$_4$ – C$_4$H$_9$], 182 (52) {M$^+$ – [2C$_4$H$_8$] – CH$_3$CNBF$_4$}, 136 (9), 57 (100). - HRMS (ESI acetonitrile): Calcd. for C$_{17}$H$_{29}$NPNi [M$^+$]: 336.1391; found 336.1400.

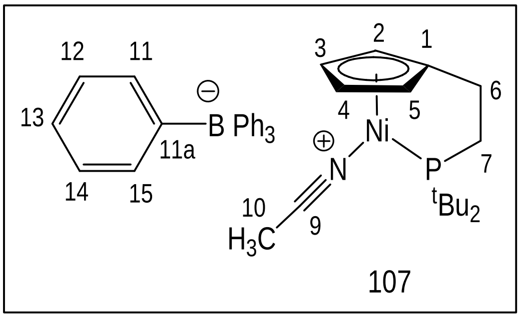
4.10.3 Synthesis of [(Di-*tert*-butylphosphanylethyl)cyclopentadienyl](acetonitrile)-nickel(II) Hexafluorophosphate (106)



A solution of **62** (0.10 g, 0.30 mmol) and silver hexafluorophosphate (0.092 g, 0.4 mmol) in acetonitrile (5 mL) was stirred for 1 h. After removal of the acetonitrile at reduced pressure, the residue was dissolved in dichloromethane (20 mL) and filtered through the celite. The dichloromethane was removed at reduced pressure and then the residue was washed with diethyl ether (2 x 30 mL) to yield 0.13 g (0.3 mmol, 90%) of **106** as a dark green solid (m.p. 230 °C decomp.).

106: IR (ATR): $\tilde{\nu}$ = 2982 cm^{-1} (w), 2917 (w), 2366 (w), 2231 (w), 2219 (w), 2166 (s), 2142 (w), 2075 (w), 2016 (w), 1953 (w), 1925 (w), 1910 (w), 1476 (m), 1371 (w), 1102 (w), 1085 (m), 1022 (m), 832 (s), 739 (w), 655 (s). - ^{1}H NMR (acetone-d_6, 400 MHz): δ = 1.52 (d, $^3J_{PH}$ = 14.0 Hz, 18 H, 6 x CH_3), 1.83 (m, 2 H, 6-H), 2.48 (s, 3 H, 10-H), 2.66 (m, 2 H, 7-H), 5.72, 6.14 [AA′BB′ line system, 4 H, 2(5), 3(4)-H] ppm. - ^{13}C NMR (acetone-d_6, 100 MHz): δ = 3.3 (s, C-10), 25.9 (d, $^2J_{CP}$ = 2.1 Hz, C-6), 28.9 (d, $^2J_{CP}$ = 3.6 Hz, 6 x CH_3), 34.9 (d, $^1J_{CP}$ = 25.0 Hz, C-7), 35.3 [d, $^1J_{CP}$ = 15.8 Hz, $C(CH_3)_3$], 97.6 [d, J_{CP} = 4.4 Hz, C-3(4)], 98.6 [d, J_{CP} = 1.7 Hz, C-2(5)], 106.5 (d, J_{CP} = 9.8 Hz, C-1), 131.6 (s, C-9) ppm. - ^{31}P NMR (acetone-d_6, 161 MHz): δ = 106.0 (s) ppm. - MS (ESI acetonitrile): *m/z* (%) = 462 (9) [$M^+ - PF_6 + Rb + CH_3CN$], 385 (2) [$M^+ - PF_6 + H_2O + CH_3O^-$], 336 (100) [$M^+ - PF_6$], 296 (5) [$M^+ + H - CH_3CNPF_6$], 294 (6) [$M^+ - H - CH_3CNPF_6$], 144 (100) [$PF_6$]$^-$. - HRMS (ESI): Calcd. for $C_{17}H_{29}NPNi$ [M^+]: 336.1391; found 336.1389, Calcd. for PF_6 [M^-]: 144.9642; found 144.9646.

