Late-Transition-Metal Cyclopentadienyl Chelate Complexes with Silylphosphane or Secondary Phosphane Tethers

Von der Naturwissenschaftlichen Fakultät der

Gottfried Wilhelm Leibniz Universität Hannover

zur Erlangung des Grades

Doktorin der Naturwissenschaften

(Dr. rer. nat.)

genehmigte Dissertation von

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2015

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Tag der Promotion:	15.07.2015

Die vorliegende Arbeit entstand in der Zeit von Juni 2011 bis April 2015 am Institut für Organische Chemie der Gottfried Wilhelm Leibniz Universität Hannover unter Anleitung von Herrn Prof. Dr. Holger Butenschön.

Herrn Prof. Dr. H. Butenschön danke ich herzlich für die interessante und herausfordernde Themenstellung, hilfreiche Diskussionen, die jederzeit freundliche Unterstützung sowie die mir gewährte Freiheit bei der Durchführung dieser Arbeit.
Herrn Prof. Dr. M. Boysen danke ich sehr für die Übernahme des Korreferats und die Hilfsbereitschaft.
Bei Herrn Prof. Dr. F. Renz bedanke ich mich für die Prüfung im Nebenfach.

Den aktuellen und ehemaligen Mitgliedern der Arbeitsgruppe Stefan Schmitz, David Schmiel, Lauren Heinisch, Sinem Tasdelen, Dr. Nico Krauße und Dr. Georg Werner gilt mein Dank für die gute Zusammenarbeit.

Bei allen Mitarbeitern der spektroskopischen und spektrometrischen Abteilungen, insbesondere bei Frau D. Körtje, Frau M. Rettstadt, Herrn Dr. J. Fohrer, Herrn Dr. G. Dräger und Herrn Dr. E. Hofer bedanke ich mich ganz herzlich für ihr Engagement und schnelle Messungen oxidationsempfindlicher Substanzen.

Ich danke Herrn Dr. M. Wiebcke und Herrn Dr. G. Dräger für die Durchführungen der Kristallstrukturanalysen.

Herrn Jan Thieleke danke ich für die Durchführung von ICP-MS Messungen.

Meinem Ehemann danke ich für seine Liebe, ständige fachliche und moralische Unterstützung sowie die Teilung der Begeisterung für die Metallorganische Chemie.

Kurzfassung

Cyclopentadienyl-Chelatkomplexe später Übergangsmetalle mit Silylphosphan- oder sekundärem Phosphan-Seitenarm

Im Rahmen dieses Forschungsprojekts wurden die ersten Cyclopentadienyl-Chelatkomplexe von späten Übergangsmetallen mit Silylphosphan- oder sekundärem Phosphan-Seitenarm synthetisiert. Über solche Komplexe wurde es bislang nur für frühe Übergangsmetalle berichtet.

Cyclopentadienylnickel(II)-Chelatkomplexe mit einem Silylphosphan-Seitenarm wurden ausgehend von neuen sterisch gehinderten *tert*-Butyldimethylsilyl- oder Triisopropylsilyl-funktionalisierten sekundären Phosphanen in der Abfolge von Deprotonierung, Reaktion mit Spiro[2.4]hepta-4,6-dien, gefolgt von der Reaktion mit Nickel(II)-Halogen-Komplexen, dargestellt. Diese Komplexe gehen Substitutionsreaktionen mit Trimethylsilylcyanid unter Bildung des entsprechenden Cyanokomplexes ein, welcher während der säulenchromatographischen Reinigung protodesilyliert wurde. Es ist gelungen, die erste Kristallstrukturanalyse mit einem sekundären Phosphan funktionalisierten Cyclopentadienylkomplexes durchzuführen.

Ein direkter Zugang zu Cyclopentadienyl-Chelatkomplexen mit sekundärem Phosphan-Seitenarm ist ausgehend vom sterisch äußerst gehinderten primären (2,4,6-Tri-*tert*-butylphenyl)phosphan möglich. Die Abfolge von Deprotonierung, Ringöffnungsreaktion mit Spiro[2.4]hepta-4,6-dien und Komplexierungsreaktionen mit Nickel(II)-Halogen-Komplexen führt zu den entsprechenden Chelaten. Durch Umsetzung dieser Komplexe mit *N*-heterocyclischen Carbenen gelangen die Darstellungen von den entsprechenden stabilen kationischen Komplexen.

Das luftstabile sekundäre Phosphan-funktionalisierte Ferrocenylderivat konnte in einer Reaktion des entsprechenden anionischen Ligandensystems mit Eisen(II)-chlorid dargestellt werden. Der Ferrocenylkomplex wurde weiter zum ersten Phosphor-verbrückten [5.5.]Ferrocenophan umgesetzt.

Cyclopentadienylkomplexe • Sekundäre Phosphane • Silylphosphane • Nickel
N-heterocyclische Carben-Komplexe • Ferrocenderivate• Ferrocenophane

Abstract

Late-Transition-Metal Cyclopentadienyl Chelate Complexes with Silylphosphane or Secondary Phosphane Tethers

In this research project, the first late-transition-metal cyclopentadienyl chelate complexes with silylphosphane or secondary phosphane functionalized tethers are presented. Previously, a few related complexes with a secondary phosphane functionalized tether were reported for early transition metals.

Nickel(II) cyclopentadienyl chelate complexes with a silylphosphane tether were prepared from the new bulky *tert*-butyldimethylsilyl or triisopropylsilyl functionalized secondary phosphanes in the sequence of deprotonation, reaction with spiro[2.4]-hepta-4,6-diene followed by treatment with nickel(II) dihalide complexes.

Halide exchange reaction in these complexes gave the respective cyano chelate by the reaction with trimethylsilyl cyanide. Under the chromatographic conditions applied, this complex underwent a protiodesilylation to give the first secondary cyclopentadienylalkylphosphane chelate complex, which has been characterized by X-ray crystallographic analysis.

A direct route to secondary phosphane functionalized chelates is feasible by the deprotonation of the extremely sterically crowded primary (2,4,6-tri-*tert*-butylphenyl)phosphane followed by cleavage of the cyclopropylring in spiro[2.4]hepta-4,6-diene and the reaction of the formed anionic ligand system with nickel(II) halide complexes. Their halide ligands were exchanged by the reaction with *N*-heterocyclic carbenes affording the corresponding stable cationic complexes.

An air stable secondary phosphane functionalized ferrocene derivative was obtained from the reaction of the respective anionic ligand system with iron(II) chloride. This complex was further converted into the first phospha-bridged [5.5]ferrocenophane.

Cyclopentadienyl complexes • Secondary Phosphanes • Silylphosphanes • Nickel *N*-heterocyclic carbene complexes • Ferrocene derivatives • Ferrocenophanes

Abbreviations

Å	Angstrom(s)
Ar	Aryl
°C	Degrees Celsius
Calcd.	Calculated
cat.	Catalyst
cm^{-1}	Wavenumber(s)
^{13}C NMR	^{13}C Nuclear Magnetic Resonance
COSY	Correlated Spectroscopy
Cp	Cyclopentadienyl (C_5H_5)
δ	Chemical shifts refered to residual solvent signals
decomp.	Decomposition
DEPT	Distortionless Enhancement by Polarisation Transfer
DME	1,2-Dimethoxyethane
EI	Electron Ionisation
ESI	Electrospray Ionization
equiv.	Equivalent(s)
eV	Electron Volt ($1.602 \cdot 10^{-19}$ J)
HASB	Hard and Soft Acids and Bases
HMBC	Heteronuclear Multiple Bond Coherence
HMQC	Heteronuclear Quantum Bond Coherence
^{1}H NMR	^{1}H Nuclear Magnetic Resonance
HRMS	High-resolution Mass Spectrometry

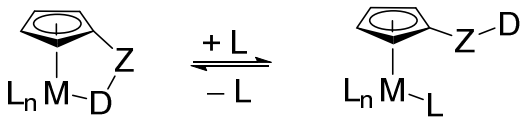
Hz	Hertz
IR	Infrared
J	Coupling Constant (NMR Spectrometry)
L	Ligand
m	Multiplet (spectral)
M^+	Parent Molecular Cation
Mes	Mesityl (2,4,6-Trimethylphenyl)
Mes*	2,4,6-Tri-*tert*-butylphenyl
MHz	Megahertz
min	Minutes
mL	Milliliter(s)
mmol	Millimol
m. p.	Melting Point
MS	Mass Spectrometry
m/*z*	Mass-to-Charge Ratio (Mass Spectrometry)
ppm	Part(s) per Million
^{31}P NMR	^{31}P Nuclear Magnetic Resonance
rac	Racemic
SIMes	1,3-Dimesityl-imidazol-4,5-dihydro-2-ylidene
THF	Tetrahydrofuran
THT	Tetrahydrothiophene
Tip	2,4,6-Triisopropylphenyl

Contents

1. Introduction

Cyclopentadienyl ligands containing donor-functionalized side chains give rise to chelate complexes unfolding a rich coordination chemistry and unusual reaction patterns at the metal centers. This class of compounds exhibits a great potential in catalytic reactions in terms of catalyst improvement, stabilization of otherwise unstable intermediates and influence on stereochemical and stereoelectronic properties.[1]

Such systems with hemilabile heterobidentante ligands possess a formally negatively charged cyclopentadienyl moiety, which is rather tightly bound to a metal, and an electroneutral group, which can readily undergo ligand exchange processes or create a vacant coordination site *via* reversible decomplexation in the course of a reaction (Scheme 1). Moreover, due to the intramolecular coordination of the donor-functionalized sidechain the cyclopentadienyl system is not able to freely rotate around the cyclopentadienyl-metal axis, giving rise to formation of stable conformers.[2]

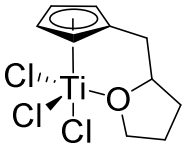


Scheme 1. General representation of a cyclopentadienyl metal complex with a hemilabile donor functionalized side chain. D = donor group, Z = linker, M = transition metal, L = ligand.[2]

The variety of the range of the donor functions in such cyclopentadienyl systems is remarkable. This includes O,[1e,3] N,[4] P,[1d] S[1d,5] and As[1d,6] donors as well as π systems such as alkene and alkyne[7] moieties; chelates **1**-**5** may serve as representative examples.[8-11]

Chelate **1** is a titanium(IV) complex with a tethered tetrahydrofuran ligand and was prepared by Qian et al. in 1989;[12] cobalt(III) complex **2** bears an internal amine ligand and was prepared by Hadjiliadis et al. in 1998;[13] **3** represents a cyclopentadienylethylphosphane nickel(II) chelate and was reported by Butenschön et al. in

2007;[14] **4** is a cationic ruthenium(II) chelate with sulfur coordination, which was prepared by Rauchfuss et al. in 1985,[15] and cobalt(I) alkene complex **5** was prepared by Okuda et al. in 1992.[10] Compared with cyclopentadienylalkylphosphane chelate complexes, the corresponding indenyl chelates are much less common. Recently, Butenschön et al. prepared chelate **6** as the first nickel complex of its kind.[16]



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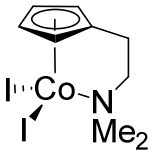

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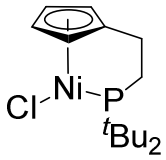

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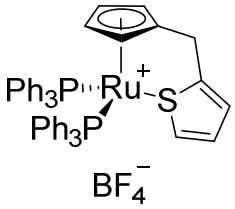

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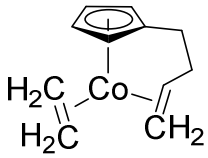

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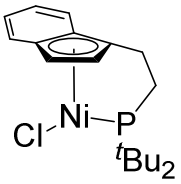
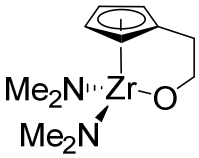


6

While the tethers in chelates such as **1**-**6** bear electroneutral ligands, a smaller number of their anionic counterparts, alkoxido, amido, and phosphido chelates have been reported as well. The alkoxido zirconium(IV) complex **7** was prepared by Hermann et al. in 1994,[17] the amido chelate **8** was prepared by Teuben et al. in 1997.[18] Finally, Miyoshi, Nakazawa et al. provided phosphido complexes **9** and **10** as hafnium(IV) and zirconium(IV) chelates, respectively, in 2003.[19]



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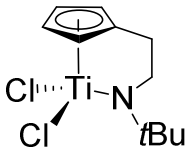

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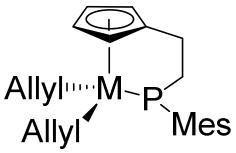
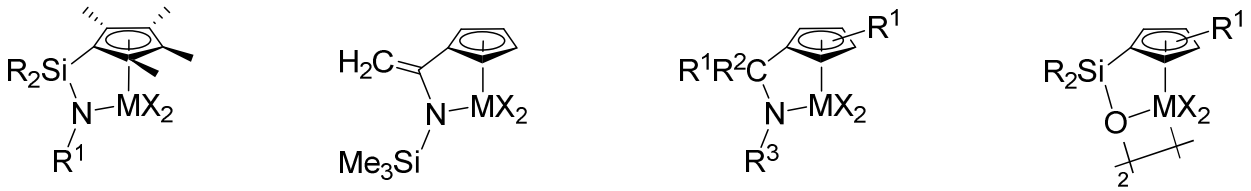
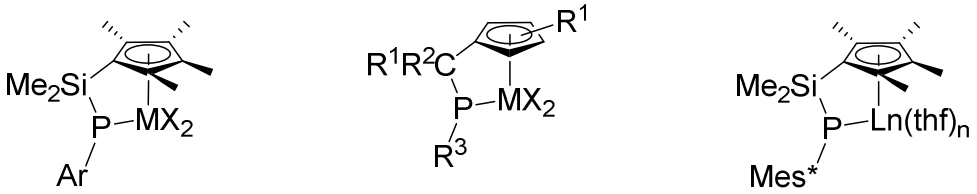


9: M = Hf
10: M = Zr

Along with scarcely reported complexes of type **7**-**10** bearing an ethylene bridge, a larger number of Si_1-bridged related titanium(IV) and zirconium(IV) complexes **A**, especially, those with an amido functionalized tether, have been described in the literature. Most of these "constrained geometry" catalysts were successfully applied in ethene/1-alkene copolymerization reactions when activated, for example, with methylalumoxane.[20]



A **B** **C** **D**



E **F** **G**

M = group 4 metal, X = halide or dialkylamide

Erker et al. reported some examples of chelates **B** and **C** that contain a vinylidene bridge (H_2C=C) as well as methylene (H_2C) and alkylidene (R^1R^2C) linkers, respectively. These "CpCN" metal catalysts produce ethene/1-octene copolymers with similarly high 1-alkene incorporations as compared to the original "CpSiN" group 4 metal complex derived systems.[21,22]

Other element combinations have been hardly explored. Royo, Cuenca et al. introduced "CpSiO" systems **D** based on group 4 metals.[23] The related "CpSiP" group 4 metal catalyst systems **E**[24] were reported in the patent literature in 1991.[25] Erker et al. have also described the first examples of C_1-bridged constrained geometry

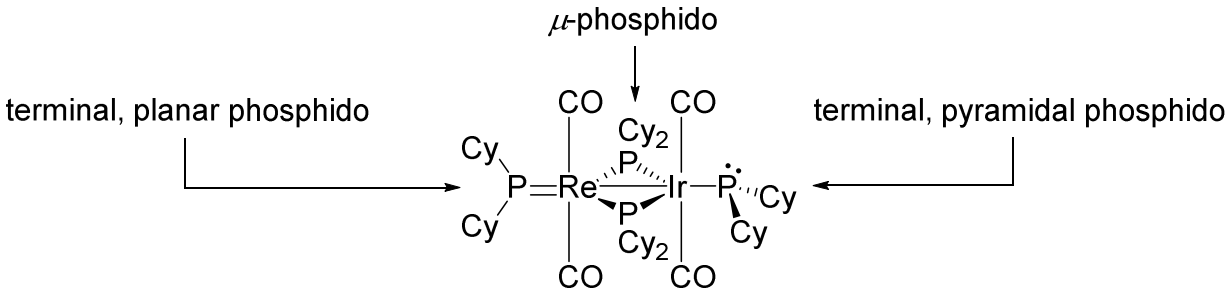
"CpCP" catalysts **F**. These titanium(IV) and zirconium(IV) complexes showed an excellent ethene/1-alkene copolymerization catalyst behavior with regard to both very high catalyst activities and high *α*-olefin incorporation.[22]

Hou et al. reported the attachment of "CpSiP" ligands to lanthanoid metals and described the first X-ray crystal structure analysis of such a "CpSiP"Ln **G** constrained-geometry complex.[26]

The concept "constrained geometry complexes" (CGCs) was introduced by Stevens et al.[25] for complexes in which a *π*-bonded group (e.g. cyclopentadienyl or a derivative) is linked to one of the other ligands at the same metal center in such a way that the ring centroid-metal-ligand angle is smaller than that in the comparable unbridged complex. Later, the term "constrained geometry complexes" was used for chelates with a coordination mode different from η^5:η^1 coordination as well as for complexes with longer ansa-bridges (e.g. $-(CH_2)_n-$; n>2).[27] Additionally, when compared to *ansa*-metallocenes, CGCs have increased stability toward methylalumoxane, are remarkably stable up to reaction temperatures of 160 °C, and give generally higher molecular weight polymers.[28]

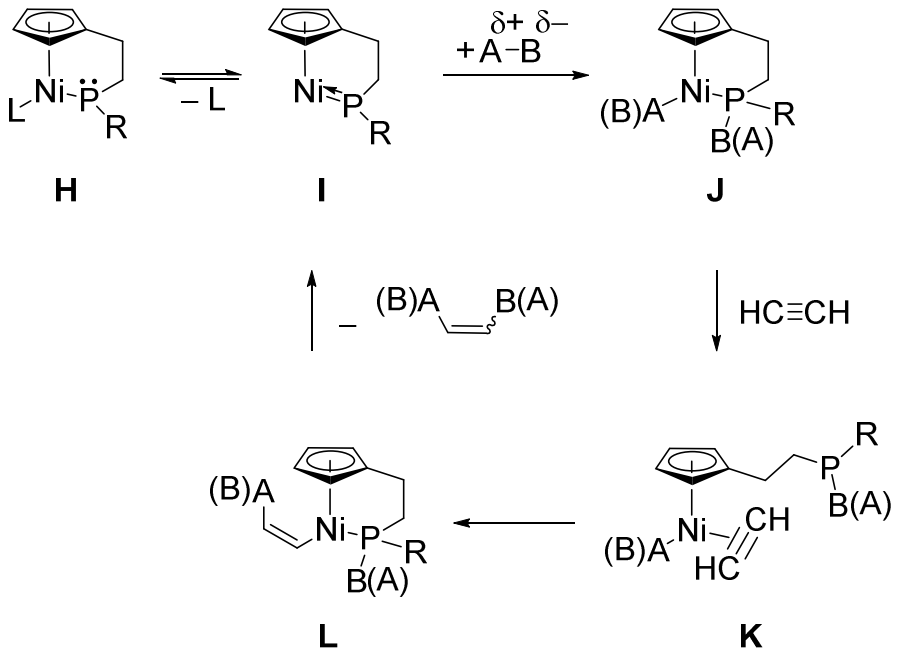
In the context of our interest in cyclopentadienylalkylphosphane chelates of cobalt[29-41] and nickel,[14,16] we noticed that their phosphido analogous had not yet been reported.

Transition metal complexes bearing terminal phosphide ligands (i.e. η^1-phosphide complexes) have attracted considerable attention.[42-45] Commonly, these are coordinatively saturated complexes in which the PR_2 fragment is pyramidal or approximately tetrahedral at phosphorus and contains a non-bonding, stereochemically active lone pair. This phenomenon is responsible for high P-nucleophilicity and basicity in the terminal phosphido ligand.[46] These Lewis bases can easily form dinuclear complexes or larger clusters containing μ-PR_2 bridge ligands.[47-49] Terminal phosphido ligands in such complexes become planar when the metal center is coordinatively unsaturated and has a low lying empty orbital of the appropriate symmetry to accept lone-pair donation in a *π*-fashion form the PR_2 group.[46] Baker et al. introduced the heterobimetallic complex **11** which clearly illustrates three types of bonding observed for nucleophilic phosphido ligands.[49,50]

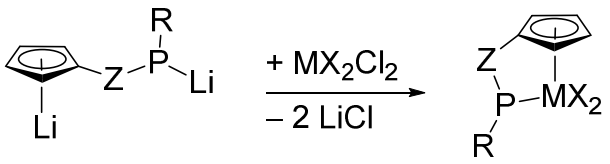


11

The underlying idea of this project is based on a cyclopentadienylethylphosphide chelate, nickel being an example for other late transition metals. The phosphido compound **H** can be represented, upon the dissociation of the ligand, as the unsaturated compound **I** with phosphorus donating its' lone pair to the metal in a *π*-fashion. The phosphido complex **I** would react with a polar compound A–B with formation of the phosphane complex **J**, which, in turn, could undergo the reaction with an alkyne, thus, inducing the dissociation of the phosphane moiety. The sequence of migratory insertion in **K** and the reductive elimination in **L** would release the catalytically active species **I** and a substituted alkene as a product. Remarkably, the whole catalytic process would proceed without change of the oxidation state of the metal.

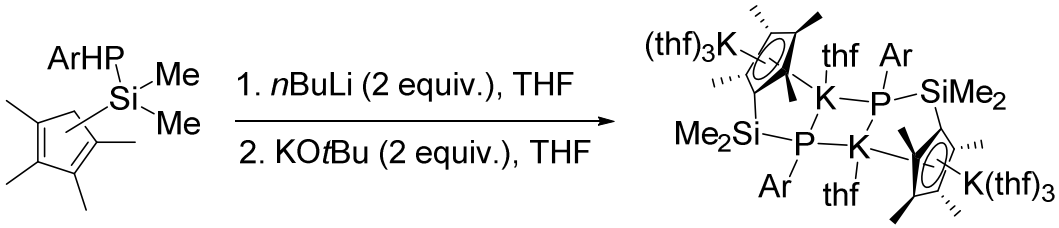


The first report of a phosphide-pendant cyclopentadienyl complex[22] was published about 10 years after the report of amide-pendant cyclopentadienyl complexes.[20] The first synthetic method describes the metathesis which involves the reaction of dilithiated “CpCP” or “CpSiP” reagents **M** with appropriate metal complexes to give the corresponding phosphido chelates **N**.[21,22]

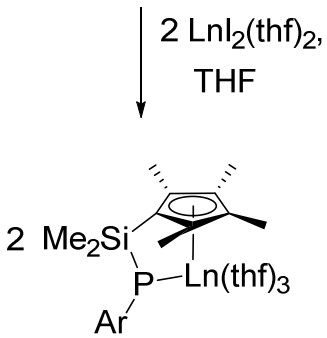


M **N**

Hou, Wakatsuki et al. reported lanthanide(II) phosphido chelates **12** and **13** prepared from the corresponding dipotassium cyclopentadienyl-phosphido complex **14**.[25]



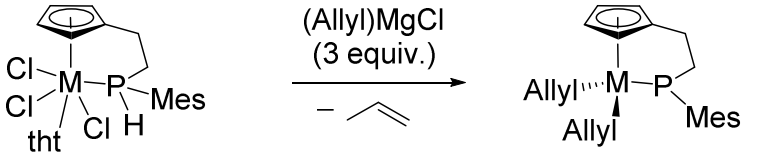
15 **14**, 88 %



Ar = Mes*

12: Ln = Sm (66 %)
13: Ln = Yb (81 %)

Miyoshi, Nakazawa et al. introduced the second method which describes the formation of zirconium(IV) and hafnium(IV) phosphido chelates **9** and **10**, respectively, from the corresponding secondary phosphane substituted complexes **16** and **17** *via* triallylation with the liberation of propene.[19]

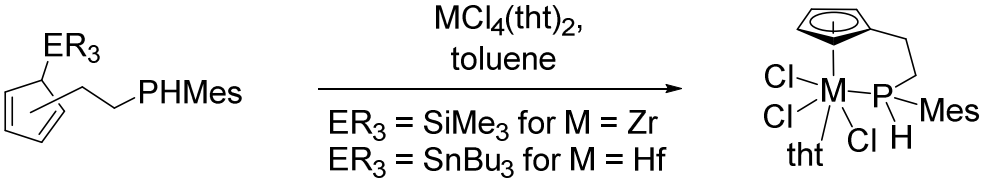


16: M = Zr
17: M = Hf

9: M = Zr, 79 %
10: M = Hf, 89 %

These systems obtained by combination of secondary phosphine-pendant and phosphide-pendant complexes of zirconium(IV) and hafnium(IV) with alkylaluminium cocatalysts were examined in the polymerization of ethylene and styrene and in the copolymerization of ethylene/styrene. The authors observed that these systems are furthermore active in the copolymerization of ethylene/styrene, and the copolymers obtained have a relatively high styrene content. Such behavior has not been observed in copolymerizations with the corresponding amido-pendant cyclopentadienyl complexes.[51]

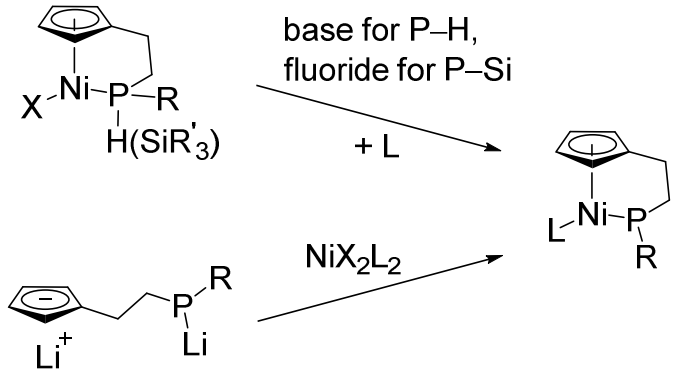
Cyclopentadienyl complexes bearing a secondary phosphane substituted chelating tether have only been reported for zirconium and hafnium by Miyoshi, Nakazawa et al. in 2002. The authors observed that the nature of ligands in metal complexes was crucial in terms of stability and therefore isolation of the formed chelate complexes **16** and **17** from trimethylsilyl- and tributylstannyl-substituted cyclopentadienyl derivatives **18** and **19**, respectively.[52]



18: $ER_3 = SiMe_3$
19: $ER_3 = SnBu_3$

16: M = Zr, 84 %
17: M = Hf, 88 %

In the scope of this work, we are aimed to investigate either one of the described methodologies in synthesis of cyclopentadienylethylphosphide complexes for late transition metals. Furthermore, the second method implies the use of the corresponding secondary phosphane substituted chelates, which have not yet been reported for late transition metals. We intend to prepare the first cyclopentadienyl complexes of late transition metals with a secondary phosphane substituted tether and to extend this class of compounds to silyl-substituted phosphane chelates, which are expected to be converted into the corresponding phosphido chelates due to the presence of reactive P–H and P–Si bonds, respectively (Scheme 2).

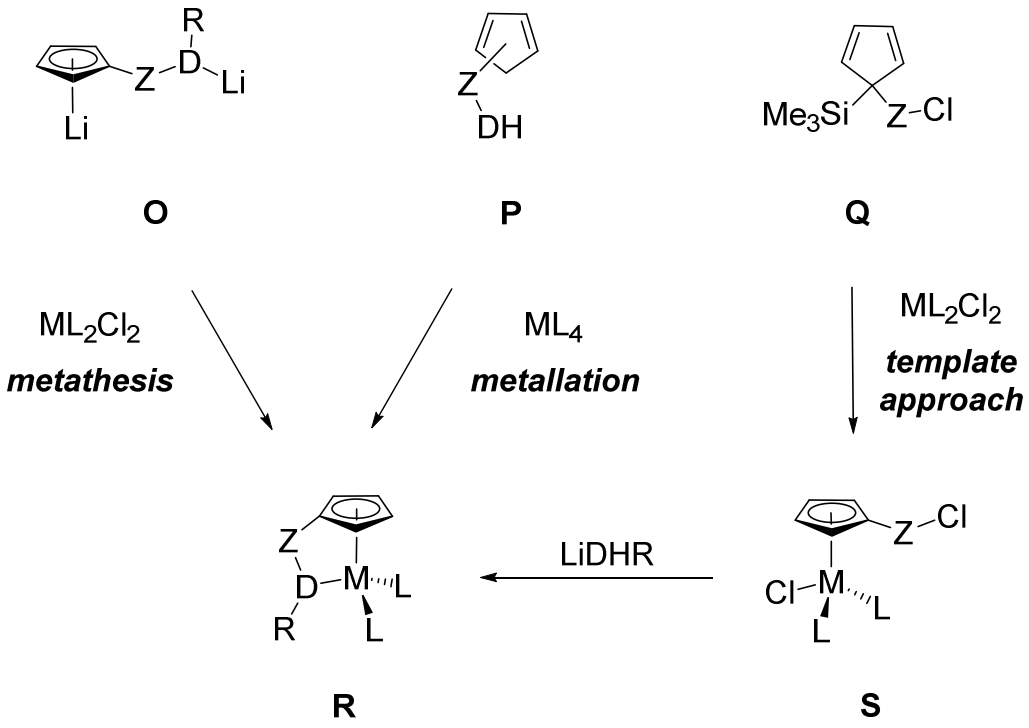


Scheme 2. Envisioned approaches to cyclopentadienylethylphosphide chelate complexes of late transition metals (nickel being an example), X = halide.

2. Results and Discussion

2.1 Synthetic Strategies to Cyclopentadienyl Chelate Complexes of Transition Metals with a Phosphido Tether

In the last two decades, numerous approaches to cyclopentadienyl complexes of transition metals **R**, namely, of group 3 and 4 metals and lanthanides, with diverse anionic tethers have been established and can be classified into three general categories: metathesis, metallation and template approach (Scheme 3).[20b]

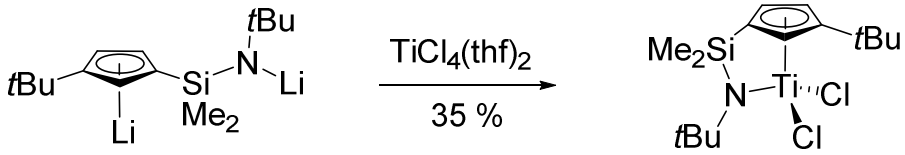


Scheme 3. Metathesis, metallation and template approaches.[20b] D = donor group, Z = linker, M = transition metal, L = anionic ligand or halide.

The metathesis methodology implies the reaction of the dilithiated species **O** with an appropriate metal reagent with salt elimination. The metallation describes the conver-

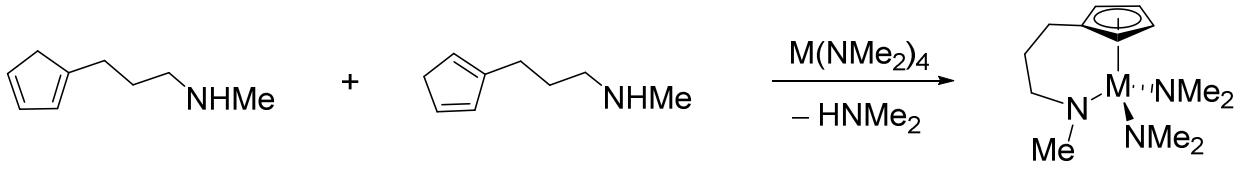
sion of the neutral functionalized cyclopentadiene **P** which is deprotonated twice upon the reaction with a metal reagent. The template approach is characterized by a stepwise attachment of a ligand to a metal center starting from the functionalized cyclopentadiene **Q** where the silyl group acts as an effective leaving group in the reaction with a metal reagent. The chelate precursor **S** can be further converted into the desired complex **R**.

The metathesis route was first applied by Okuda et al. in the synthesis of the first group 4 constrained geometry catalyst **21** by treating $TiCl_4(thf)_2$ with the dilithiated reagent **20**.[53]



20 **21**

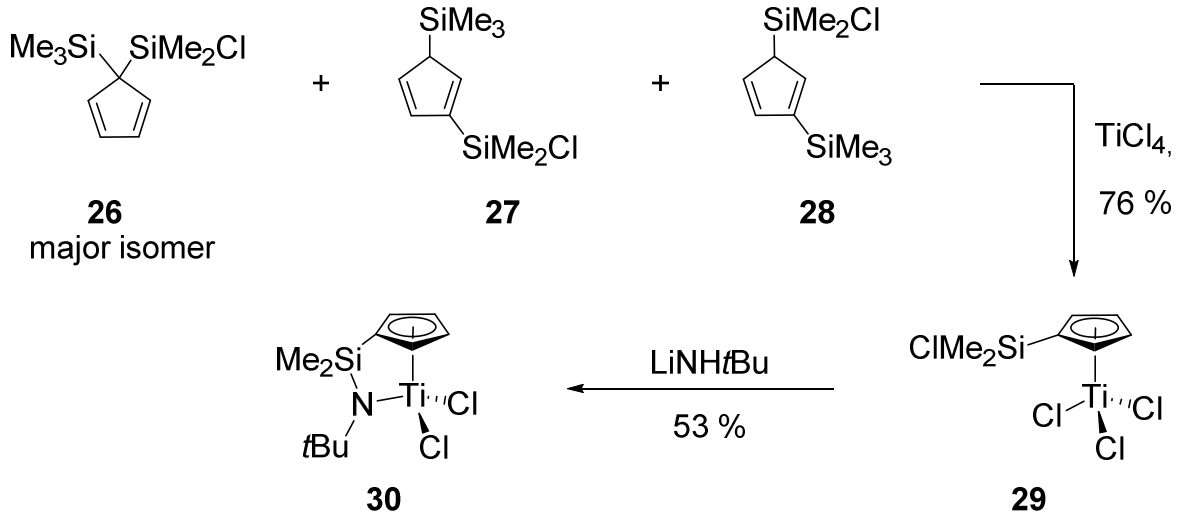
The metallation approach was first applied by Teuben et al. in the preparation of zirconium(IV) and hafnium(IV) amido chelates **24** and **25**, respectively, with a propylene spacer. The driving force of these reactions is the formation of volatile amines formed by the double deprotonation of the secondary amine substituted cyclopentadiene isomers **22** and **23**.[54]



22 **23**

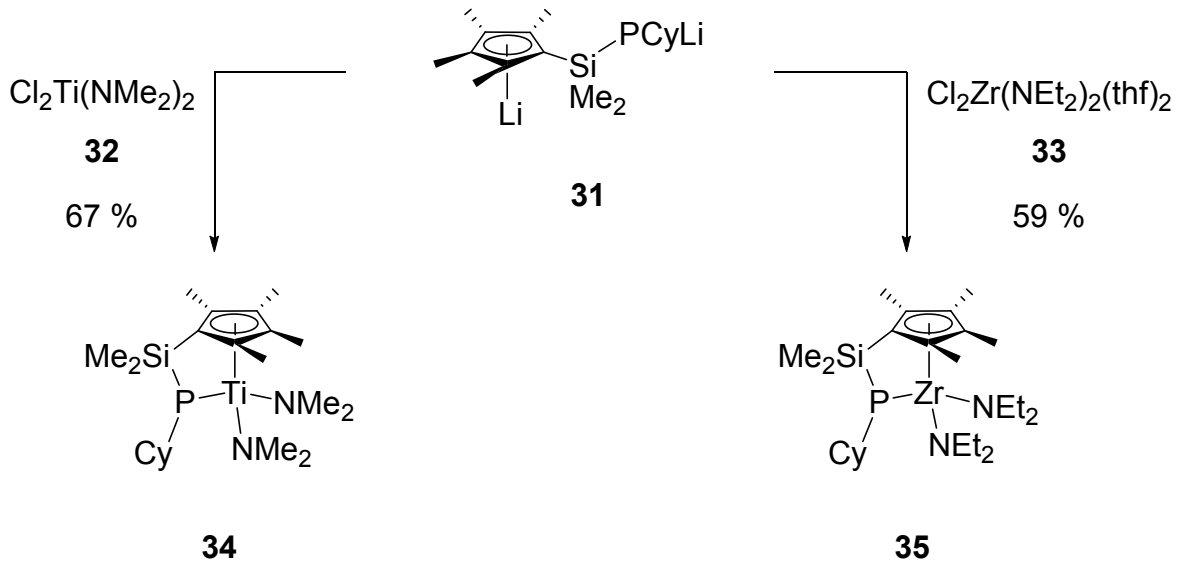
24: M = Zr, 94 %
25: M = Hf, 58 %

The template approach was first applied by Royo et al. by the preparation of the titanium(IV) amido chelate **30** from the silylated cyclopentadiene isomers **26**, **27** and **28** *via* the intermediate **29**.[23a]



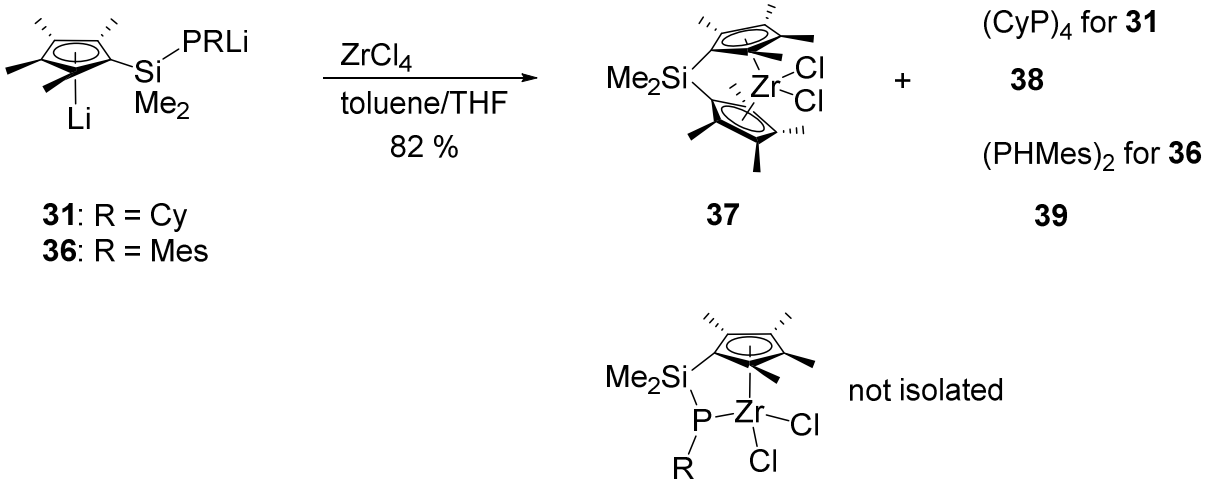
In syntheses of cyclopentadienyl complexes of transition metals with a phosphido tether both, the metathesis[21,22,25,55] and the template approach[19] have successfully been applied.

Erker et al. reported the synthesis of silylene- and methylene-bridged cyclopentadienyl phosphido chelates[22b,24,55] *via* the metathesis route. The authors noted that the nature of the employed metal reagent was crucial for the stability and isolation of the formed phosphido complexes.



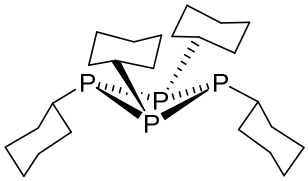
By the reaction of the dilithiated reagent **31** with $ZrCl_4$ or $TiCl_4$ complicated product mixtures were observed, while the reactions of **31** with the corresponding group 4 metal dichlorobis(dialkylamido) reagents **32** and **33** gave the desired phosphido complexes **34** and **35** in good yields.[24]

Hey-Hawkins et al. observed an unexpected P–Si cleavage in the reaction of dilithiated reagents **31** and **36** with $ZrCl_4$, obtaining the *ansa*-metallocene **37** instead of the expected cyclopentadienyl derivative [{(η^5-C_5Me_4)$SiMe_2$PR}$ZrCl_2$].[56] Along with **37** the formation of the oxidation side products $(CyP)_4$ (**38**)[57, 58] and $(PHMes)_2$ (**39**)[59], respectively, was detected by ^{31}P NMR spectroscopy. The authors noted, that these results are in contradiction with those originally reported by Dow Chemical Co. in a patent application, where the formation of the expected monocyclopentadienyl derivative [{(η^5-C_5Me_4)$SiMe_2$PPh}MCl_2] (M = Ti or Zr) from the corresponding dilithio reagent Li_2[(C_5Me_4)$SiMe_2$PPh] was described.[25]



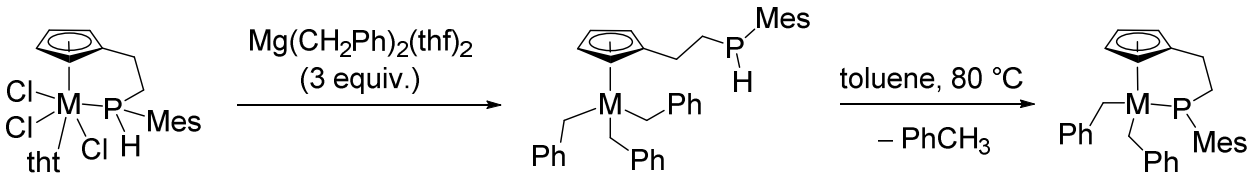
A possible mechanism for the formation of the (tetracyclohexyl)cyclotetraphosphine (**38**) or the diphosphine **39** during these complexation reactions has not yet been proposed. Originally, **38** was prepared by Issleib et al. from the reaction of cyclohexylphosphine with the corresponding organophosphonous dihalide.[57] The cyclotetraphosphine ring in **38** is puckered with cyclohexyl groups alternating above and below the phosphorus ring, where the P–P distances correspond to a single bond. The phosphorus atoms have a pyramidal environment and occupy the equatorial posi-

tions in the chair configuration of the cyclohexyl rings. The non-planarity of the cyclotetraphosphine is possibly caused by bond angle and torsional angle requirements as no interaction between the substituent groups have been found.[58]



38

The template approach to the ethylene bridged cyclopentadienyl phosphido chelates was applied by Miyoshi, Nakasawa et al. starting from the corresponding secondary phosphane substituted complexes (*vide supra*). The formation of zirconium(IV) and hafnium(IV) phosphido chelates **42** and **43**, respectively, from the corresponding secondary phosphane substituted complexes **16** and **17** *via* intermediate isolable complexes **40** and **41** with a non-coordinated secondary phosphane tether was reported. The authors were not able to isolate phosphides **42** and **43** as a solid due to their slow decomposition in solution.[19]

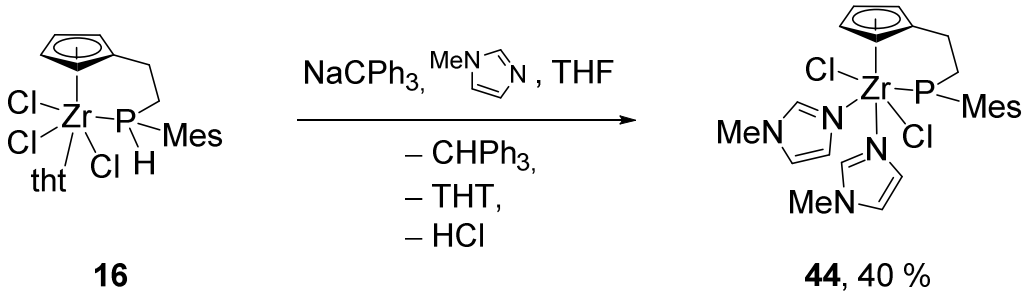


16: M = Zr
17: M = Hf

40: M = Zr, 88 %
41: M = Hf, 91 %

42: M = Zr
43: M = Hf

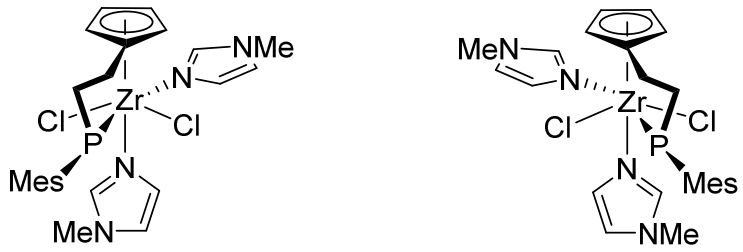
A single crystal X-ray structural analysis was performed on zirconium(IV) complex **44** obtained in moderate yields from **16** by the sequence of a monotritylation, a ligand exchange reaction with *N*-methylimidoazole and the liberation of triphenylmethane.[19]



16 **44**, 40 %

2.2 Characteristic Features of Cyclopentadienyl Chelate Complexes of Transition Metals with a Phosphido Tether

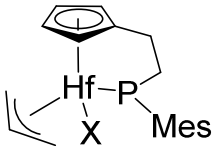
The structural and the spectroscopic analyses of some mentioned cyclopentadienyl chelate complexes of early transition metals with a phosphido tether showed interesting results. A single crystal X-ray structural analysis of the zirconium(IV) complex **44** demonstrates that the asymmetric unit contains a pair of the enantiomers **44a** and **44b**.



44a **44b**

The zirconium-phosphorus distances of 260.0 pm for **44a** and 259.7 pm for **44b** show that the Zr–P bond is shorter than that in the comparable tertiary phosphine-pendant complex [{η^5-$C_5H_4(CH_2)_2PPh_2$-κP}$ZrCl_3$(thf)] (284.7 pm).[60] This indicates that the Zr–P bond in **44** bears a considerable double bond character. The phosphorus atom has a distorted trigonal-planar geometry with the sum of bond angles of 341.7° (**44a**) and 342.4° (**44b**), indicating that the phosphorus atom has some sp^2-hybridization character.[61] The ^{31}P NMR spectrum of **44** shows a signal at δ = 162.8 ppm demon-

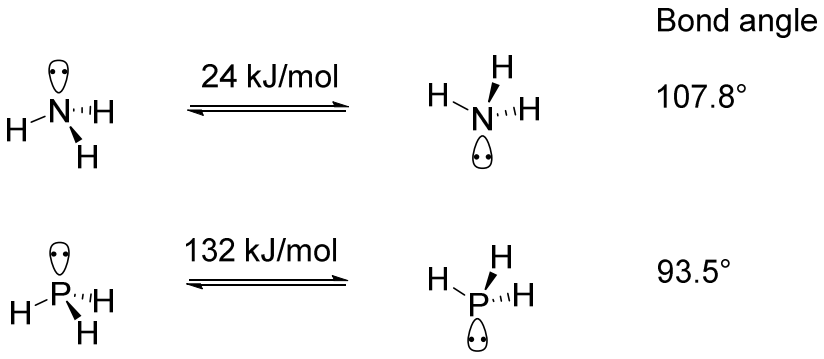
strating a huge downfield shift of about 185 ppm difference relative to a secondary phosphine substituted precursor **16** (δ = –20.6 and –22.9 ppm).[19,52]



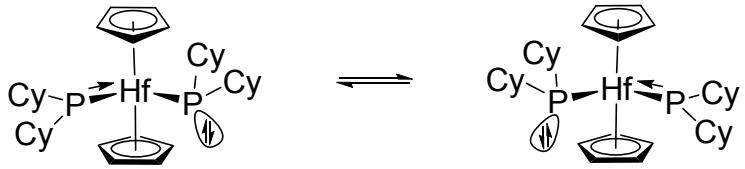
45: X = C_6F_5
46: X = NPh_2
47: X = NEt_2

Hafnium(IV) complexes **45**-**47**, where the metal atom is also an asymmetric center, may exist each as a couple of two diastereomers, assuming that the phosphorus atom takes pyramidal geometry. The ^{31}P NMR spectra of these complexes show only one signal for each complex indicating either a planar geometry of the phosphorus atom or a rapid inversion between the enantiomeric trigonal geometries.[19]

Tricoordinate phosphorus species, unlike the corresponding nitrogen compounds, are configurationally stable and usually do not undergo inversion under ambient conditions. The inversion barrier of phosphines is generally 125-145 kJ/mol.[62] For example, PH_3 has an inversion barrier of 132 kJ/mol compared to 24 kJ/mol for NH_3.[63] The higher energy demand for the phosphorus inversion results from the strong geometric distortion necessary to form the trigonal planar transition state. Larger bond angles require less distortion than smaller bond angles. The bond angles in the trivalent phosphorus compounds are smaller than those of the trivalent nitrogen or carbon tetravalent species.[64]

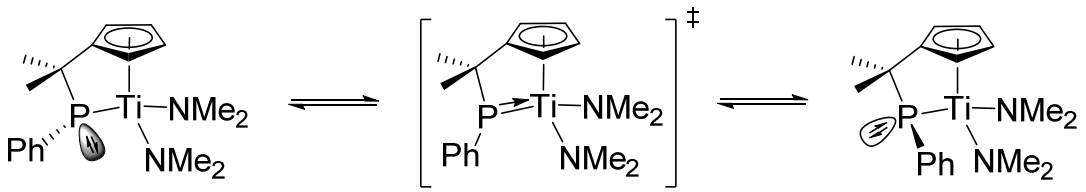


There are, however, a number of cases where a *σ*-bonded metal electrophile strongly interacts with the phosphorus lone pair, the phenomenon responsible for the planarity at phosphide phosphorus.[49] Low temperature ^{31}P NMR allowed the assignment of two signals due to the distinct, localized hafnium-phosphorus *σ*-bond (*δ* = –15.3 ppm) and hafnium-phosphorus *π*-bond (*δ* = 270.2 ppm) in bis(phosphido)hafnocene complex **48**, which was described by Baker et al. At ambient temperature the single and double hafnium-phosphorus bonds undergo rapid exchange to give an averaged, delocalized phosphorus-hafnium-phosphorus structure (*δ* = 160.0 ppm) in solution.[65]



48a **48b**

The **48a**-**48b** interconversion probably represents a process that is closely related to the dynamic process which was observed by Erker et al. for the titanium(IV) complex **49**. The DFT (Density Functional Theory) calculations of the **49a**-**49b** interconversion process indicate that the *π*-bonded structure **50** represents a transition state rather than a high-lying intermediate. From the temperature-dependent 600 MHz ^{1}H NMR spectra in a Freon ($CDFCl_2$/CDF_2Cl/CD_2Cl_2) solvent mixture a Gibbs activation energy of $\Delta G^{\ddagger}$ (213 K) = 39 kJ/mol was obtained for the phosphorus inversion process of complex **49**. At 298 K only symmetry-averaged NMR spectra of complex **49** were observed. The ^{31}P NMR resonance of **49** showed a marked temperature-dependent chemical shift (*δ* = 3.0 ppm at 298 K and *δ* = –13.0 ppm at 193 K).[55,66]

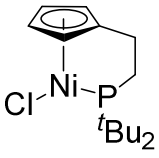


49a **50** **49b**

Encouraged by the results for early transition metals, we envisaged syntheses of cyclopentadienyl complexes of late transition metals with a phosphido tether *via* metathesis and template approaches, since such complexes have not been reported until now.