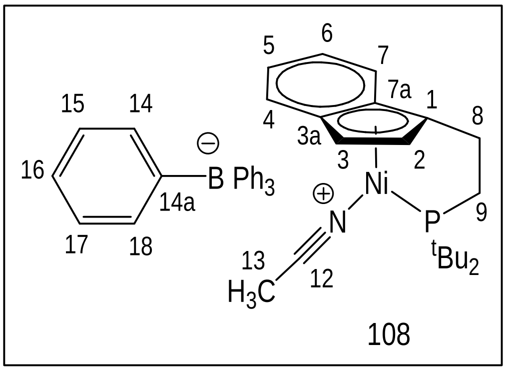
4.10.4 Synthesis of [(Di-*tert*-butylphosphanylethyl)cyclopentadienyl](acetonitrile)-nickel(II) Tetraphenylborate (107)



A solution of **62** (0.10 g, 0.3 mmol) and sodium tetraphenylborate (0.20 g, 0.6 mmol) in acetonitrile (5 mL) was stirred for 2 h. After removal of the acetonitrile at reduced pressure, the residue was dissolved in dichloromethane (20 mL) and filtered through celite. Dichloromethane was removed at reduced pressure and residue was washed with diethyl ether (2 x 30 mL) to yield 0.18 g (0.28 mmol, 92%) of **107** as a light green solid (m.p. 167 °C).

107: IR (ATR): $\tilde{\nu}$ = 2963 cm^{-1} (w), 2917 (w), 2361 (w), 2262 (w), 2183 (w), 2157 (w), 2039 (w), 2023 (w), 2010 (w), 1957 (w), 1259 (s), 1092 (s), 1013 (s), 862 (w), 794 (s), 743 (w), 731 (m), 704 (m). - ^{1}H NMR (acetone-d_6, 400 MHz): δ = 1.49 (d, $^3J_{PH}$ = 13.9 Hz, 18 H, 6 x CH_3), 1.76 (m, 2 H, 6-H), 2.22 (s, 3H, 10-H), 2.58 (m, 2H, 7-H), 5.63, 6.08 [AA′BB′ line system, 4 H, 2(5), 3(4)-H], 6.79 (dd, $^3J_{HH}$ = 7.2, 7.1 Hz, 4 H, 13-H), 6.92-6.96 [m, 8 H 11(15)-H], 7.33-7.36 [m, 8 H, 12(14)-H] ppm. - ^{13}C NMR (acetone-d$_6$, 100 MHz): δ = 3.5 (s, C-10), 26.2 (d, $^2J_{CP}$ = 2.3 Hz, C-6), 29.2 (d, $^2J_{CP}$ = 3.4 Hz, 6 x CH_3), 35.3 (d, $^1J_{CP}$ = 25.2 Hz, C-7), 35.7 [d, $^1J_{CP}$ =15.8 Hz, *C*(CH$_3$)$_3$], 97.9 [d, J_{CP} = 4.5 Hz, C-3(4)], 98.9 [d, J_{CP} = 1.7 Hz, C-2(5)], 106.8 (d, J_{CP} = 9.8 Hz, C-1), 131.8 (s, C-9), 122.2 (d, $^4J_{B\text{-}C}$ = 0.6 Hz, C-13), 125.9 [dd, $^3J_{B\text{-}C}$ = 2.7 Hz, C-12(14)], 136.9 [dd, $^2J_{B\text{-}C}$ = 1.5, 1.2 Hz, C-11(15)], 164.6 (4-line multiplet, $^1J_{B\text{-}C}$ = 49.2 Hz, C-11a) ppm. - ^{31}P NMR (acetone-d$_6$, 161 MHz): δ = 106.0 (s) ppm. - MS (ESI acetonitrile): *m/z* (%) = 462 (7) [M$^+$ – BPh$_4$ + Rb + CH$_3$CN], 385 (1) [M$^+$ – BPh$_4$ + H$_2$O + CH$_3$O$^-$], 336 (100) [M$^+$ – BPh$_4$], 319 (100) [BPh$_4$]$^-$, 295 (6) [M$^+$ – CH$_3$CNBPh$_4$], 294 (10) [M$^+$ – H – CH$_3$CNBPh$_4$]. - HRMS (ESI acetonitrile): Calcd. for $C_{17}H_{29}NPNi$ [M$^+$]: 336.1391; found 336.1386, Calcd. for $C_{24}H_{20}B$ [M$^-$]: 319.1658; found 319.1669.