2.3 Attempted Metathesis Reactions towards Cyclopentadienyl Chelate Complexes of Late Transition Metals with a Phosphido Tether

Earlier reports of our group showed that cyclopentadienyl complexes of late transition metals with a tertiary phosphane substituted ethylene tether, such as **3** and **51**-**53**, are easily accessible *via* salt-elimination reactions.[14,40,67]



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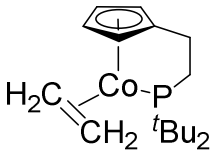

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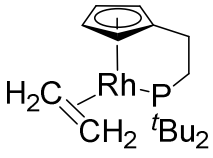

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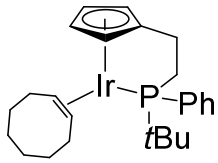
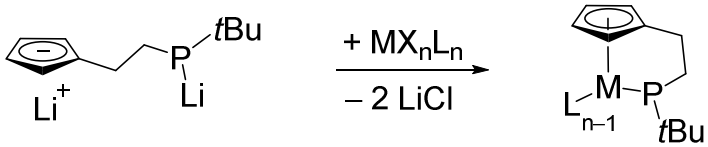


53

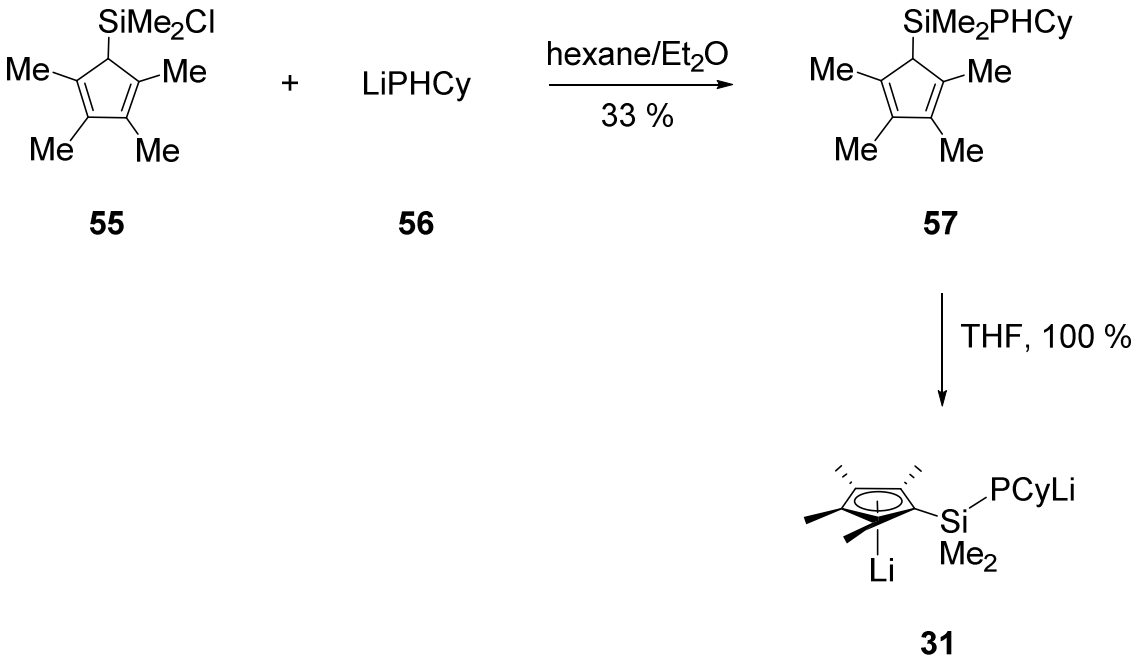
The conversion of the dilithiated compound **54** with an appropriate metal reagent should deliver the desired phosphido complex **T**. Thereby, the *tert*-butyl substituent at phosphorus is the group of the first choice as, compared to the phenyl group, it has been proven to be successful in crystallization of complexes **3** and **51**.[14,40]



54 **T**

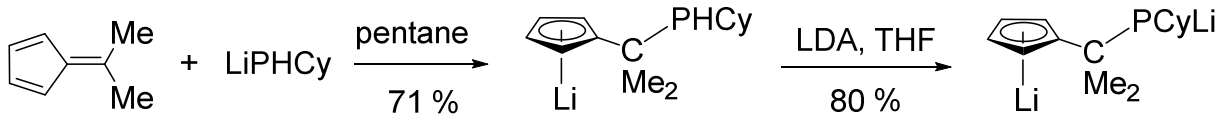
M = late transition metal; L = ligand

Most of cyclopentadienyl phosphido complexes of early transition metals were prepared from the corresponding dilithiated cyclopentadienyl phosphido reagents which are connected either by a silylidene or by an alkylidene bridge.[21,22,24,26] The dilithiated silylidene linked cyclopentadienyl phosphide **31** was prepared by double lithiation of the corresponding PH-functionalized cyclopentadiene derivative **57**, which is accessible by the salt elimination reaction of (dimethylchlorosilyl)tetramethylcyclopentadiene (**55**) and lithium cyclohexylphosphide (**56**). The ^{1}H NMR and ^{13}C NMR spectra of **31** and **57** are featured by the presence of diastereotopic methyl groups bound to the silicon atom as well as by diastereotopic hydrogen and carbon atoms of the cyclohexyl groups. [68]



55 **56** **57** **31**

The dilithiated alkylidene linked cyclopentadienyl phosphide **60** was prepared by treatment of the monolithiated PH-functionalized cyclopentadienyl derivative **59**, which, in turn, was obtained by the addition of the phosphide **56** to 6,6-dimethylfulvene (**58**).[55] Fulvenes have extensively been used as precursors for substituted cyclopentadienyl ligands.[69] It is well established that diverse nucleophiles can add to the electrophilic fulvene C6-carbon atom to obtain the corresponding cyclopentadienides.[70]

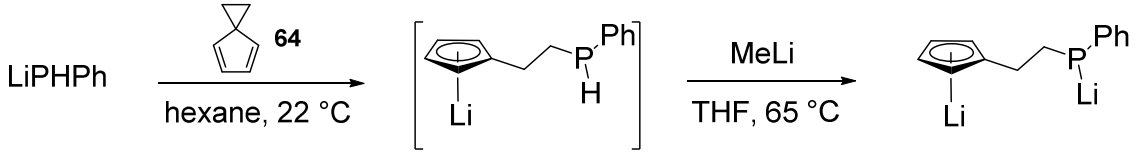


58 **56** **59** **60**

The authors observed a doublet for the methyl groups in the tether, induced by the P,H-coupling, each for **59** and **60**.[55]

(2-Phosphanylethyl)cyclopentadienyl ligands are usually prepared by the reaction of a lithium phosphide with spiro[2.4]hepta-4,6-diene (**64**).[1d] The nucleophilic cyclopropane ring opening of **64** was first established by Kauffmann et al.,[71] representing a general method of synthesis of numerous systems, which contain an ethylene spacer between the cyclopentadienyl ligand and the appended phosphane or arsenic group. The driving force of this ring opening reaction is the release of ring-strain accompanied by the formation of the aromatic cyclopentadienide.

The only known dilithiated cyclopentadienyl phosphido reagent which is connected by the ethylene spacer was reported by Hey-Hawkins et al. The authors reported the synthesis of the solvent-free dilithiated cyclopentadienylethylphosphine **63** by treatment of the monolithiated compound **62** with methyllithium in 56 % yield from lithium phenylphosphide (**61**). The intermediate **62**, which was converted further without isolation, was prepared by cleavage of the cyclopropylring in spiro[2.4]hepta-4,6-diene (**64**) by the phosphide **61**. The asymmetry of the substitution at phosphorus in **63** is reflected in the ^{1}H NMR spectrum as multiplets for the non-equivalent hydrogen atoms of the cyclopentadienyl moiety. Interestingly, for the CH_2-group directly bound to phosphorus distinct signals for the diastereotopic hydrogen atoms could be observed, whereas for the CH_2-group next to the cyclopentadienyl group a triplet, induced by the H,H-coupling, was reported.[68]

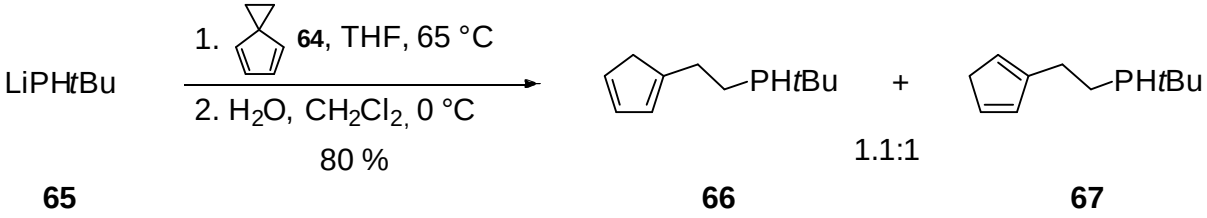


61 **62** **63**, 57 %

Consequently, the reaction between lithium *tert*-butylphosphide[72] (**65**) and spiro[2.4]-hepta-4,6-diene[73] (**64**) was intended.

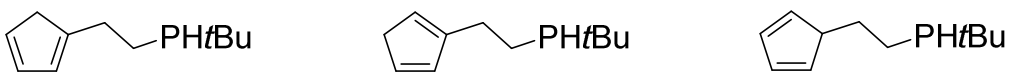
2.3.1 Synthesis of (2-*tert*-Butylphosphanylethyl)cyclopentadienes 66 and 67

Lithium *tert*-butylphosphide (**65**) was treated with **64** in THF and then hydrolyzed, leading to a 1.1:1 mixture (^{31}P NMR analysis) of isomeric secondary phosphanes **66** and **67** as colorless oils, respectively, in 80 % yield. The mixture could not be separated. The reaction does not proceed in weakly or non-coordinating solvents such as diethyl ether or hexane, respectively. Compounds **66** and **67** are like many other primary and secondary phosphanes extremely sensitive to air. The cyclopentadienes **66** and **67** were stored at –30 °C in order to prevent the dimerization to dicyclopentadienes.[74]



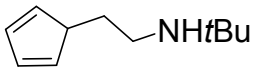
65 **66** **67**

In the ^{31}P{^{1}H} NMR spectrum the resonances of the two (**66** and **67**) of three possible regioisomers (**66**, **67** and **68**) were observed at δ = –23.8 and –23.9 (major isomer) ppm. The preferred formation of **66** and **67** can be explained by the increased thermodynamic stability of the disubstituted alkenes compared with the monosubstituted ones.



66 **67** **68**

The constitutions were confirmed by HSQC, HMBC and H,H-COSY NMR measurements. The chemical shifts in the ^{1}H NMR spectrum of **66** and **67** are nearly the same for all hydrogen atoms except for the methylidene protons (2.90 ppm for $CpCH_2$ in **66** and 2.96 ppm for $CpCH_2$ in **67**) as well as for the protons of the cyclopentadiene moiety which appear as multiplets. In the ^{1}H NMR spectrum two multiplets for the CH_2-group directly bound to phosphorus at δ = 1.54-1.73 and δ = 1.96-2.08 ppm were observed, indicating the diastereotopic nature of the hydrogen atoms. A multiplet at δ = 2.45-2.68 ppm was assigned to the CH_2-group directly bound to the cyclopentadienyl moiety. These results are in contradiction with those reported for the related compounds **69**, **70** and **71**[18] containing a secondary amine function.



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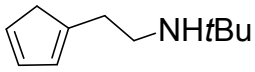

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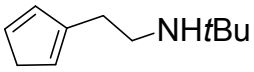
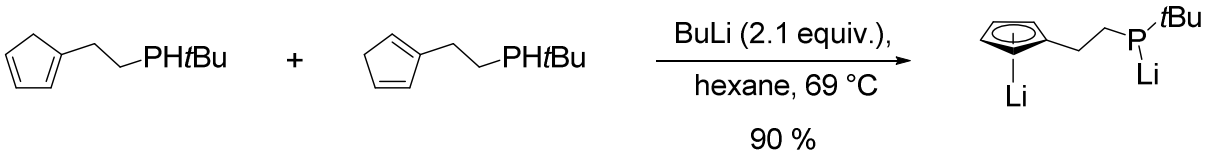


71

69, **70** and **71** were obtained by Teuben et al. as a 0.4:1:1 mixture of 1-, 2- and 3-substituted isomers, respectively, as air stable compounds. The symmetry is particularly reflected by the signals for both CH_2-groups either directly bound to nitrogen or next to the cyclopentadiene moiety, which appear as triplets in the ^{1}H NMR spectra of **69**, **70** and **71**.[18]

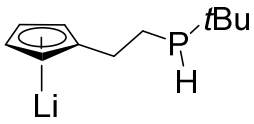
2.3.2 Synthesis of Dilithio (2-*tert*-Butylphosphidoethyl)cyclopentadienyl (54)

Compounds **66** and **67** were treated with butyllithium (2.1 equiv.) in hexane delivering the dilithio salt **54** as a pyrophoric yellowish solid in 90 % yield (purity ≥ 80 % according to ^{31}P NMR analysis).



66 **67** **54**

54 was characterized by ^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectroscopy. The proton coupled ^{31}P NMR spectrum shows a multiplet at δ = –47.8 ppm indicating a shielding effect of lithium as compared to hydrogen atom. In addition to this signal, a doublet of multiplets at δ = –23.8 ppm (ca. 10 %) with the coupling constant of 191.6 Hz, which was assigned to **72** as a result of a partial hydrolysis of **54**, was observed.



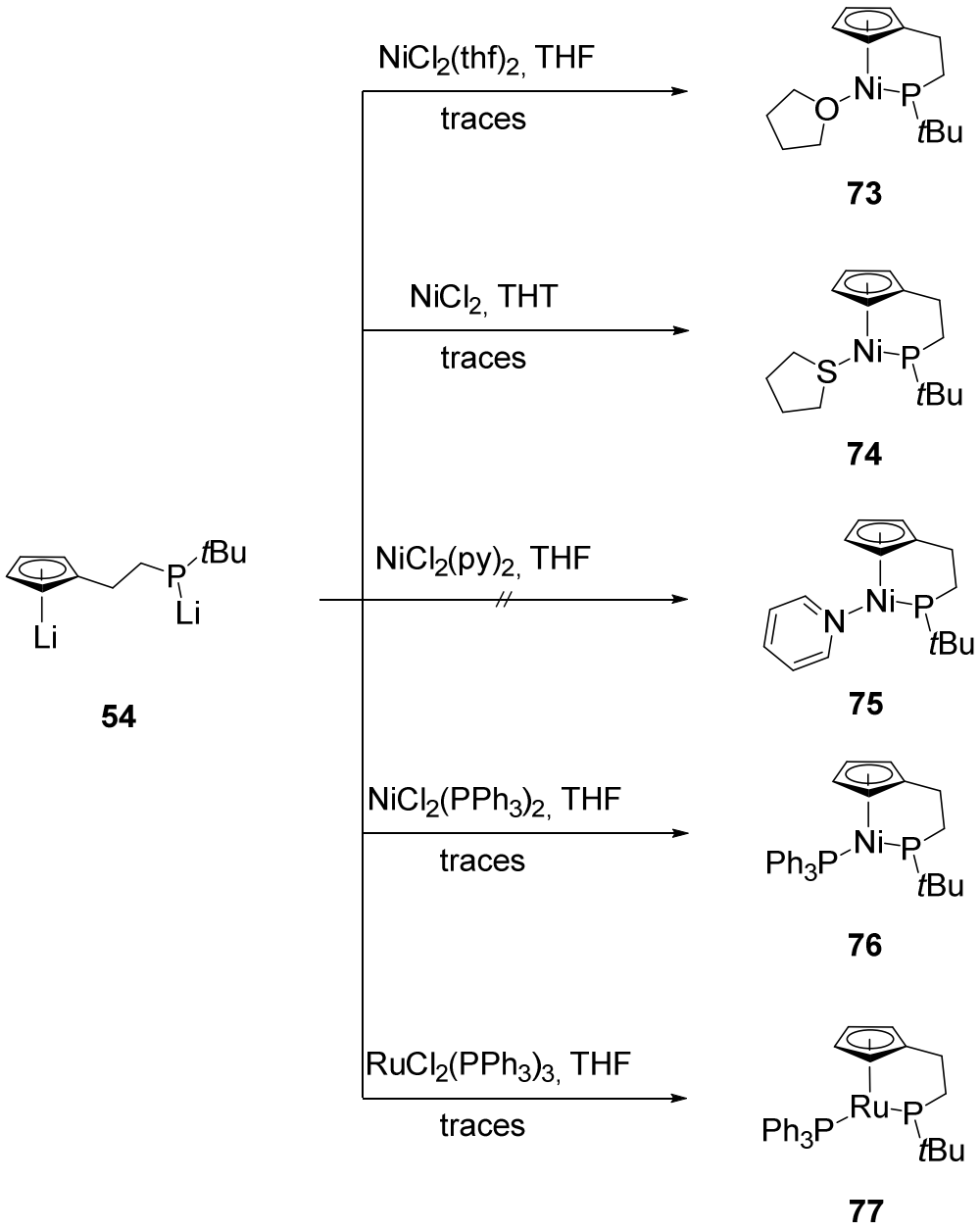
72

The partial hydrolysis of **54** to **72** could have taken place during purification and isolation procedures, and indicates that the phosphine moiety is more basic than the cyclopentadienyl group. Issleib and Kümmel reported the experimental solution-phase acidities of several secondary phosphines in tetrahydrofuran, the pK_a values range from 21 to 36.[75] Cyclopentadiene has a pK_a value of 16, being one of the most acidic hydrocarbons.[76]

The asymmetry of the substitution at phosphorus in **54** is reflected in the ^{1}H NMR and ^{13}C NMR spectra as distinct signals of the diastereotopic hydrogen and carbon atoms in the cyclopentadienyl ring and in the ethylene bridge. In the ^{1}H NMR spectrum multiplets at δ = 2.01-2.04 ppm and at δ = 2.55-2.61 ppm for the CH_2-group next to phosphorus and for CH_2-group next to the cyclopentadienyl group, respectively, were observed. The signals for the CH-group of the cyclopentadienyl moiety appear as multiplets at δ = 5.37-5.38 and 5.51-5.52 ppm in the ^{1}H NMR spectrum and as two signals at δ = 102.3 and 102.8 ppm in the ^{13}C NMR spectrum.

2.3.3 Conversion of 54 with Middle and Late Transition Metal Reagents

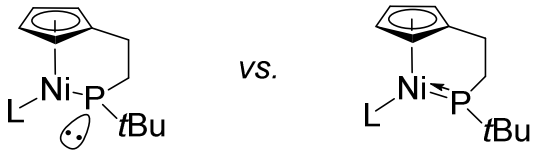
Next, the reactions of dilithio reagent **54** with a variety of late transition metal reagents based on nickel(II) and ruthenium(II) chloro complexes, were tested (Scheme 4).



Scheme 4. Attempted metathesis reactions towards phosphido chelate complexes. $NiCl_2(thf)_2$,[77] $NiCl_2(py)_2$,[78] $RuCl_2(PPh_3)_3$[79] and were prepared according to the procedures described in literature.

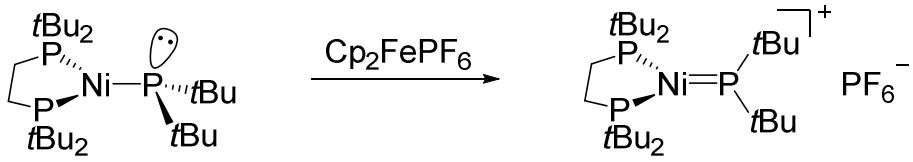
The general procedure for the metathesis reactions consisted of treating cold suspensions (–100 °C) of the appropriate metal reagents in THF with the solution of **54** in THF followed by slow warming to 22 °C. The analysis of **74** and **75** by NMR spectroscopy was not possible to perform due to locking problems. One of the possible reasons could be the magnetic nature of the samples. The NMR spectroscopy analysis of **73**, **76** and **77** showed a complicated mixture of compounds which could not be identified. All attempts to isolate the desired phosphido chelates by column chromatography or by crystallization failed. Longer reaction times did not positively influence the results. However, the ESI-HRMS spectrometry analysis indicated masses for $[M+H]^+$ for the complexes **73**, **74**, **76** and **77**, showing that the phosphido complexes have likely been formed but decomposed, presumably, due to their unstable nature.

The choice of a ligand at the metal center as well as the nature of a substituent at the phosphorus atom could play a crucial role in providing stability for phosphido chelates. It was not possible to determine, whether compounds **73**, **74**, and **76** exist as complexes with a pyramidal phosphido substituent **U** or with a planar phosphido moiety **V**. Complex **V** is characterized by an electron-rich metal center due to the additional *π*-donation from the phosphido *p*-lone pair. The reduction of the electron density at nickel can presumably be achieved through the introduction of an electron-withdrawing ligand.



U **V**

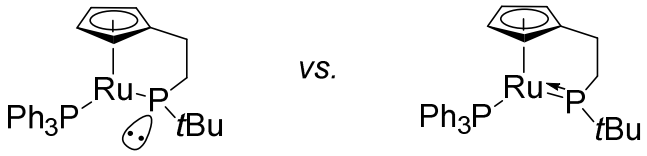
Hillhouse et al. reported the oxidation of the nickel(I) complex with a pyramidal phosphido group **78** to the corresponding cationic nickel(II) complex **79** with a planar phosphido moiety.[80]



78 **79**

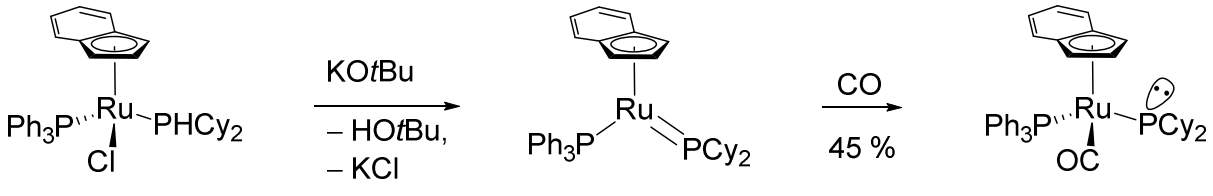
The authors showed that one-electron oxidation of nickel promoted *π*-donation of the phosphido lone pair to an empty metal-based molecular orbital, which was previously singly occupied. These results were confirmed by the crystal structure analyses of **78** and **79**.[80]

Similar to the nickel complexes **U** and **V**, the unsaturated ruthenium(II) compound **77** can be represented as **77a**, featuring a 16-electron complex where the phosphido ligand participates only in *σ*-bonding, or as **77b**, where the 18-electron count is formally achieved through the additional formation of a metal-phosphorus *π*-bond.



77a **77b**

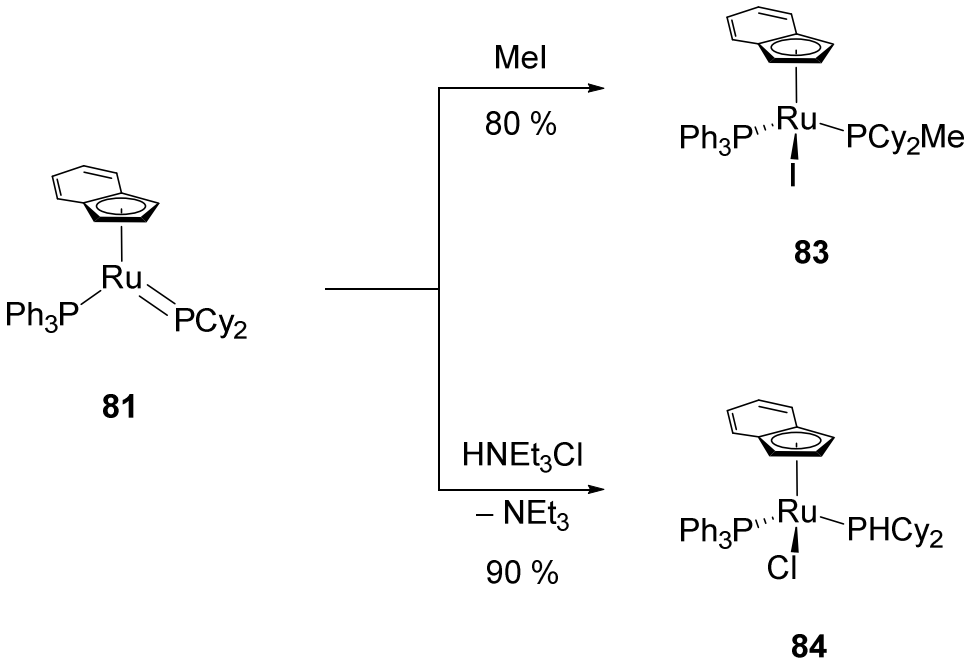
Rosenberg et al. reported the indenyl ruthenium(II) phosphido complex **81**, prepared from the corresponding secondary phosphine substituted complex *rac*-**80** by deprotonation.



80 **81** **82**

Functional unsaturation at ruthenium was demonstrated by ready formation of the complex *rac*-**82** with a pyramidal phosphido function by addition of carbon monoxide.[81]

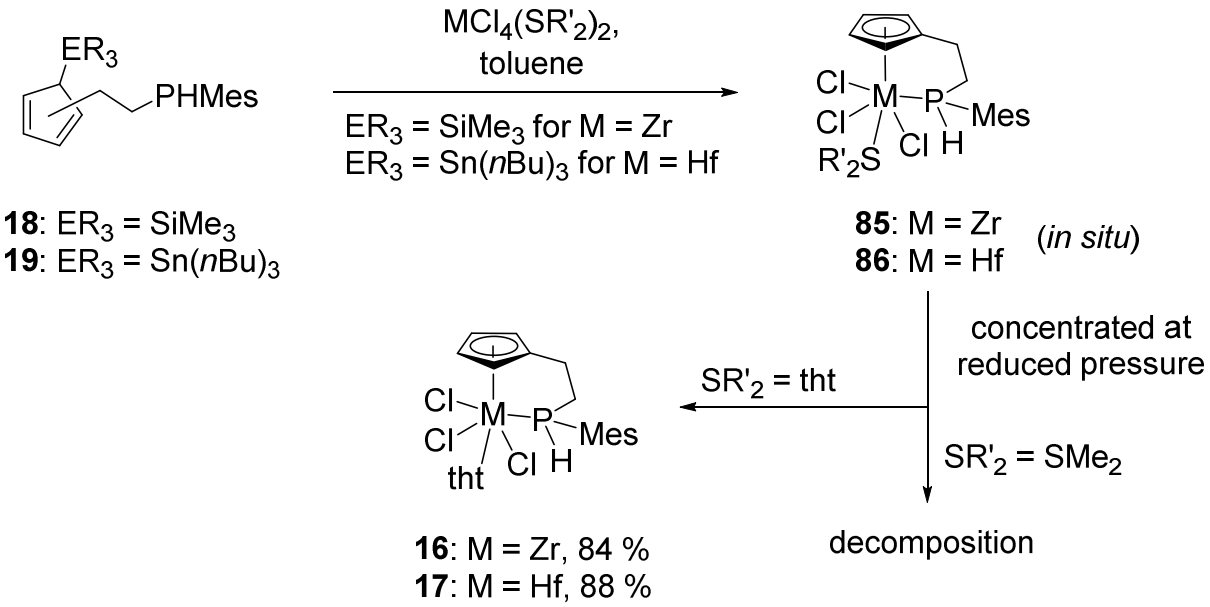
The addition reactions of **81** indicated the bond polarity in $Ru^{\delta+}=P^{\delta-}$. In the reaction of methyl iodide with **81** $Me^{\delta+}$ was delivered to the phosphido ligand and $I^{\delta-}$ coordinated to ruthenium, generating *rac*-**83**. **81** could be also protonated by $HNEt_3Cl$: this delivered Cl^- to ruthenium, generating *rac*-**84**.[81]



Next, the application of the template approach to the desired phosphido chelates was intended, which implies the synthesis of the complexes with secondary phosphanes or silyl substituted phosphanes in the tether. The advantage of this methodology consists in the introduction of a variety of ligands bound to a metal center, preforming in that way an appropriate precursor for the corresponding phosphido complexes.

2.4 Synthesis of Cyclopentadienyl Complexes of Late Transition Metals with a Secondary Phosphane Functionalized Sidechain

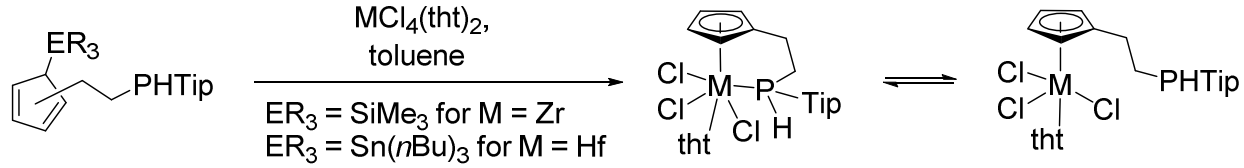
Cyclopentadienyl complexes of transition metals with a secondary phosphane substituted chelating sidechain have only been reported for zirconium and hafnium by Miyoshi, Nakazawa et al. It was found that the selection of the kind of the ligand in metal reagents was very important. $ZrCl_4(SMe_2)_2$ and $HfCl_4(SMe_2)_2$ reacted with the trimethylsilyl substituted cyclopentadienyl derivatives **18** and **19** to give the chelates **85** and **86**, respectively, *in situ* (controlled by ^{31}P NMR spectroscopy). However, either one of the complexes decomposed when the solvent was removed. The analogous reaction with $ZrCl_4(tht)_2$ or $HfCl_4(tht)_2$ gave access to the isolable secondary phosphane substituted chelate complexes **16** and **17**.[52]



The authors also noted that the bulkiness of the substituent at the phosphorus atom strongly affected the coordination mode of the secondary phosphane group in solution. When the substituent is the mesityl group, the phosphine-coordinated compounds **16** and **17** are stable, when the substituent is a bulkier 2,4,6-

triisopropylphenyl group, the phosphine-coordinated (**89** and **90**) and -dissociated species (**91** and **92**), prepared from the precursors **87** and **88**, are in equilibrium.

These phenomena were controlled by the ^{31}P NMR spectroscopy analysis of the reaction mixtures. The ratio of **89** and **91** at 22 °C was approximately 3 to 1 in benzene and toluene. The corresponding hafnium complexes **90** and **92** showed the same behavior.[52]

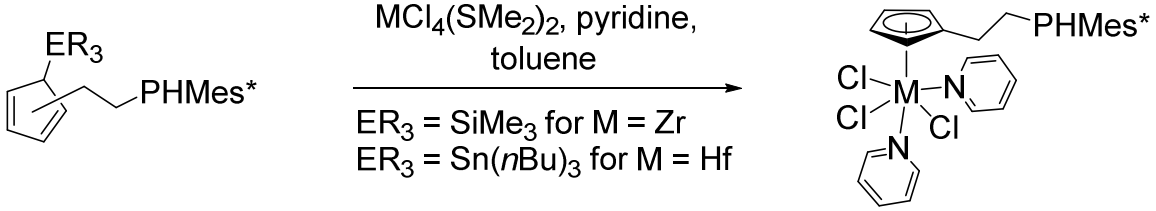


87: $ER_3 = SiMe_3$
88: $ER_3 = Sn(n\text{Bu})_3$

89: M = Zr
90: M = Hf

91: M = Zr
92: M = Hf

In case of an extremely overcrowded 2,4,6-tri-*tert*-butylphenyl substituent, the phosphine-coordinated species are not observed at all. By the reaction of **93** and **94** with $ZrCl_4(SMe_2)_2$ and $HfCl_4(SMe_2)_2$ in the presence of pyridine only the non-chelated species **95** and **96** were obtained in excellent yields.[52]



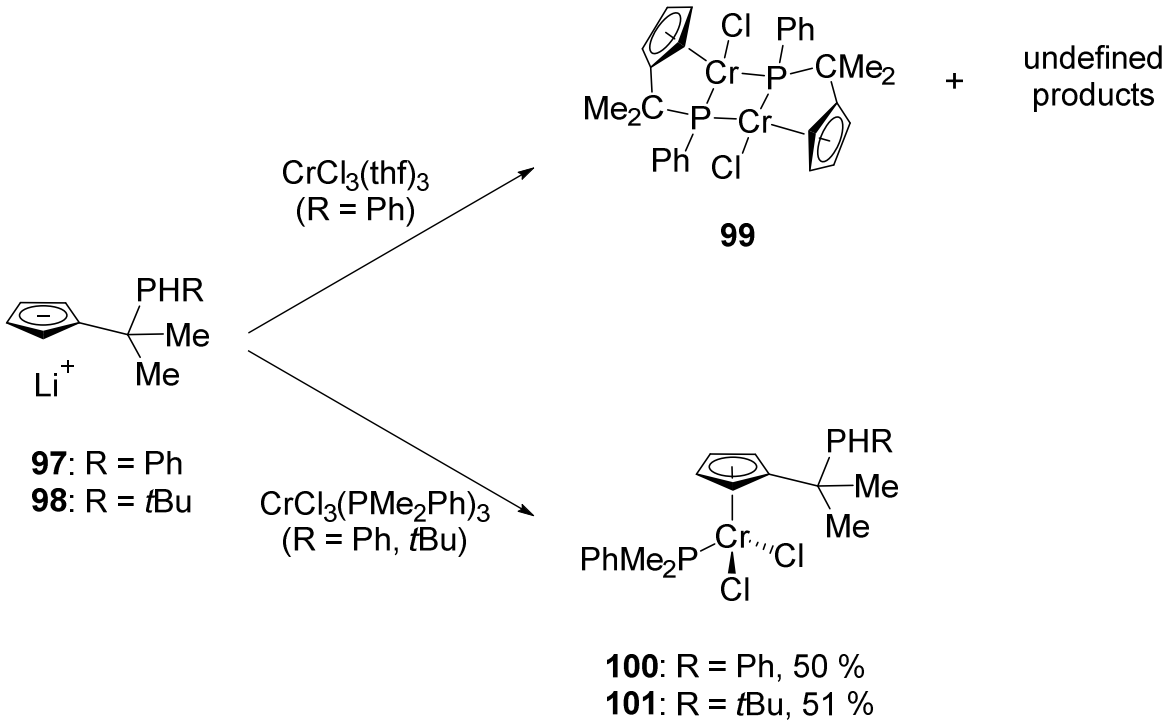
93: $ER_3 = SiMe_3$
94: $ER_3 = Sn(n\text{Bu})_3$

95: M = Zr, 91 %
96: M = Hf, 89 %

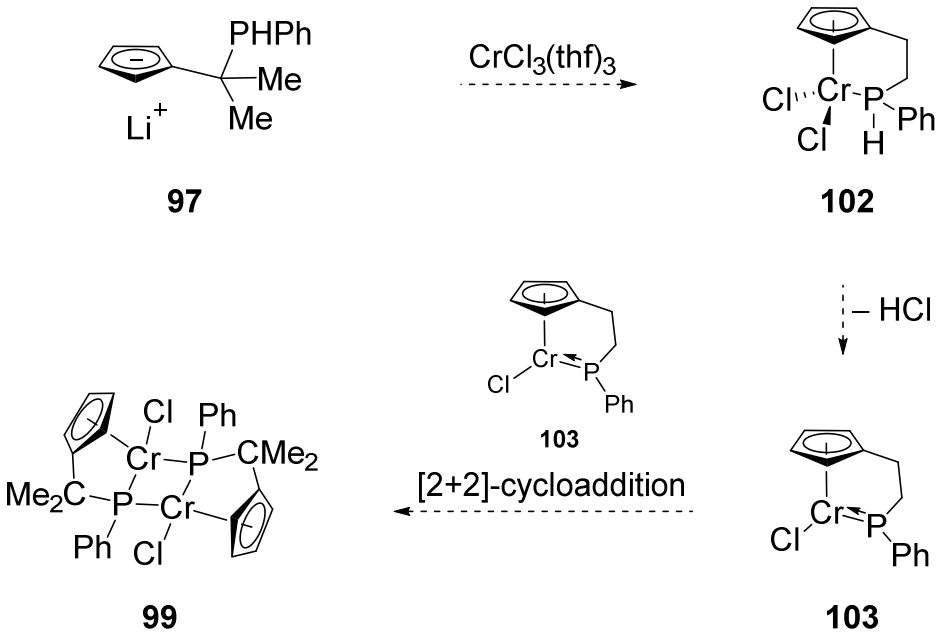
Hey-Hawkins et al. reported the synthesis of the first PH-functionalized (phosphanylalkyl)cyclopentadienyl complexes of chromium(III), where the secondary phosphane group, however, is not coordinated to the metal. Again, dependent on the nature of ligands in metal complexes, different compounds were obtained. By the reaction of

97 with $CrCl_3(thf)_3$ a phosphanido-bridged dimer **99** along with undefined product mixtures were obtained. However, the authors were able to detect the formation of 6,6-dimethylfulvene in the reaction mixture, which indicates the decomposition of **97** in the course of the reaction. Similarly, the decomposition was observed by the reaction of **97** on the protonation with gaseous hydrogen chloride in diethyl ether under the formation of phenylphosphine, lithium chloride and 6,6-dimethylfulvene.

Analogous results were obtained by the reaction with aluminium(III) chloride for which the elimination of hydrogen chloride was proposed as the first reaction step. The authors propose the similar reaction of **97** with $CrCl_3(thf)_3$, which attacks the cyclopentadienyl group under the elimination of lithium chloride and/or the phosphanyl group liberating hydrogen chloride. The activation of the PH proton and the elimination of hydrogen chloride could be avoided when $CrCl_3(PMe_2Ph)_3$ was employed as starting material for the reactions with **97** and **98** under the formation of PH-functionalized non-chelates **100** and **101**. The authors propose that the change of the chromium(III) reagent was responsible for the prevention of the attack of the metal at the phosphanyl group.[82]

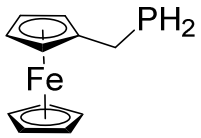


Presumably, **99** was formed in the course of the [2+2]-cycloaddition reaction of **103** which, in its turn, was likely the result of the elimination of hydrogen chloride in **102**.

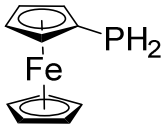


2.4.1 Synthesis of 1,1'-Di[(2-*tert*-butylphosphanyl)ethyl]ferrocene (114)

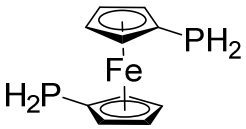
In search for stable compounds, which could confirm the successful nucleophilic opening of the spirocyclopropyl ring of spiro[2.4]hepta-4,6-diene (**64**), the preparation of PH-functionalized ferrocene derivatives was envisaged. The air-stable primary phosphane functionalized ferrocene compound **104** was originally prepared by Henderson et al.[83] Taking into account that such primary phosphine substituted ferrocene compounds as **105**[84] and **106**[85], where the phosphino moiety is directly bound to the cyclopentadienyl ring, are oxidized in air within 3-5 days, the presence of the alkyl spacer in **104** must play a significant role in terms of air stability in the ferrocenyl-phosphine system.[86]



104

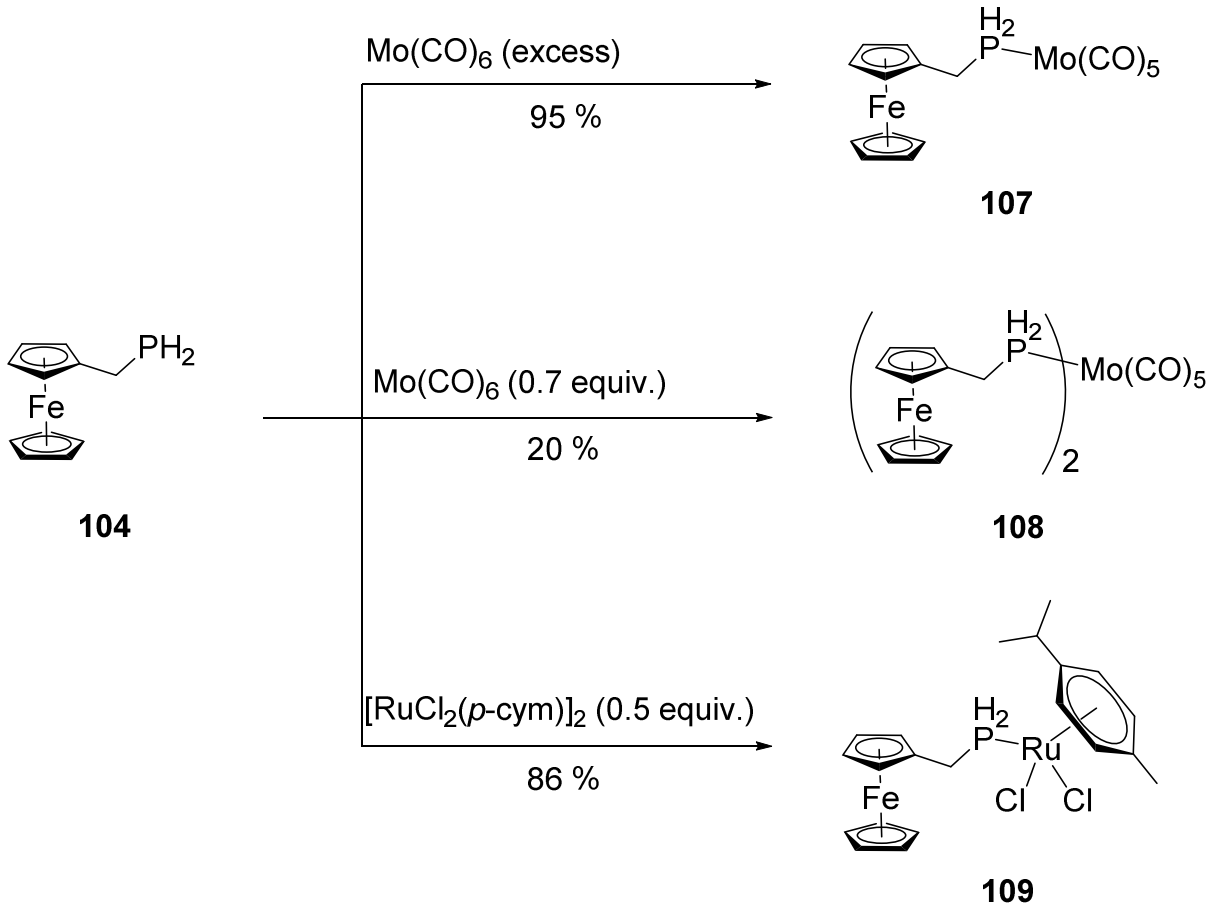


105



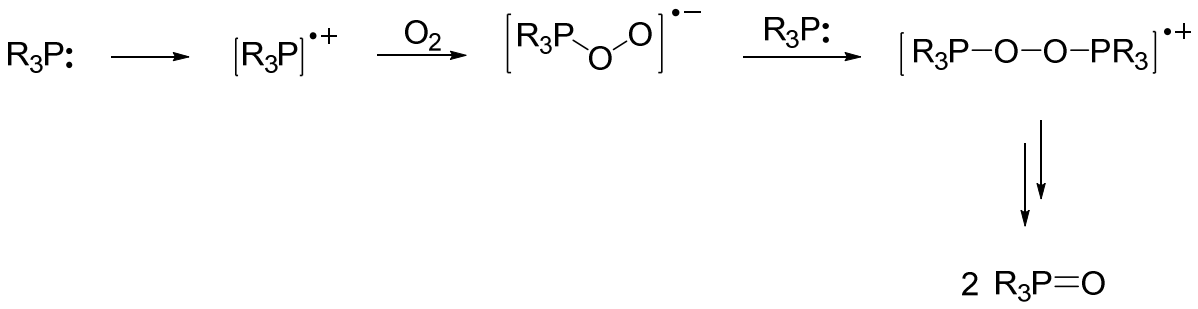
106

Some molybdenum and ruthenium complexes such as **107**, **108** and **109**, respectively, were prepared, in order to show that **104**, despite its air-stability, still displays normal coordinative behavior.[83]