4.10.5 Synthesis of {[1-(Di-*tert*-butylphosphanylethyl)indenyl](acetonitrile)}nickel(II) Tetraphenylborate (108)



108

A solution of **63** (0.10 g, 0.3 mmol) and sodium tetraphenylborate (0.20 g, 0.6 mmol) in acetonitrile (5 mL) was stirred for 2 h. After removal of the acetonitrile at reduced pressure, the residue was dissolved in dichloromethane (20 mL) and filtered through celite. Dichloromethane was removed at reduced pressure and residue was washed with diethyl ether (2 x 30 mL) to yield 0.18 g (0.28 mmol, 92%) of **108** as a light green solid (m.p.151 °C).

108: IR (ATR): $\tilde{\nu}$ = 2963 cm^{-1} (w), 2917 (w), 2361 (w), 2262 (w), 2183 (w), 2157 (w), 2039 (w), 2023 (w), 2010 (w), 1957 (w), 1259 (s), 1092 (s), 1013 (s), 862 (w), 794 (s), 743 (w), 731 (m), 704 (m). - ^{1}H NMR (acetone-d$_6$, 200 MHz): δ = 1.23 (d, $^3J_{PH}$ = 13.9 Hz, 9 H, 3 x CH_3), 1.46 (d, $^3J_{PH}$ = 13.9 Hz, 9 H, 3 x CH_3), 2.24 (s, 3 H, 13-H), 2.79–2.95 (m, 2 H, 8-H), 3.35–

3.45 (m, 2 H, 9-H), 5.85 (dd, ${}^3J_{HH}$ = 4.3, 3.7 Hz, 1 H, 3-H), 6.75 (s, 1 H, 2-H), 6.78-6.82 [m, 4 H, 16-H], 6.89-6.97 [m, 9 H, 5-H, 15(17)-H], 7.21–7.34 (m, 2 H, 6-H, 7-H), 7.35 [br, 8 H, 14(18)-H], 7.6 (d, ${}^3J_{HH}$ = 7.6 Hz, 1 H, 4-H] ppm. - ^{13}C NMR (acetone-d_6, 100 MHz, BB): δ = 4.0 (s, C-13), 26.9 (d, ${}^2J_{CP}$ = 3.6 Hz, C-8), 28.5 (d, ${}^2J_{CP}$ = 3.6 Hz, 3 x CH_3), 28.9 (d, ${}^2J_{CP}$ = 3.9 Hz, 3 x CH_3), 34.5 (d, ${}^1J_{CP}$ = 23.2 Hz, C-9), 36.5 [d, ${}^1J_{CP}$ = 15.4 Hz, $C(CH_3)_3$], 37.4 [d, ${}^1J_{CP}$ = 14.9 Hz, $C(CH_3)_3$], 83.2 (d, J_{CP} = 9.2 Hz, C-3), 108.5 (s, C-2), 120.9 (s, C-5), 121.3 (s, C-6), 122.9 (d, ${}^4J_{B-C}$ = 0.5 Hz, C-16), 126.6 [d, ${}^3J_{B-C}$ = 2.7 Hz, C-15(17)], 126.7 (s, C-7), 127.9 (s, C-1), 128.4 (s, C-3a), 129.8 (s, C-4), 130.4 (s, C-7a), 130.9 (s, C-12), 137.7[dd, ${}^2J_{B-C}$ = 1.5, 1.2 Hz, C-14(18)], 165.8 (4-line multiplet, ${}^1J_{B-C}$ = 49.1 Hz, C-14a) ppm. - ^{31}P NMR (acetone-d_6, 161 MHz): δ = 47.5 (s) ppm. - MS (ESI acetonitrile): m/z (%) = 716 (12) [M^+ + B], 435 (8) [$M^+ - C_{20}H_{19}B$], 386 (100) [$M^+ - C_{24}H_{20}B$], 372 (28) [$M^+ - C_{25}H_{22}B$], 319 () [BPh_4], 305 (16) [$C_{19}H_{28}P + H_2O$], 289 (8) [$C_{19}H_{30}P$]. HRMS (ESI acetonitrile): Calcd. for $C_{21}H_{31}NPNi$ [M^+]: 386.1548; found 386.1548, Calcd. For $C_{24}H_{20}B$ [M^-]: 319.1658; found 319.1656.

5. References

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