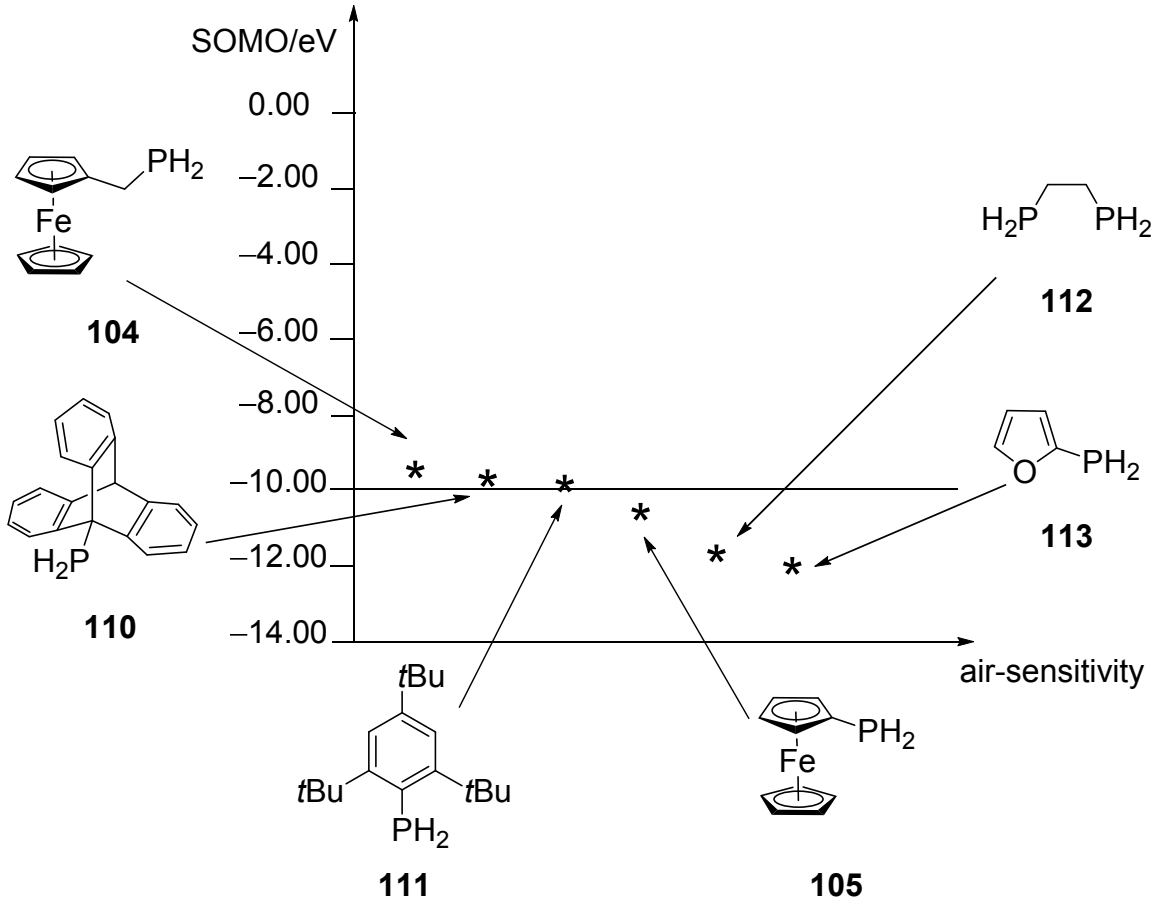
The air-stability of **104** cannot be explained by the steric hindrance; the electronic nature of the primary phosphine could be the protecting factor. It was recently established that the formation of the corresponding radical cation of a phosphine by photolysis led to its oxidation via a radical mechanism (Scheme 5). The formed phos-

phine radical cation reacts with oxygen to generate the peroxy radical anion. The repeated oxidation of the phosphine generates the peroxy radical cation that leads to the phosphine oxide.[87]



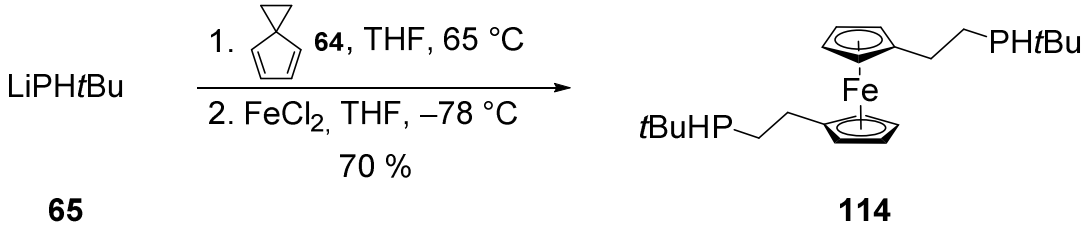
Scheme 5. Postulated steps in the photolytic oxidation of phosphines.[87,88]

Harriman, Higham et al. carried out a series of DFT calculations, which form the basis of a model capable of predicting the air-stability of phosphines. According to this model, the radical cation SOMO (Single Occupied Molecular Orbital) energy for a phosphine is the key to its air-stability/sensitivity.[88] The radical cations of the air-stable phosphines have a higher energy SOMO than their air-sensitive counterparts, with a calculated threshold value of –10 eV. This means that a radical cation generated from a stabilized SOMO has sufficient reactivity to react with oxygen. This model would explain the air-stability of primary phosphines such as **104**, **110** and **111** as well as the air-sensitivity of **105**, **112** and **113** (Scheme 6).[88]



Scheme 6. Plot of the radical cation SOMO energies for the primary phosphines **104**, **105** and **110**-**113**.[88] The air-sensitivity correlates with the estimated reaction rate of the phosphines with oxygen.

In this work, the anionic ligand system obtained *in situ* from **65** and **64** was treated with anhydrous iron(II) chloride, giving the ferrocene derivative **114** in 70 % yield as a yellow solid, which is stable in air at least for several weeks.

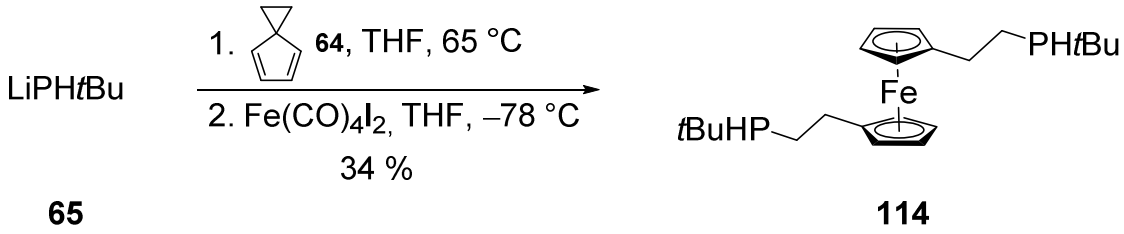


65 **114**

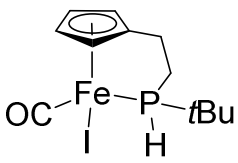
According to the DFT calculations[89] [RB3LYP, 6-31G(D)] the SOMO energy for the radical cation **114** lies at an energy of –8.8 eV. This is in accord with the air-stability of **114**.

Remarkably, the NMR spectra (^{1}H, ^{13}C, ^{31}P) show only one set of signals, although the compound bears two stereogenic phosphorus atoms. In the proton coupled ^{31}P NMR spectrum only one doublet of multiplets at δ = –23.6 ppm with the P–H coupling constant of 199.2 Hz is observed. In the ^{1}H NMR spectrum two multiplets each for the CH_2-group next to the phosphorus atom at δ = 1.50-1.61 and δ = 1.92-2.03 ppm as well as for the CH_2-group next to the cyclopentadienyl moiety at δ = 2.36-2.46 and δ = 2.51-2.61 ppm were observed, indicating the diastereotopic nature of the hydrogen atoms in the tether. In the IR spectrum a sharp P–H band at 2262 cm^{-1} was observed. Given that there is no clear reason to expect exclusive stereospecific formation of either the *R,R/S,S* or the *R,S/S,R* (*meso*) diastereomer, the reason for this phenomenon could be the remote position of the stereogenic phosphorus atoms rendering the hydrogen, carbon and phosphorus atoms in **114** not sufficiently different for resolution by NMR spectroscopy.

The analogous reaction with $Fe(CO)_4I_2$[90] instead of $FeCl_2$ delivered again complex **114**, though in lower yields. The desired chelate **115** was not observed.



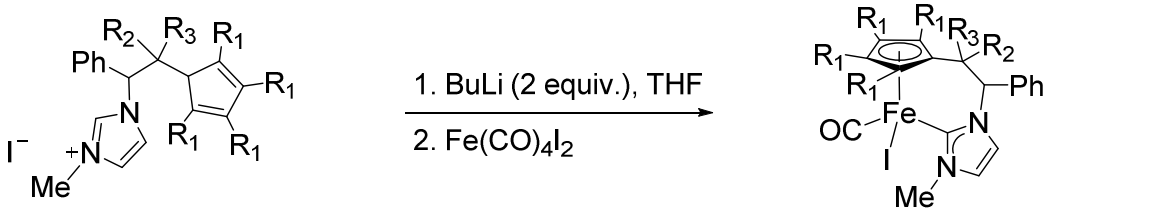
65 **114**



115

not formed

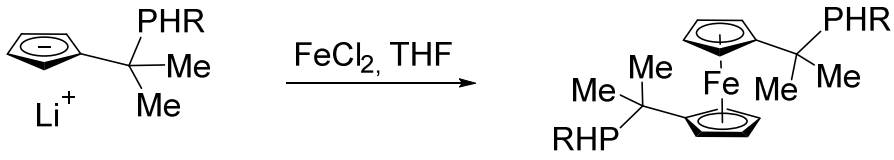
$Fe(CO)_4I_2$ had previously successfully been applied in the synthesis of cyclopentadienyl iron(II) complexes **118** and **119** with a chelating N-heterocyclic carbene ligands *via* double deprotonation of the cyclopentadienyl functionalized imidazolium salts **116** and **117**.[91] The authors observed only one diastereomer in both cases, although, due to the presence of the asymmetric iron atom and the mono-phenyl substituted carbon atom in the spacer, the formation of two diastereomers in each case is possible.



116: R_1 = Me, R_2 = R_3 = H
117: R_1 = H, R_2 = R_3 = Ph

117: R_1 = Me, R_2 = R_3 = H, 77 %
119: R_1 = H, R_2 = R_3 = Ph, 36 %

Hey-Hawkins et al. earlier prepared similar 1,1'-disubstituted ferrocenes **121** and **122**, which were obtained by the reactions of lithium reagents **97** and **120** with anhydrous iron(II) chloride. The authors report the NMR evidence for the formation of one diastereomer for **121**, whereas in case of **122** with bulky mesityl groups the formation of both possible diastereomers was observed. Compounds **121** and **122** are reported to be air-stable at least for several days.[92]

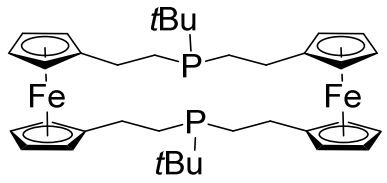


97: R = Ph
120: R = Mes

121: R = Ph, 59 %
122: R = Mes, 55 %

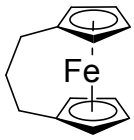
2.4.2.1 Synthesis of 1,16-Di-*tert*-butyl-1,16-diphospha[5.5]ferrocenophane (123)

Further derivatizations of the ferrocene compound **114** might be possible due to the presence of the reactive P–H bond. In this work, the synthesis of the phosphorus-bridged [5.5]ferrocenophane **123** was intended, since such heteroatom-bridged ferrocenophanes are rear and known only for the arsenic- and tin-bridged related compounds **129**,[93] **132**-**133**,[94,95] respectively (*vide infra*).



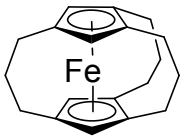
123

Ferrocenophanes belong to the class of metallocenophanes in which the metallocenes units are joined intramolecularly by an atomic or a molecular bridge.[96] The nomenclature of ferrocenophanes is derived from the system proposed by Smith et al.[97] and Vögtle et al.[98] for naming bridged organic aromatic cyclophanes and metallocenophanes. The ferrocenophanes (FCPs) are designated [m][n][o][p]FCP and [m.n.o.p]FCP, where the numbers in square brackets denote the length of the bridges. The first class describes such derivatives in which one ferrocene nucleus is connected by one or more bridges between the cyclopentadienyl rings (compounds **124** and **125**). The second class consists of compounds where two or more ferrocene nuclei are connected by one or more bridges (complex **126**).



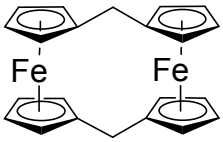
124

[3]ferrocenophane



125

[3][3][3]ferrocenophane

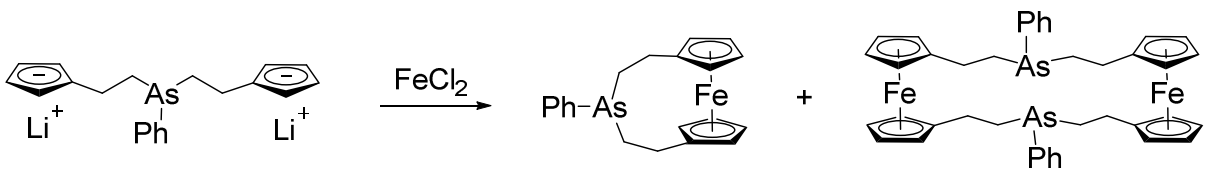


126

[1.1]ferrocenophane

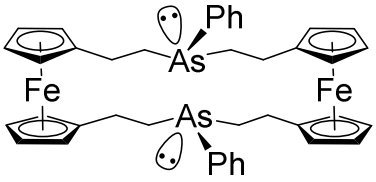
Multinuclear [m.n.o.p…]ferrocenophanes have received considerable attention due to the potential interactions between the metal centers, which might give rise to unique physical and chemical phenomena. Even though the metal atoms in these systems do not exhibit direct bond characteristics, electronic communication between the metals is possible via through-bond and/or through-space processes. The nature of the connecting bridges would also have influence on the properties of metallocenophanes.[99] Multinuclear [m.n]ferrocenophanes with heteroatomic bridges were for the most part reported for [1.1]ferrocenophanes containing group 12 (Hg),[100] 13 (B, Ga, In),[101-103] 14 (Si, Sn)[104-106] or 15 (P, As)[107,108] elements.

Kauffmann et al. reported [5.5]ferrocenophane **129** with arsenic bridges obtained as a side product in 2 % yield along with the major product [5]ferrocenophane **128** from the dilithiated arsen-bridged cyclopentadienyl derivative **127** by the reaction with anhydrous iron(II) chloride. In the ^{1}H NMR spectrum of **128** multiplets for either the ethylene bridges (δ = 1.85-2.30 ppm) and for the cyclopentadienyl protons (δ = 4.00-4.20 ppm) were observed. Similar results were obtained for **129**, except that in the ^{1}H NMR spectrum two multiplets each for two CH_2-groups of the ethylene bridges with δ = 1.85-2.30 ppm for the CH_2-group next to the arsenic atom and with δ = 1.85-2.30 ppm for the CH_2-group directly bound to the cyclopentadienyl moiety were observed.[93]

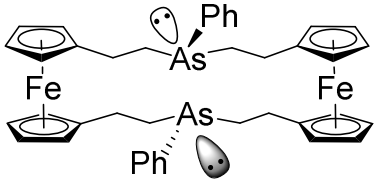


127 **128**, 78 % **129**, 2 %

The authors did not comment further on the spectroscopic and structural analysis of **129**, although, due to the presence of two asymmetric arsenic atoms in the compound, the formation of two isomers **129a** and **129b** with *cis*- and *trans*-configuration of the phenyl groups, respectively, is possible.

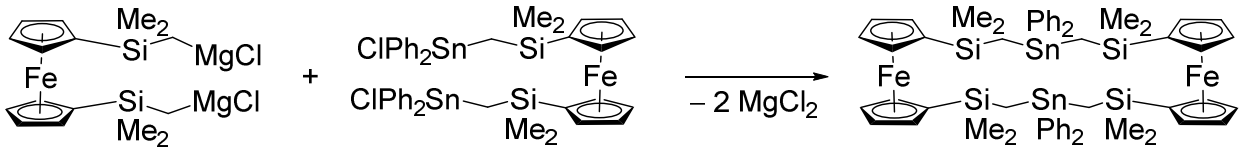


129a

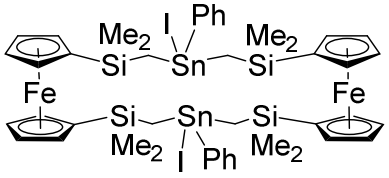


129b

Jurkschat et al. reported the synthesis of the silicon- and tin-containing ferrocenophane **132** by the reaction of the di-Grignard compound **130** with the organotin chloride **131**. Further reaction of **132** with iodine delivered **133** as a mixture of two isomers. The ^{119}Sn NMR spectrum shows two signals at δ = –13.1 and –13.4 ppm, whereas in the ^{29}Si NMR spectrum only one resonance is observed. However, the crystal structure analysis showed only the formation of the *trans*-isomer of **133**.[95]

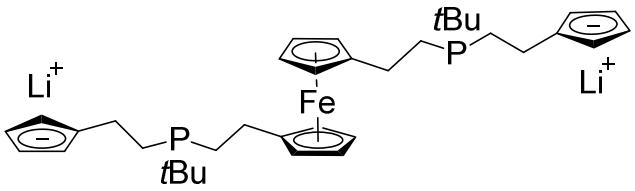


130 **131** **132**, 80 %

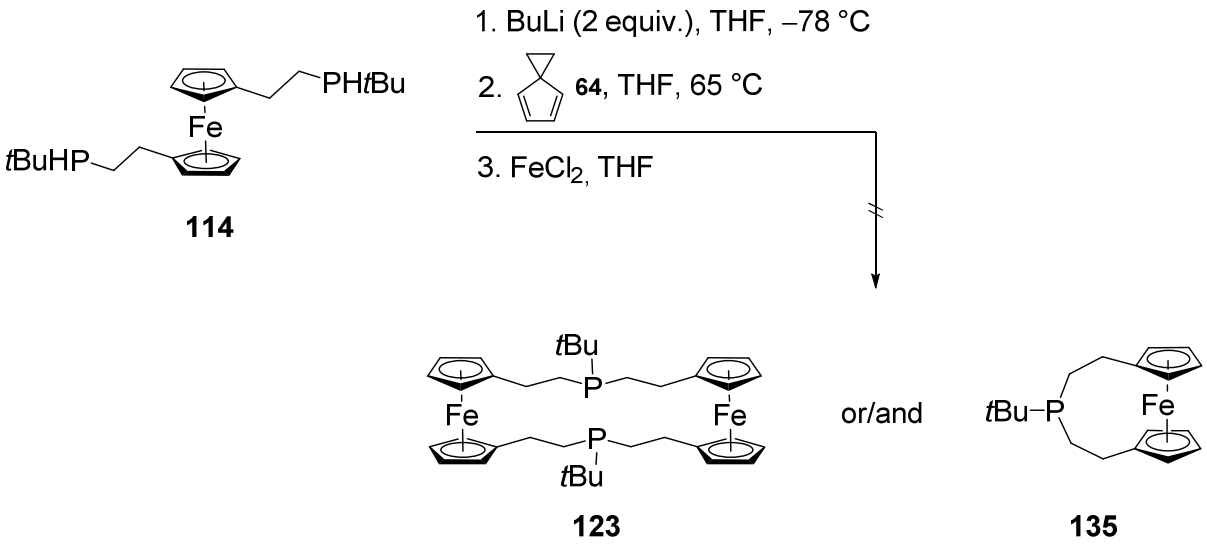


133, 99 %

Similar to the route of Kauffmann et al., the synthesis of **123** was attempted by the sequence of the double lithiation of the ferrocene **114**, treatment with **64** and the complexation reaction of the intermediate **134** with anhydrous iron(II) chloride. The analysis of the crude reaction mixture did not give any hint on the formation of the desired complex **123** as well as the possible [5]phosphaferrocenophane **135**. The low solubility of the crude reaction mixture in polar solvents indicates the polymeric nature of the formed products.

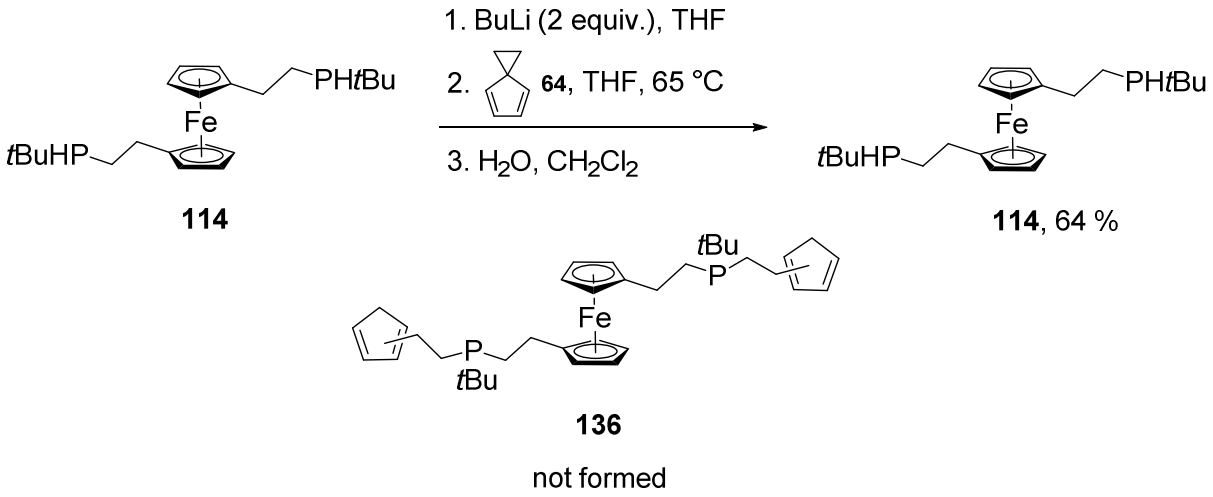


134

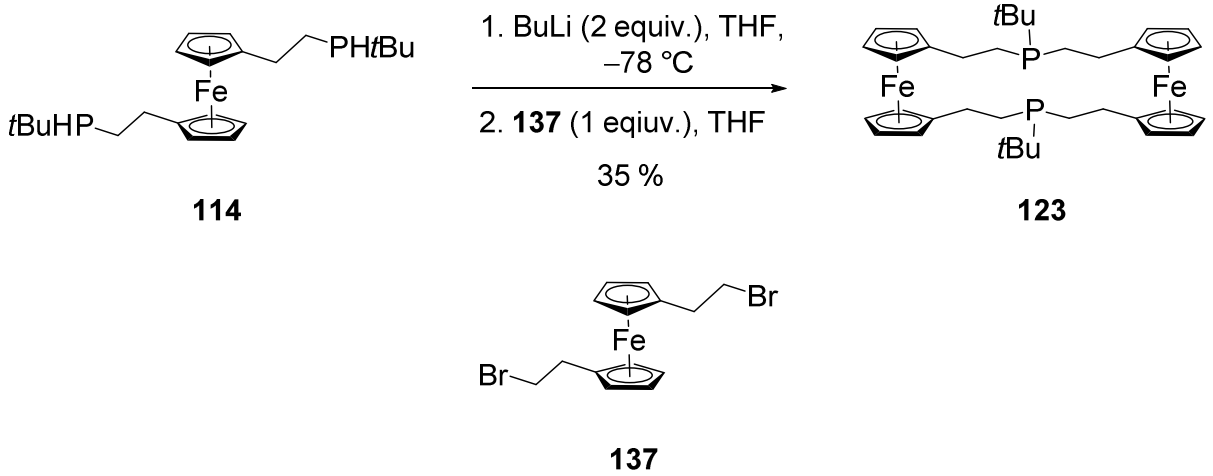


114 **123** **135**

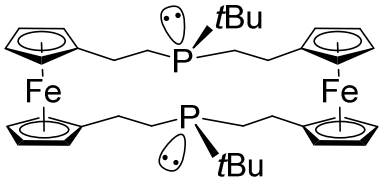
The analogous reaction of **114** with the aqueous quench instead of the complexation step did not deliver the expected compound **136** indicating that the nucleophilic ring opening reaction of **64** did not take place, presumably, due to the steric bulk of the phosphane group in **114**. Ferrocene **114** could be recovered in 64 % yield.



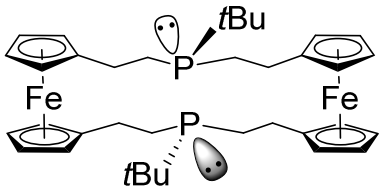
Next, the method of Jurkschat et al. was envisaged which implies the reaction of two ferrocene derivatives each with nucleophilic and electrophilic functions, respectively. **114** was first double lithiated and then treated with 1,1'-di-(2-bromoethyl)ferrocene[109] (**137**) delivering the desired complex **123** in 35 % yield.



In the ^{1}H, ^{13}C and ^{31}P NMR spectra of **123** two isomers in a 1.1 to 1 ratio (^{31}P NMR analysis) were observed, which can most likely be represented as *cis*- and *trans*-isomers **123a** and **123b**, respectively. In the ^{31}P NMR spectrum the major isomer appears at δ = 0.8 ppm, the signal at δ = 0.9 ppm refers to the minor isomer.



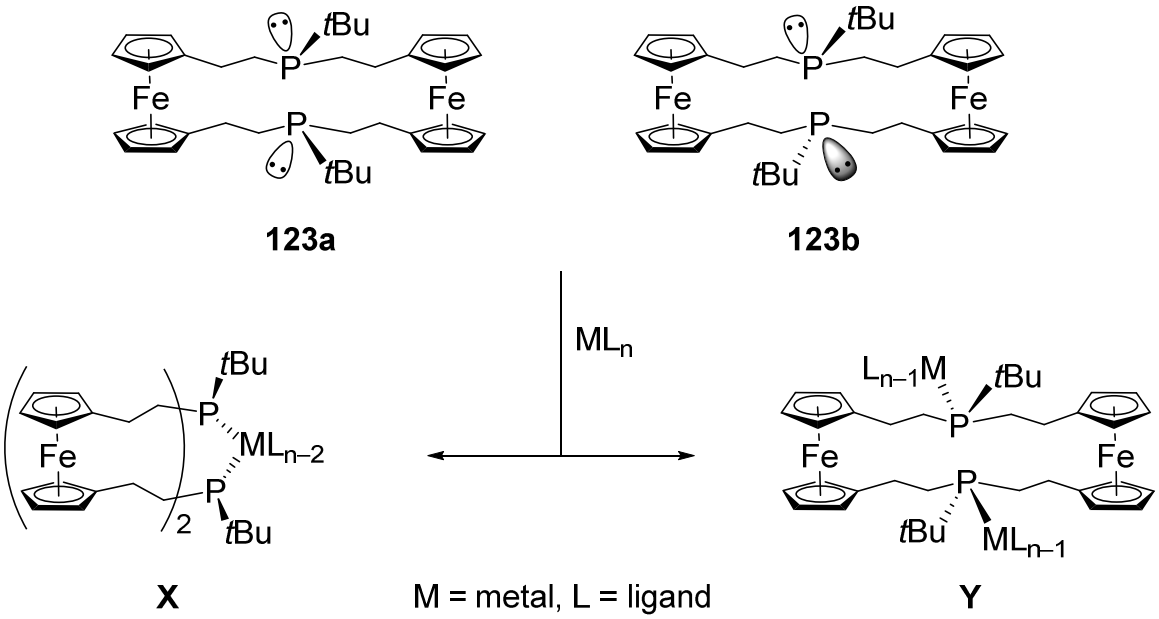
123a



123b

Recrystallization of **123** from CH_2Cl_2/ethyl acetate (2 to 1 ratio) allowed a nearly full separation of **123a** and **123b**, with the minor isomer remaining in the mother liquor. According to the ^1H und ^{13}C NMR spectra, both isomers were featured by the diastereotopic hydrogen and carbon atoms in the ethylene bridges and in the cyclopentadienyl moieties. The ^1H NMR spectra of both isomers display the same shift for the *tert*-butyl group at δ = 0.97 ppm with a coupling constant of 11.4 Hz. The signals for the CH_2-groups of the ethylene bridges as well as for the cyclopentadienyl protons of both isomers appear as multiplets. The differences between the isomers become apparent in the ^{13}C NMR spectra: while both isomers exhibit each five signals for the cyclopentadienyl groups and a doublet for the CH_3-group of the *tert*-butyl moiety, a number of signals for the CH_2-groups as well as for the quaternary carbon atoms of the *tert*-butyl groups is different for each isomer. The major isomer is characterized by four distinct singlets for the CH_2-groups as well as one singlet assigned to the quaternary carbon atom of the *tert*-butyl group. In the ^{13}C NMR spectrum of the minor isomer two doublets for the CH_2-groups ($^1J_{P,C}$ = 2.5 Hz, $^2J_{P,C}$ = 5.2 Hz) and a doublet for the quaternary carbon atom with a coupling constant of 9.3 Hz were observed.

Considering the results reported by Jurkschat et al. for the selective crystallization of the *trans*-isomer **133** as the more thermodynamically stable product and the spectroscopic results for **123** in this work, the major isomer corresponds likely to the trans-isomer **123b**. Further distinction between the isomers might be achieved through the complexation reactions with appropriate metal reagents. The *cis*-isomer **123a** should form the chelate complex **X** by the reaction with the metal reagent, whereas the *trans*-isomer **123b** would probably react twice to form the doubly substituted complex **Y**.

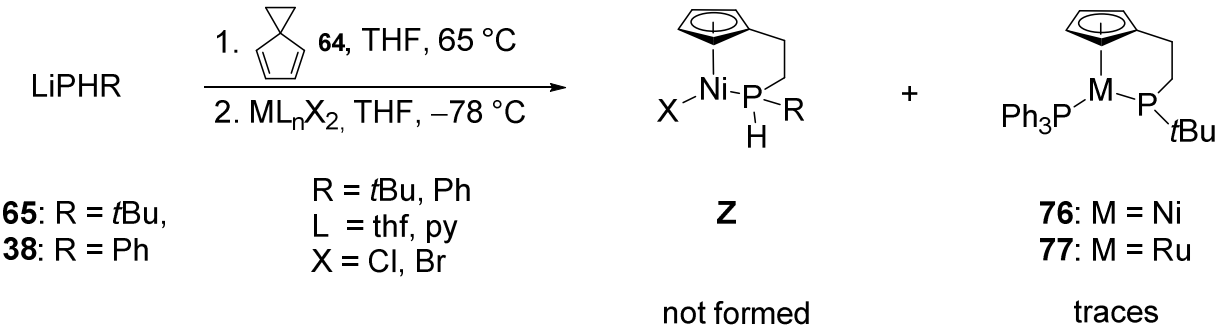


2.4.3 Attempted Syntheses of Cyclopentadienyl Complexes of Late Transition Metals with a *tert*-Butylphosphane or a Phenylphosphane Substituted Chelating Sidechain

Under analogous reaction conditions applied for the synthesis of **114**, the anionic ligand system obtained *in situ* from lithium phosphides **65** and **138**[110] and spiro[2.4]-hepta-4,6-diene (**64**) was treated with a diversity of nickel(II) and ruthenium(II) halide complexes. When $NiCl_2(thf)_2$, $NiBr_2(thf)_2$[111] or $NiCl_2(py)_2$ were employed, the desired PH-functionalized chelates were not observed even in traces. Instead, only oily brownish decomposition products were obtained, which could not be identified by the spectrometric and spectroscopic analyses.

The ESI-HRMS spectrometry analysis of the reaction mixtures from the corresponding reactions with $NiCl_2(PPh_3)_2$ and $RuCl_2(PPh_3)_3$ indicated masses for $[M+H]^+$ for the phosphide complexes **76** and **77**, showing that the secondary phosphane substituted complexes have likely been formed but decomposed, presumably, due to the activation of the PH proton and the elimination of hydrogen halide. A similar explanation was suggested by Hey-Hawkins et al. in the syntheses of the related chromium(III)

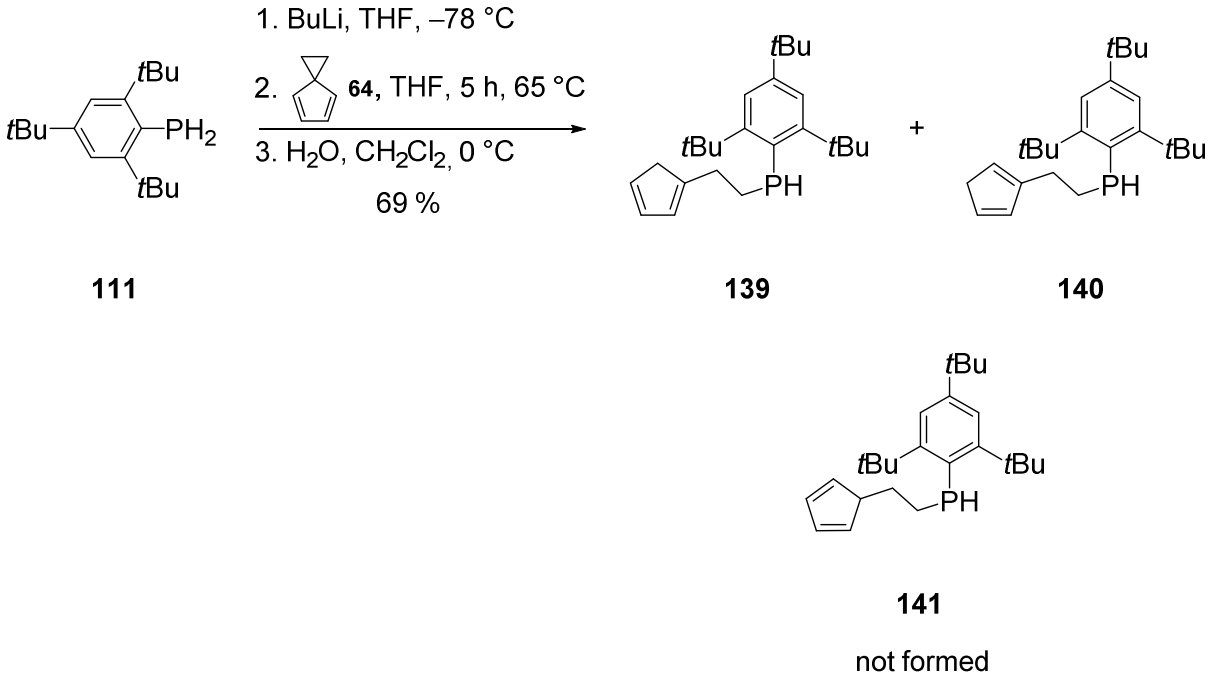
complexes.[82] The employment of bulkier substituents at phosphorus was envisaged in order to kinetically stabilize the secondary phosphane substituted chelates.



2.4.4 Synthesis of (2,4,6-Tri-*tert*-butylphenyl)phosphane Functionalized Cyclopentadienes 139 and 140

(2,4,6-Tri-*tert*-butylphenyl)phosphane (**111**)[111] is a particularly bulky primary phosphane with the calculated SOMO energy for the radical cation higher than –10 eV (*vide supra*). The combination of the steric and the electronic effects explain the air-stability of **111**.[88]

Phosphane **111** was deprotonated with butyllithium, treated with **64** in THF and then hydrolyzed, leading to a 1.4:1 mixture (^{31}P NMR analysis) of isomeric secondary phosphanes **139** and **140** as colorless solids, respectively, in 69 % yield. However, the nucleophilic ring opening reaction in **64** by **111** required nearly five hours to be completed (visual from the discoloration of the reaction mixture) as compared to the corresponding reaction of lithium *tert*-butylphosphide (**65**) (one hour). The separation and the assignment of the major and minor isomers could not be achieved. The cyclopentadienyl derivatives **139** and **140**, being stable in air for an indefinite time, were stored at –30 °C in order to prevent the dimerization to dicyclopentadienes.



111 **139** **140**

141

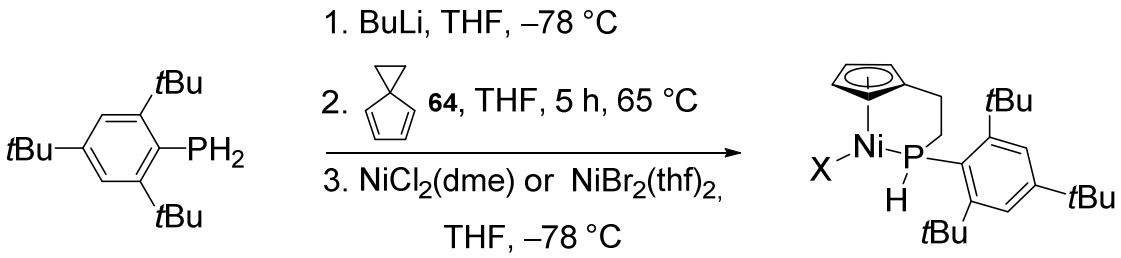
not formed

Similar to the results obtained for the thermodynamically stable isomers **66** and **67**, only two (**139** and **140**) of three possible regioisomers (**139**, **140** and **141**) were observed.

In the proton coupled ^{31}P NMR spectrum two doublets were observed at δ = –72.4 (major isomer, $^{1}J_{P,H}$ = 221.0 Hz) and δ = –72.6 (minor isomer, $^{1}J_{P,H}$ = 221.5 Hz) ppm. Similar to **66** and **67** (vide supra), the chemical shifts in the ^{1}H NMR spectrum of **139** and **140** are nearly the same for all hydrogen atoms except for the methylidene protons (2.83 ppm for $CpCH_2$ for the major isomer and 2.92 ppm for $CpCH_2$ for the minor isomer) as well as for the protons of the cyclopentadiene moiety which appear as multiplets. In the ^{1}H NMR spectrum two multiplets for the CH_2-group next to phosphorus at δ = 1.51-1.64 and δ = 1.78-1.96 ppm were observed, the CH_2-group next to the cyclopentadienyl moiety exhibits two multiplets at δ = 2.28-2.42 and δ = 2.45-2.59 ppm, indicating the diastereotopic nature of the hydrogen atoms. The P–H vibration was observed in the IR spectrum as a sharp absorption band at 2388 cm^{-1}.

2.4.5 Synthesis of Cyclopentadienyl Nickel Complexes 142 and 143 with 2,4,6-Tri-*tert*-butylphenylphosphane Functionalized Chelating Tether

Having showing that the steric bulk does not prevent the lithiated phosphine **111** from the opening of the cyclopropyl ring in **64**, the new bidentate ligand system was to be coordinated as a chelate to nickel. The aqueous work up in the synthesis of **139** and **140** was replaced by the addition of the reaction mixture to suspensions of $NiCl_2$(dme) or $NiBr_2(thf)_2$ in THF leading to the chelates **142** and **143** in 48 % and 69 % yields, respectively. Crystallization from toluene afforded **142** and **143** as red-purple crystals, which were, however, too small for the crystal structure analysis. If crystalline, **142** and **143** can be handled in air at least for two hours, but they decompose within several minutes in solutions under aerobic conditions. The complexes could not be purified by column chromotography based on silica gel or aluminium oxide, as they decomposed immediately. **142** and **143** show good solubility in polar solvents being insoluble in nonpolar media.



111

142: X = Cl, 48 %
143: X = Br, 69 %

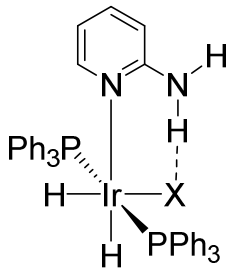
The obtained chelates were fully characterized. Both complexes are featured by the diastereotopic hydrogen and carbon atoms in the ethylene bridges, in the cyclopentadienyl groups as well as in the aryl moieties. In the ^{1}H NMR spectra two multiplets for the CH_2-group next to phosphorus for either complex (δ = 2.11-2.14 and δ = 2.39-2.50 ppm for **142** and δ = 2.19 and δ = 2.41-2.49 ppm for **143**) were observed. The signals for the CH_2-groups next to the cyclopentadienyl moiety are shifted to higher

fields in both cases (multiplets at δ = 1.27-1.32 ppm for **142** and δ = 1.27-1.37 ppm for **143**) in comparison to the ligand systems **139** and **140**. Each of the proton coupled ^{31}P NMR spectra show a doublet of multiplets at δ = 0.8 ppm ($^{1}J_{P,H}$ = 343.8 Hz) for **142** and at δ = –5.7 ppm ($^{1}J_{P,H}$ = 349.9 Hz) for **143**, demonstrating the shifts to lower field compared with **139** or **140** (δ = –72.4 ppm, $^{1}J_{P,H}$ = 221.0 Hz). Further confirmation of the coordination of the secondary phosphine functionalized tether to nickel is the difference between the coupling constants for the P–H bonds of the coordinated and not coordinated phosphanes being more than 120 Hz. It is known, that the values for the coupling constants of the phosphorus-hydrogen bonds increase with the decreasing electron density on phosphorus.[112] This is achieved here by the incorporation of the lone pair of the phosphorus atom into the coordination to the metal. For example, PH_3 has a $^{1}J_{P,H}$ coupling constant of 189 Hz, whereas in its complexes $[Cr(CO)_4(PBu_3)(PH_3)]$ and Me_3BPH_3 the values of 307 and 366 Hz, respectively, were observed.[112]

In the IR spectra of **142** and **143** each a P–H vibration was observed as a weak broad absorption band at 2348 and 2357 cm^{-1}, respectively, whereas the P–H vibration of **139** as well as of **140** appears as a sharp middle absorption band at 2388 cm^{-1}.

Remarkably, the difference in the melting points between **142** (174-175 °C) and **143** (104-105 °C) is 70 °C. A possible explanation for this phenomenon is the presence of intermolecular halogen-hydrogen interactions, which are stronger in the chloro substituted complex than in the bromo substituted one. Brammer, Orpen et al. reported that halogens bound to transition metals are good hydrogen bonding acceptors.[113,114] The metal-assisted H-bonding[115] phenomenon is based on the strongly polarized character of the metal-halogen bond resulting in an enhanced partial negative charge of the halogen. The strength of M–X···H–D interaction [M = transition metal, X = halogen, D = donor (O, N, C)] decreases in the order M–F > M–Cl > M–Br > M–I for the acceptors and O–H > N–H > C–H for the donors.[116] Crabtree, Eisenstein et al. determined hydrogen strength bonds in Ir–X···H–N **144** by the combination of NMR methods and *ab initio* calculations, observing analogous trends reported by Brammer, Orpen et al. (*vide supra*) The greatest value of 5.2 kcal/mol was obtained for the

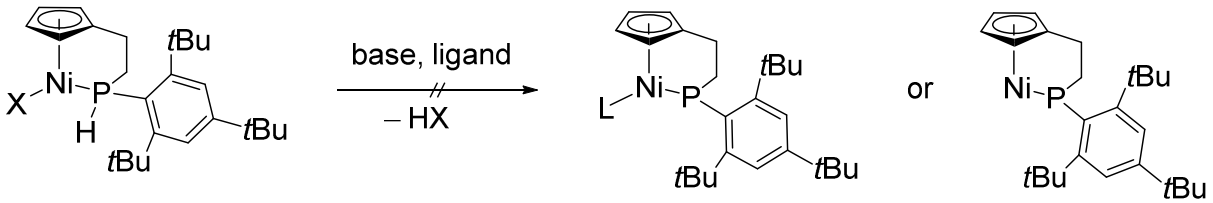
fluoride substituent, for the chloride, bromide and iodide substituents the values of 9, 8 and 5 kJ/mol were calculated, respectively.[117]



144

2.4.6 Reactions of Chelates 142 and 143 with *N*-Heterocyclic Carbenes

The chelates **142** and **143** were subjected to the deprotonation reactions with DBU, butyl lithium and methyl lithium in the presence of a variety of ligands under different reaction conditions. The desired complex **145** or its coordinatively unsaturated version **146** were not observed according to the spectrometric analyses, even when the ligands were used in great excess. In each case, brownish solids hardly soluble in any solvent were obtained.



142: X = Cl
143: X = Br

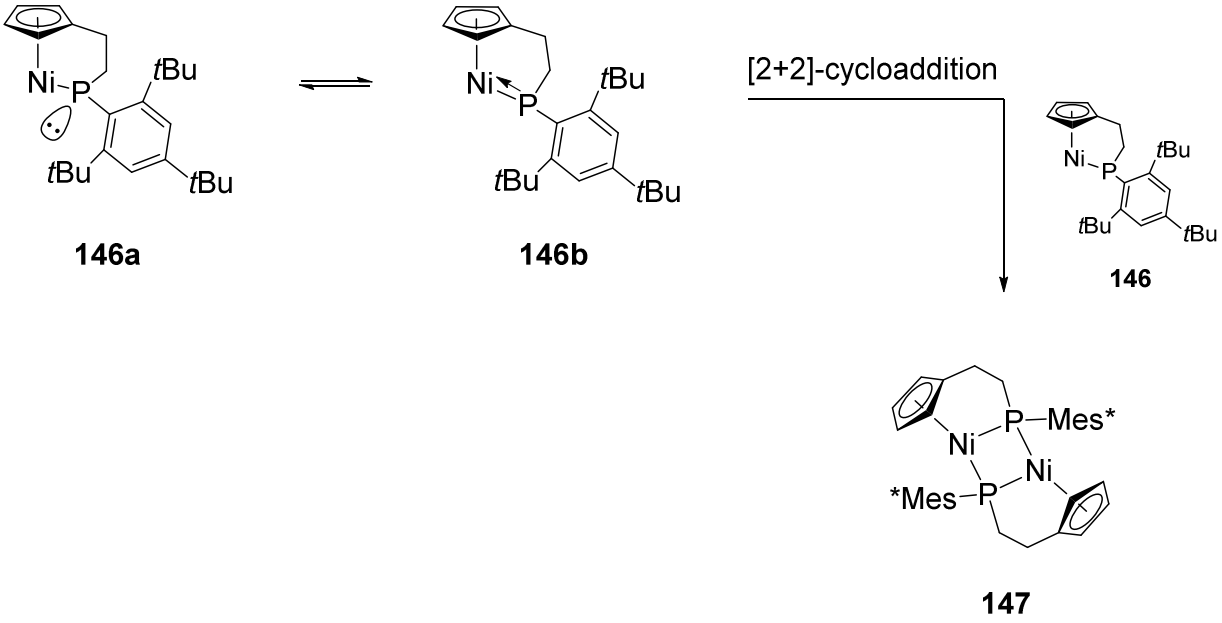
145 **146**

base: DBU, BuLi, MeLi
ligand: THF, acetonitrile, pyridine, PPh_3, 4-isocyanobenzonitrile

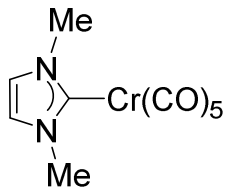
Compound **146** could also react with itself in a [2+2]-cycloaddition delivering the bimetallic phosphido bridged complex **147**, similar to that proposed for the formation of

99 (*vide supra*). The spectrometric analysis of the crude reaction mixture did not give any hint on the formation of **147**.

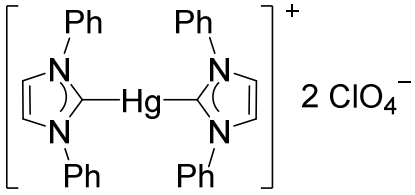
A possible explanation for the failed reactions is that the phosphido species **146** was likely formed in the course of the deprotonation reaction and the dissociation of a halide but did not react with the ligands, following other reaction paths. Based on these results, the syntheses of the secondary phosphane chelates with N-heterocyclic carbenes (NHCs) were envisaged, which are to be converted into the corresponding phosphido chelates simply by the deprotonation reactions.



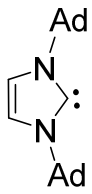
Since the first report of the chromium(0) NHC complex **148** by Öfele et al.[118] and the mercury(II) complex **149** by Schönherr et al.,[119] N-heterocyclic carbenes have gained enormous popularity in organometallic chemistry.[120] In 1991, the isolation of the first stable 1,3-di-1-adamantylimidazol-2-ylidene (**150**) was reported by Arduengo et al.[121]



148

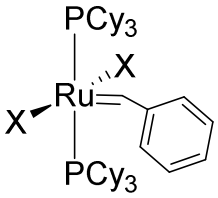


149

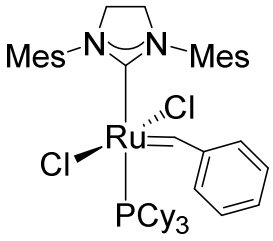


150

Grubbs et al. introduced the ruthenium metathesis catalyst **152** (Grubbs 2nd generation catalyst), which was obtained through the replacement of the tricyclohexyl phosphine group in **151a**-**c** (Grubbs 1st generation catalyst) the by the NHC carbene of the type imidazole-2-ylidene, resulting in the increased catalyst activity and stability.[122]



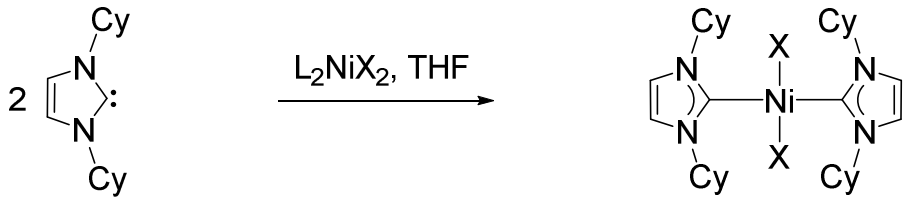
151a: X = Cl,
151b: X = Br,
151c: X = I



152

The excellent *σ*-donating characteristics of NHC carbenes allow them to form strong bonds to metals that prevent ligand dissociation, making them ubiquitous as supporting ligands in transition-metal catalysis.[120,123] For Arduengo carbenes the singlet ground state was calculated to be preferred,[124] mainly, due to the p_π-donation from the nitrogen atoms into the empty p_π-orbital of the carbene carbon atom.[120j]

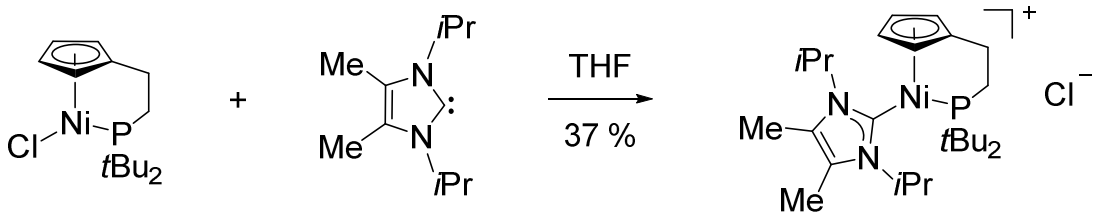
The first NHC carbene functionalized nickel(II) complex **154a-b** was prepared by Herrmann et al. in the ligand exchange reaction of the imidazol-2-ylidene **153** with nickel(II) halide complexes.[125]



153

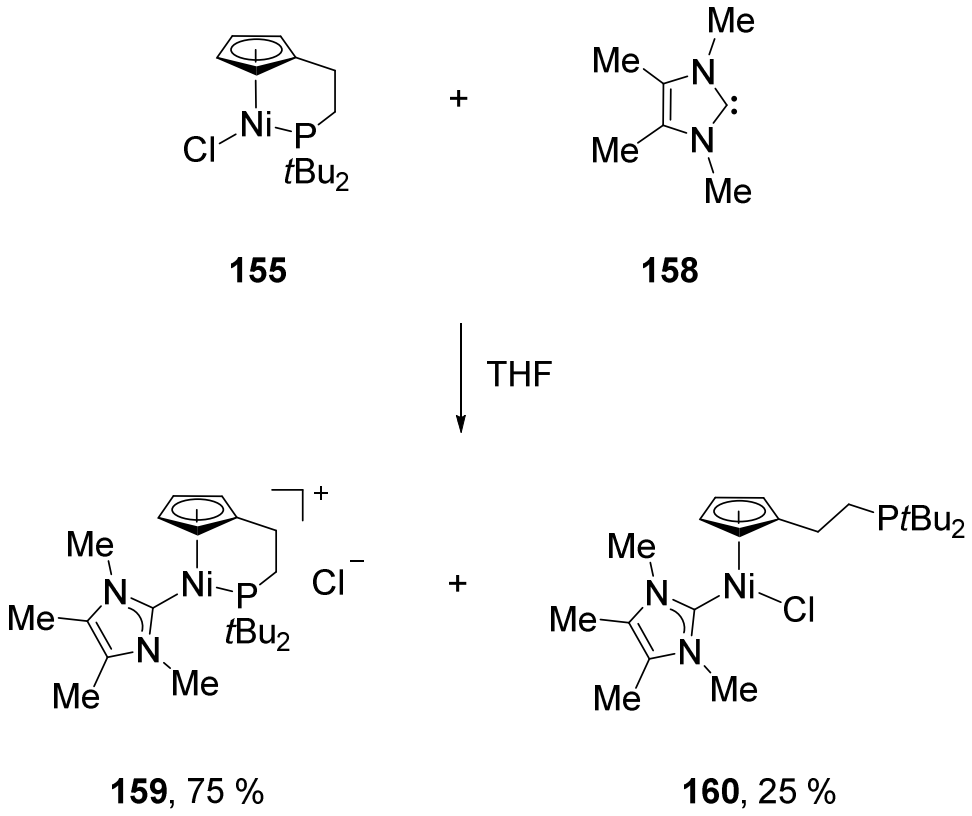
154a: X = Cl, 76 %
154b: X = Br, 87 %

Butenschön et al. reported a series of nickel(II) chelate complexes bearing imidazol-2-ylidene ligands. Complex **155** reacts with 1,3-di-*iso*-propyl-3,4-dimethylimidazol-2-ylidene (**156**) to the cationic nickel(II) complex **157**.[126]



155 **156** **157**

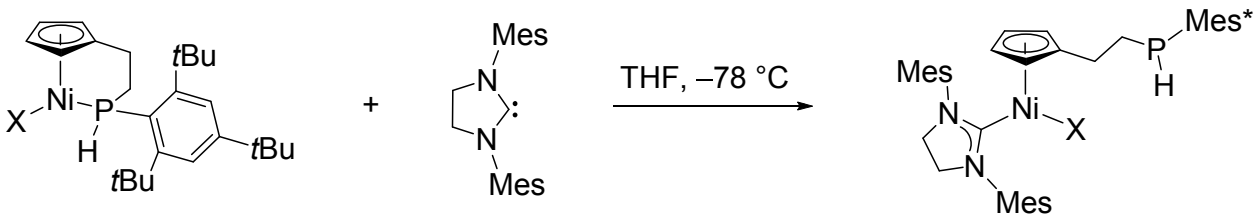
The corresponding reaction of **155** with a less bulky 1,3,4,5-tetramethylimidazol-2-ylidene (**158**) delivered a mixture of the cationic complex **159** and the decoordinated species **160** in a three to one ratio, respectively.[126]



The ^{31}P NMR spectra show the resonances at δ = 95.7 and 100.1 ppm for **157** and **159**, respectively, while the signal at δ = 31.2 ppm for **160** confirms the decoordination of the phosphane moiety. The ^{13}C NMR spectra of **157** and **159** show each a doublet for the carbene carbon atom at δ = 159.2 ($^2J_{P,C}$ = 14.8 Hz) and δ = 159.6 ($^2J_{P,C}$ = 17.0 Hz), respectively, supporting the coordination of the phosphane group to nickel. The formation of **160** indicates that the NHC has better σ-donating properties than the di-*tert*-butylphosphanyl group.

Encouraged by these results, the reactions of **142** and **143** with 1,3-bis-(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene (**161**), abbreviated as SIMes, were envisaged. **161** was isolated and structurally characterized by Arduengo et al. as a free carbene which is thermodynamically stable under inert atmosphere.[127]

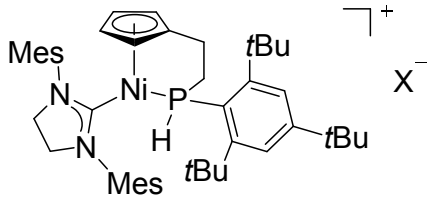
Treatment of **142** and **143** with **161** delivered the complexes quite stable **162** and **163** with the decoordinated tethers in 63 % and 85 % yields, respectively. The formation of the cationic nickel complexes **164** and **165** was not observed.



142: X = Cl
143: X = Br

161

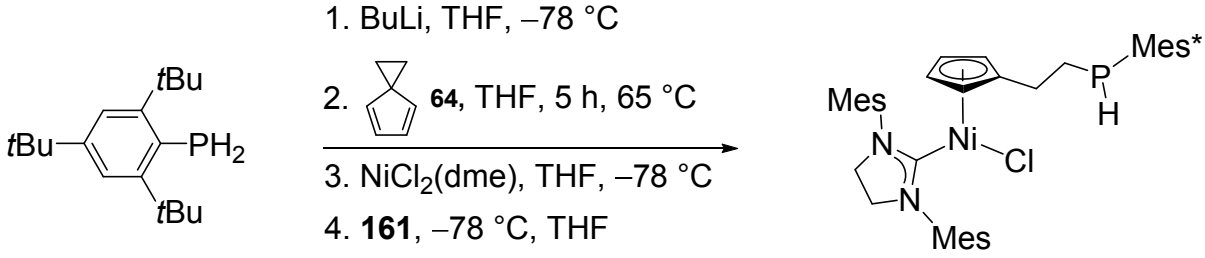
162: X = Cl, 63 %
163: X = Br, 85 %



164: X = Cl
165: X = Br

not formed

Alternatively, **162** was obtained in a one-pot reaction from the phosphane **111** in a sequence of deprotonation, nucleophilic ring opening reaction in **64**, complexation reaction with $NiCl_2$(dme) and, finally, treatment with the carbene **161**, though, in moderate yields.



111

162

The proton coupled ^{31}P NMR spectra of **162** and **163** show each a doublet of multiplets at δ = –73.1 ppm ($^1J_{P,H}$ = 221.7 Hz) for **162** and at δ = –73.0 ppm ($^1J_{P,H}$ = 222.1 Hz) for **163**. These results are consistent with those reported for free ligands **139** and

140. The formation of the non-chelated complexes **162** and **163** can be explained by, otherwise, the overcrowded situation at nickel centers in **164** and **165**. The decoordination of the phosphane tether demonstrates better σ-donation properties of SIMes than those of the phosphane moiety. The ^{13}C NMR spectra of **162** and **163** show each a singlet for the carbene carbon atom at δ = 202.7 and 202.0 ppm, respectively. These are in accord with the results reported for [NiCp(Br)(SIMes)].[128] In the IR spectra of **162** and **163** each a P–H vibration was observed as a weak absorption band at 2405 and 2394 cm^{-1}, respectively. However, the ESI-HRMS spectrometry analysis indicated masses for $[M–X]^+$ (X = Cl for **162**, X = Br for **163**) indicating the lability of the nickel-halide bonds in complexes of this type.

The presence of the chloride atom in **162** was definitely confirmed by the qualitative ICP-MS (Inductively-Coupled-Plasma Mass Spectrometry) measurement. Figure 1 shows signals for ^{13}C-, ^{35}Cl- and ^{64}Ni-isotopes reflected by the slopes of different intensities, being, though, the smallest for ^{35}Cl.

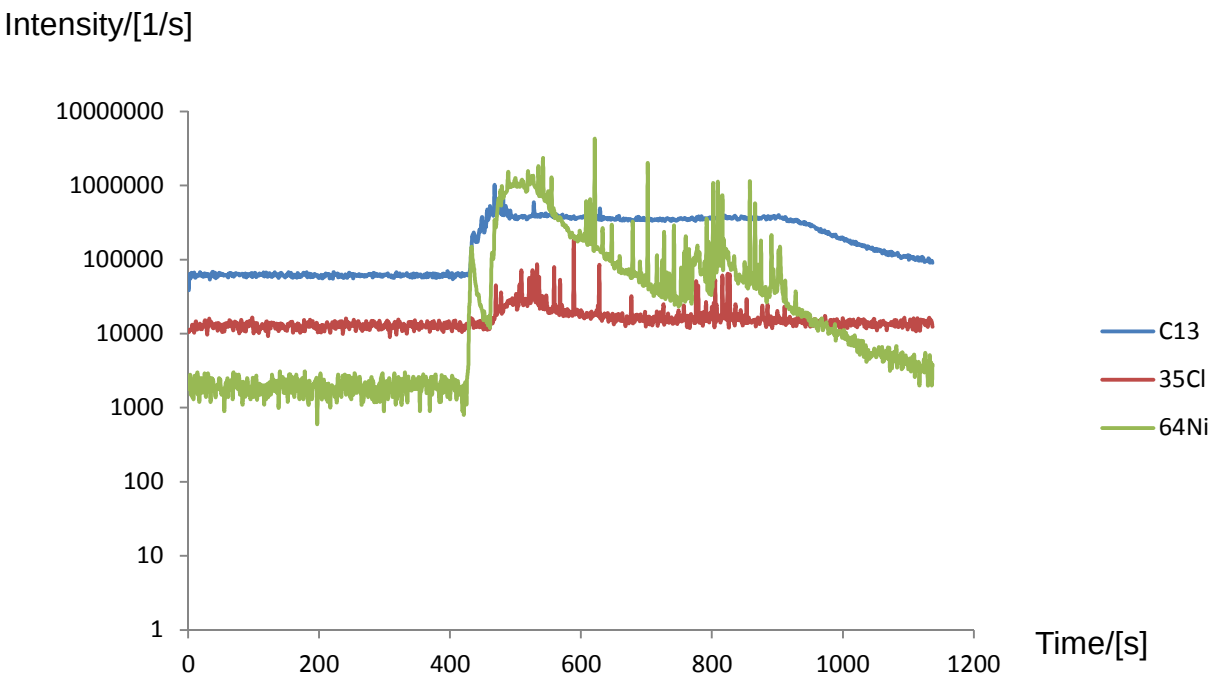
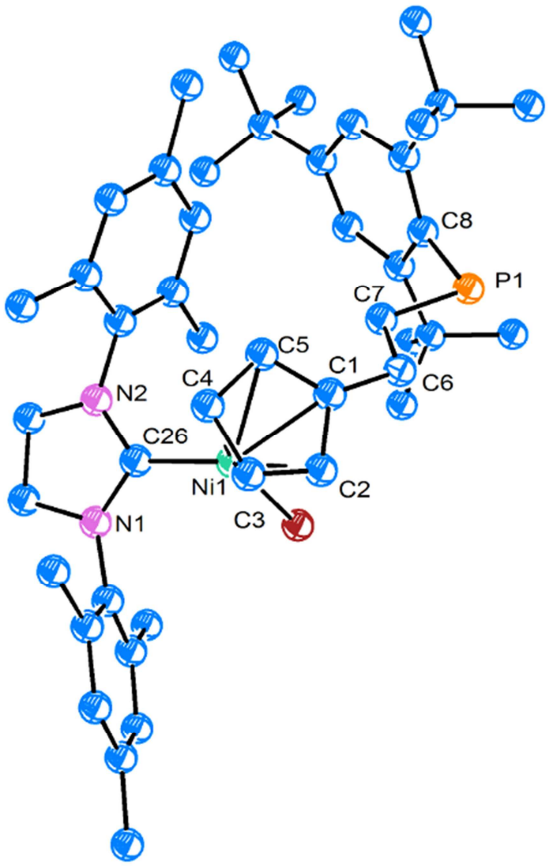
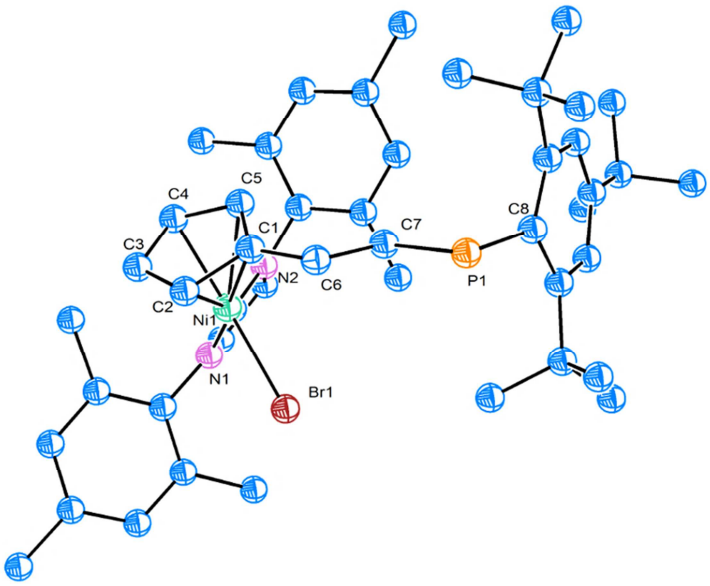


Figure 1. Qualitative ICP-MS analysis of **162**.

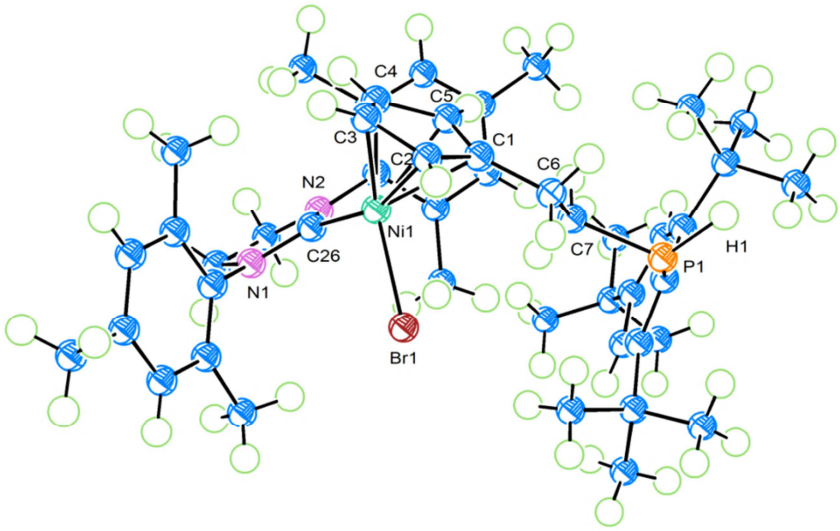
Crystallization of **163** from hexane/ethyl acetate (1:2) at –30 °C afforded red crystals suitable for the X-ray crystal structure analysis. Attempts to the crystallization of **162** from different solvents failed in the scope of this work. Figure 2 represents several aspects of the crystal structure of **163** with the views B-C (hydrogen atoms omitted for clarity) from different sides and with the view A, highlighting the P–H bond. **163** crystallizes in a monoclinic crystal system with the space group $P2_1/c$ (Nr. 14). The phosphorus atom has a distorted pyramidal environment with some angles significantly deviating from the pyramidal angles (C8–P1–C7 98.2°, C8–P1–H1 123°, C7–P1–H1 117°). This distortion is presumably due to a large difference in the steric bulk between the 2,4,6-tri-*tert*-butylphenyl group and the hydrogen atom bound to phosphorus.



View A



View B

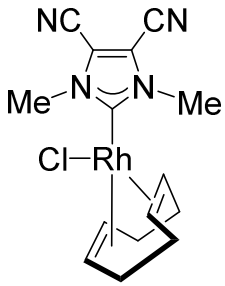


View C

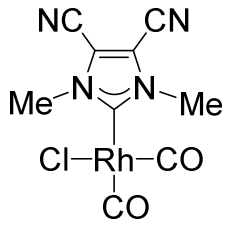
Figure 2. Crystal structure of **163** (views A-C, 50 % probability level). Key atoms are labeled. Selected bonds lengths [ppm] and angles [°]: Ni1–C1 222.4(6), Ni1–C2 214.5(8), Ni1–C3 215.4(9), Ni1–C4 203.9(8), Ni1–C5 219.7(6), Ni1–Br1 230.1(1), Ni1–C26 187.7(7), P1–H1 160(1), P1–C7 186.2(9), P1–C8 186.2(8); Br1–Ni1–C26 98.6(2), N1–C26–N2 98.6(2), Br1–Ni1–C26 126.4(5), C7–P1–H1 117(4), C8–P1–H1 123(4), C7–P1–C8 98.2(4).

Having showed, that **142** and **143** react with NHCs to form stable complexes, the reactions with less bulky NHCs were envisaged.

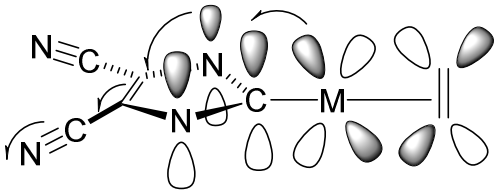
The electronic properties of NHCs can be tuned by the saturation/unsaturation in the backbone.[129] Bielawski et al. have prepared a series of NHC-rhodium(I) complexes in order to investigate the *π*-backbonding effects from the metal center to the NHC moieties bearing electron-withdrawing groups. As an example, the IR spectroscopic analyses of the nitrile substituted complexes **164** and **165** with COD and carbon monoxide ancillary ligands, respectively, were closely investigated. When the COD ligand was replaced by two carbon monoxide groups, which are excellent *π*-acceptor ligands, the corresponding nitrile absorption was shifted to lower energy ($\Delta\tilde{\nu}$ = 4 cm^{-1}), demonstrating that the carbonyl ligands diminish the ability of the rhodium atom to *π*-back-bond to the NHC.[130]

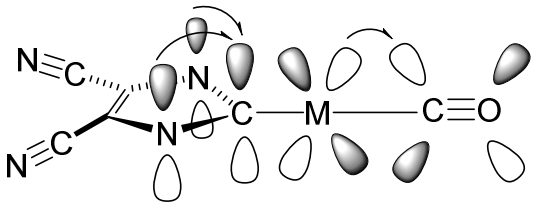


164

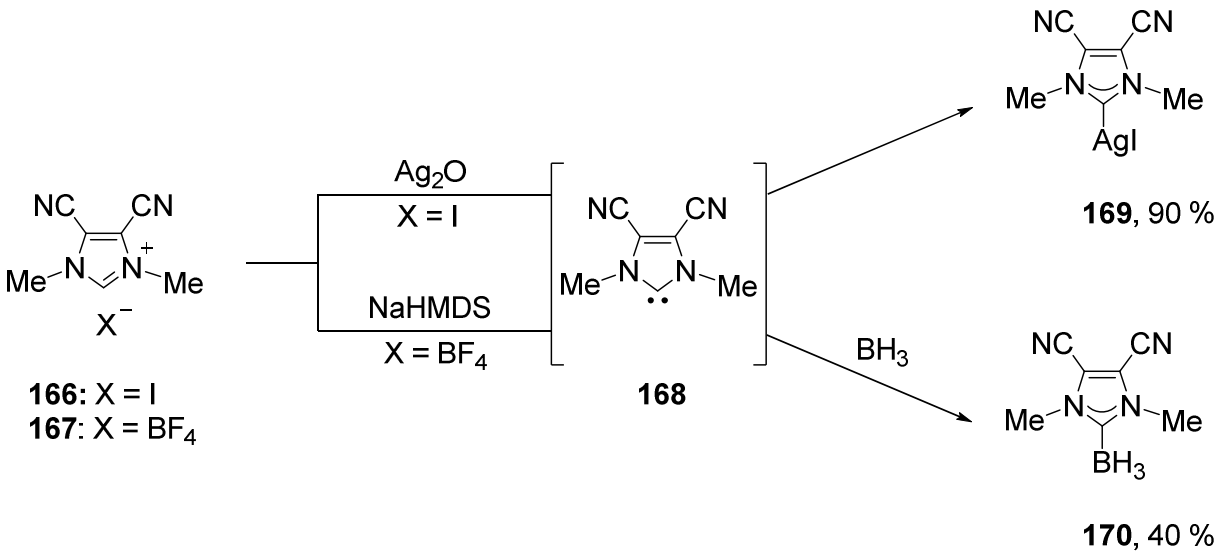


165

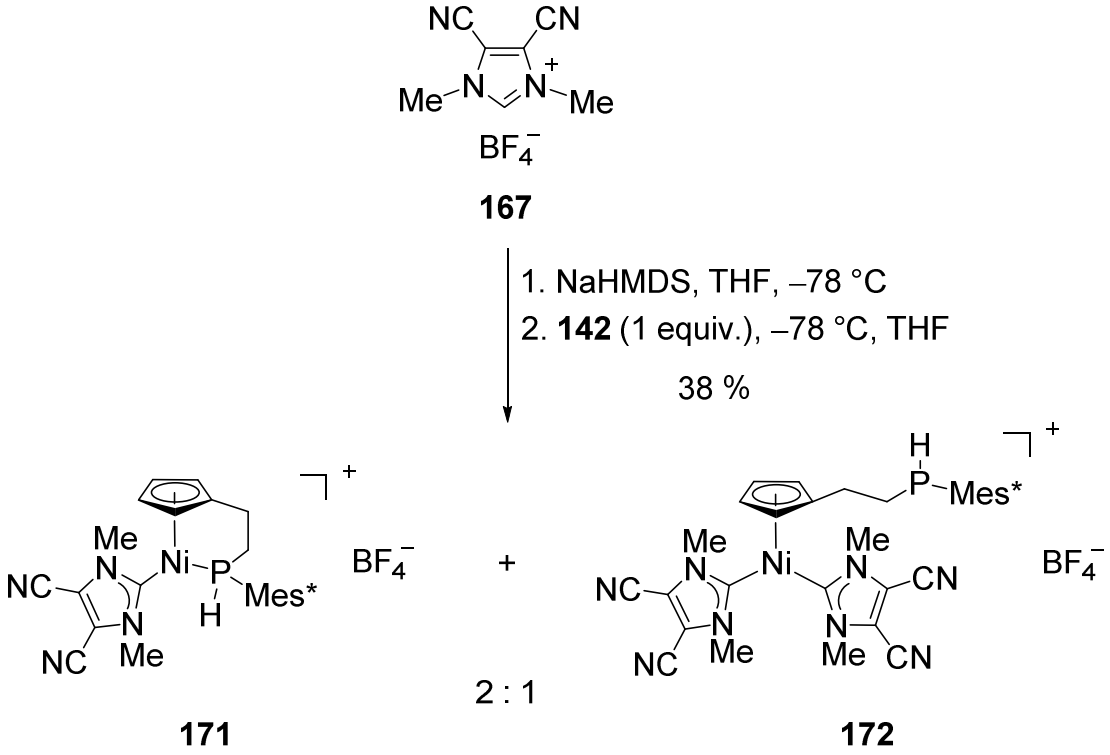




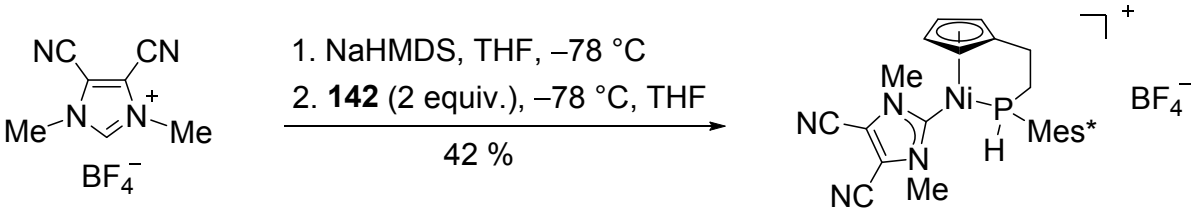
Consequently, the reaction of **142** with 1,3-dimethyl-4,5-dicyanoimidazol-2-ylidene (**168**), abbreviated to Im(CF$_3$)$_2$*N*Me$_2$, was envisaged. Usually, Im(CF$_3$)$_2$*N*Me$_2$ functionalized compounds, such as **169**[130] and **170**,[131] are prepared by the *in situ* deprotonation of the imidazolium salts **166** or **167**[130] and treatment with the appropriate reagents. The isolation of the free **168** has not been reported, presumably, due to its instability.



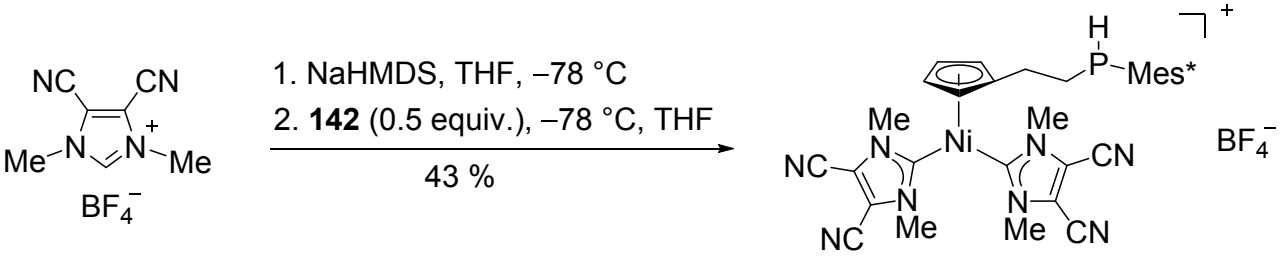
In this work, **167** (1 equiv.) was treated with NaHMDS followed by the addition of this reaction mixture to the solution of **142** (1 equiv.) in THF at –78 °C, delivering the chelate **171** and the decoordinated species **172** in a ratio of 2:1 (^{31}P NMR analysis), respectively.



The salts **171** and **172** could not be separated due to their similar solubility characteristics. The corresponding reaction with two equivalents of **142** delivered exclusively **171** in 42 % yield, whereas the employment of 0.5 equiv. of **142** led solely to **172** in 43 % yield.



166 **171**

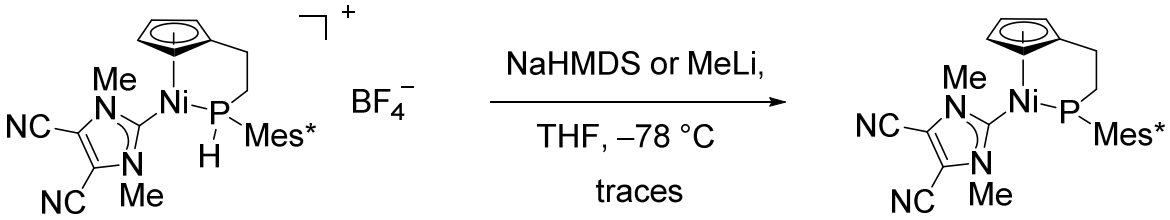


166 **172**

171 and **172** were characterized by spectrometric and spectroscopic analyses. For **171**, the ^{31}P NMR spectrum exhibits a signal at δ = –10.6 ppm demonstrating the chelation of the phosphane group, while the signal at δ = –74.4 ppm for **172** clearly shows the dissociation of the phosphane moiety. The ^{1}H NMR spectrum of **171** shows a doublet of doublet of doublets (δ = 6.68 ppm) for the phosphorus bound hydrogen atom with the coupling constants of $^{1}J_{P,H}$ = 353.3, $^{2}J_{C,H}$ = 11.7 and $^{3}J_{C,H}$ = 4.0 Hz. In case of **172** a doublet of multiplets at δ = 4.73 ppm ($^{1}J_{P,H}$ = 219.6 Hz) was observed which is shifted to higher fields in comparison with **171**. For **171**, the *ortho*-*tert*-butyl groups of Mes* as well as the *N*-methyl groups appear each as two broad singlets. The corresponding signals for **172** were observed each as a singlet. The ^{13}C NMR spectrum of **171** is featured by a doublet at δ = 182.1 ppm ($^{2}J_{P,C}$ = 14.7 Hz) which was assigned to the carbene carbon atom, whereas the corresponding signal for the non-chelated **172** appears as a singlet at δ = 180.8 ppm. The signal for the carbene carbon atom in **171** is only slightly shifted to the lower field as compared to

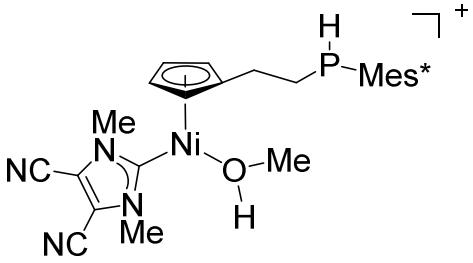
172, indicating almost similar donating properties of the phosphane and the Im$(CF_3)_2$*N*Me_2 groups. In the IR spectra of **171** and **172** each a C≡N vibration at 2241 and 2242 cm^{-1}, respectively, was observed. For **172**, a further weak band at 2392 cm^{-1} was assigned to the P–H vibration. The corresponding vibration was not observed in case of **171**.

Consequently, **171** was treated with bases such as NaHMDS and methyl lithium in THF at –78 °C, though, the outcomes of the reactions in both cases did not differ.



171 **173**

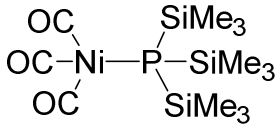
The analysis of the reaction mixture by NMR spectroscopy was not possible to perform due to locking problems. One of the possible reasons could be the magnetic nature of the sample. The ESI-HRMS spectrometry analysis indicated masses for $[M+H]^+$ and $[M+MeOH]^+$, the latter can be, probably represented as a dissociated species **174** in the course of the conversion of **173** with methanol during the measurement. The phosphido complex has likely been formed but decomposed, probably, due to its unstable nature.



174

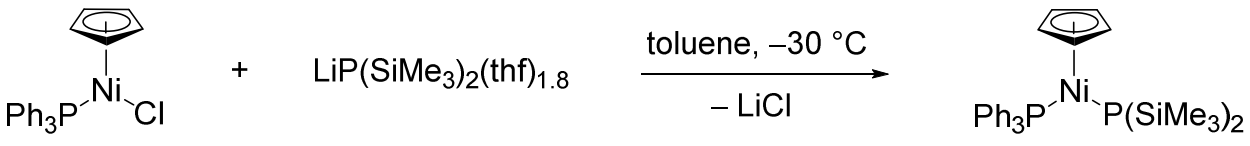
2.5 Synthesis of Cyclopentadienyl Nickel(II) Complexes Bearing a Silylphosphane Substituted Chelating Tether

Since the report on the first silylphosphane, H_3SiPH, by Fritz et al.[132] in 1953, a large number of novel Si–P containing compounds have been synthesized and widely applied.[133] The first transition metal complex incorporating a silylphosphane ligand **175** was prepared by Schumann, Stelzer et al. Although the silylphosphanes are air-sensitive, the nickel complex **175** was reported to be stable under aerobic conditions.[134]

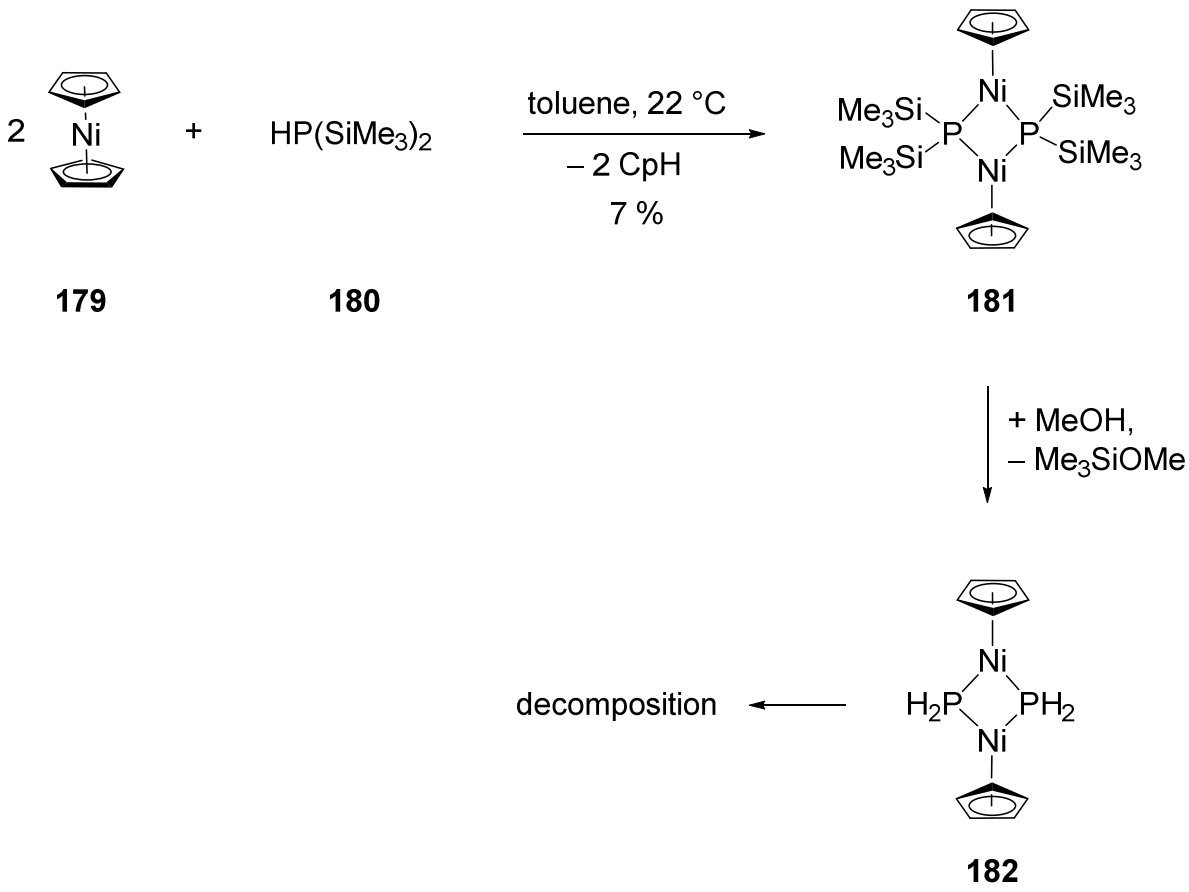


175

Schäfer et al. introduced the cyclopentadienyl nickel(II) complex with a silylphosphido ligand **178**, prepared from **176** and **177**, and the corresponding silylphosphido-bridged dinuclear complex **181**, which was obtained from the reaction of nickelocene (**179**) with the secondary silylphosphane **180**. The authors obtained the unstable phosphido-bridged compound **182** (^{31}P NMR analysis) after the protiodesilylation of **181** *via* alcoholysis with methanol.[135] Investigations on the high reactivity of silylphosphanes bonds towards basic and acidic hydrolysis as well as alcoholysis, which resulted in the cleavage of the silyl groups, were earlier carried out by Fritz et al.[136]

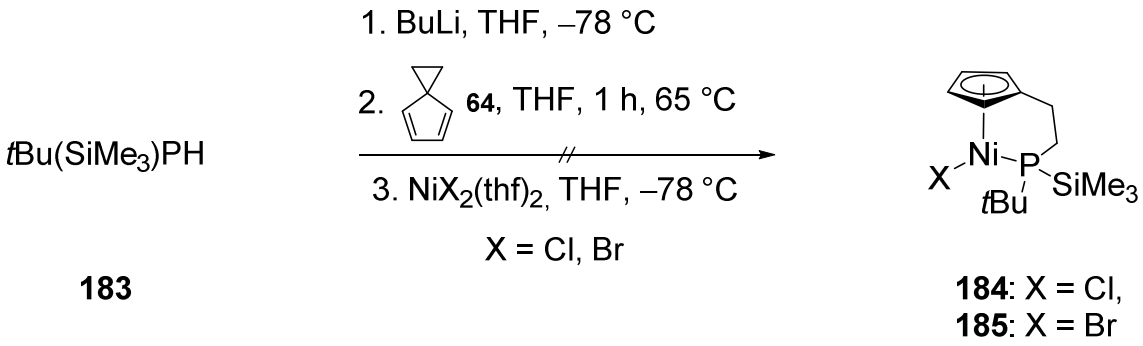


176 **177** **178**



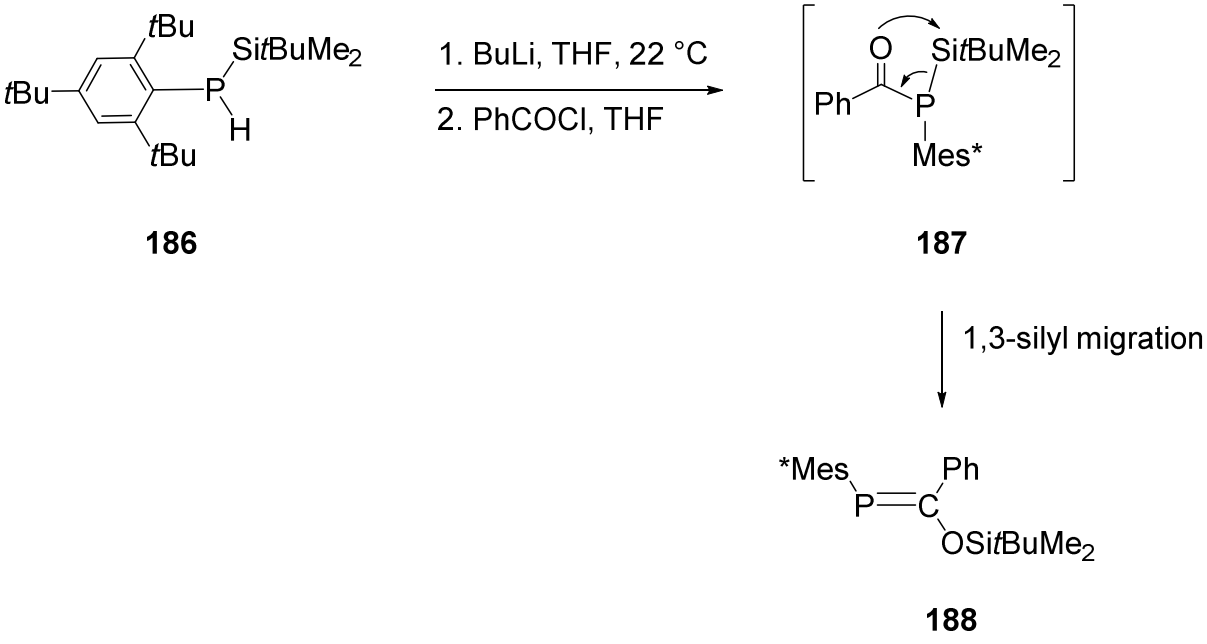
Interestingly, cyclopentadienyl complexes with a silylphosphane functionalized chelating tether have not yet been reported. Actually, the silyl group can be selectively cleaved by a fluoride source,[137] leading to the desired phosphido chelates. Consequently, the syntheses of cyclopentadienyl nickel(II) complexes with a trimethylsilylphosphanyl group functionalized chelating tether was envisaged. Previously, Becker, Schneider et al. reported the lithiation of (*tert*-butyl)(trimethylsilyl)phosphane (**183**) which was further successfully applied in nucleophilic reactions.[138] In this work, **183** was first deprotonated with butyllithium and then treated with **64** followed by the addition of the reaction mixture to suspensions of $NiCl_2(thf)_2$ or $NiBr_2(thf)_2$ in THF by –78 °C. The desired chelates **184** and **185** were not observed by the spectrometric and spectroscopic analyses of oily brown products. The interpretations of the results were difficult due to the formation of the complicated mixtures of undefined products. These results resemble those observed for the corresponding reactions of lithium *tert*-butylphosphane (**65**). The employment of bulkier substituents at

phosphorus was envisaged in order to kinetically stabilize silylphosphane substituted chelates.



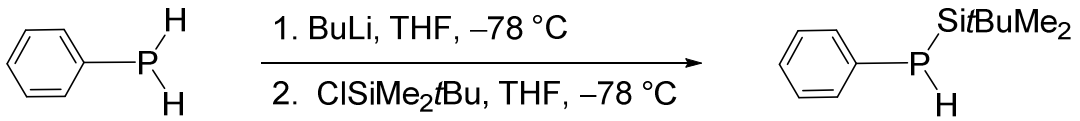
2.5.1 Synthesis of Novel Bulky Secondary Silylphosphanes

Only few reports on secondary phosphanes bearing such bulky silyl substituents as *tert*-butyldimethylsilyl or triisopropylsilyl groups have appeared in the literature.



An extremely overcrowded secondary silylphosphane **186** was introduced by Yoshifuji, Inamoto et al. The sequence of lithiation and the nucleophilic addition-elimination reaction with benzoyl chloride led presumably, to the acylsilylphosphane intermediate **187** which undergoes 1,3-silyl migration under the formation of the alkylidenephosphine **188**.[139]

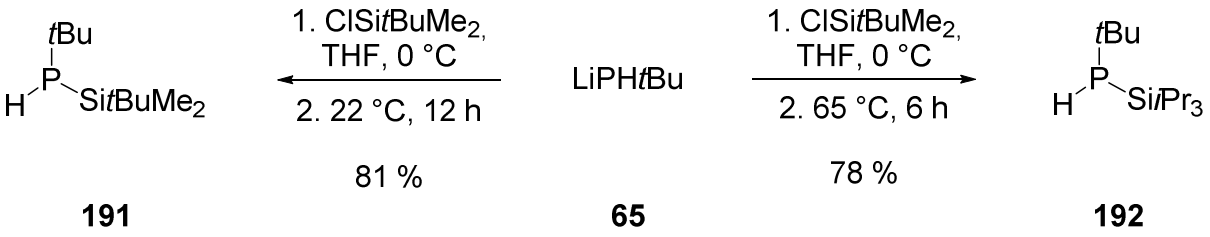
A less bulky phenyl substituted silylphosphane **190** was prepared by Wang et al. However, the authors did not report on the spectroscopic analysis of **190**.[140] In this work, **190** was obtained as an extremely pyrophoric colorless oil by the lithiation of phenylphosphane (**189**) followed by the quench with *tert*-butyldimethylsilyl chloride. **190** was characterized by the ^{1}H, ^{13}C and ^{31}P NMR spectroscopy. In the proton coupled ^{31}P NMR spectrum a doublet of multiplets at δ = –130.3 ppm ($^{1}J_{P,H}$ = 203.5 Hz) was observed. The signal is shifted to the higher fields as compared to **189** (δ = –121.8 ppm) assuming a shielding effect of the silyl substituent as compared to the hydrogen atom. In the ^{1}H NMR spectrum of **190** the signals for the methyl groups bound to silyl as well as the resonances for the phenyl hydrogen atoms appear as multiplets, presumably, due to their diastereotopic nature because of the stereogenic phosphorus atom. The ^{13}C NMR spectrum is featured by two distinct signals for the methyl groups which appear as a doublet at δ = –5.06 ppm ($^{2}J_{P,C}$ = 13.9 Hz) and as singlet at δ = –4.29 ppm.



189 **190**

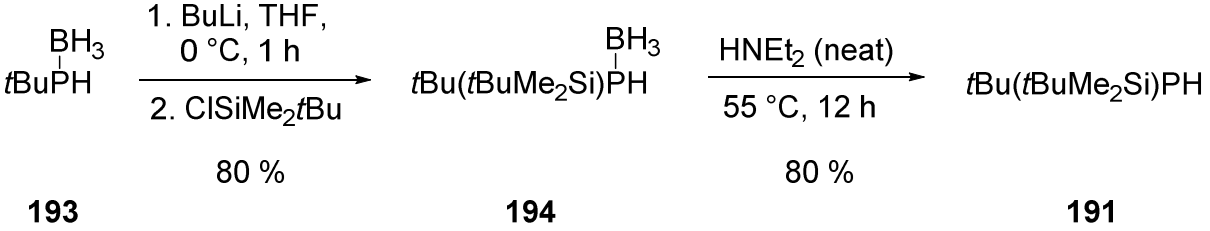
The corresponding *tert*-butyl substituted secondary silylphosphanes have not yet been reported. Thus, **65** was treated with *tert*-butyldimethylsilyl chloride or triisopropylsilyl chloride affording highly pyrophoric new silylphosphanes **191** and **192** in 81 % and 78 % yields, respectively. Regarding the formation of **192**, a longer reaction time was required (visual from the discoloration of the reaction mixture) as compared

to **191**. This is, presumably, due to the enhanced steric bulk in **192**. Both phosphanes could be purified by vacuum distillation without decomposition.



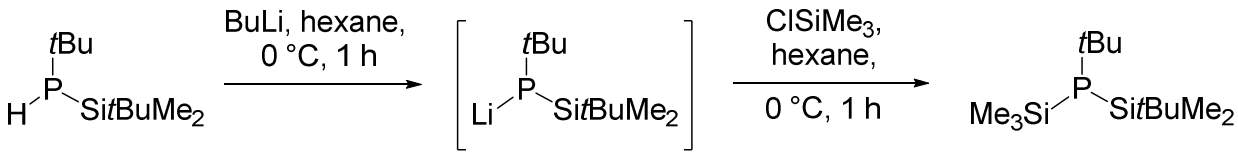
In the proton coupled ^{31}P NMR spectrum of **191** a doublet of multiplets at δ = –95.3 ppm ($^{1}J_{P,H}$ = 194.6 Hz) was observed. The signal is shifted to the higher fields as compared to *tert*-butylphosphine[138] (δ = –78.3 ppm) due to the shielding effect of the silyl substituent as compared to the hydrogen atom. In the ^{1}H NMR spectrum of the signals for the methyl groups bound to silyl appear as doublets with different coupling constants ($^{2}J_{C,H}$ = 6.6 Hz and $^{2}J_{C,H}$ = 3.1 Hz), probably, due to their diastereotopic nature because of the stereogenic phosphorus atom. Most likely, for the same reason the resonances of the isopropyl CH-groups appear as multiplets in the ^{1}H NMR spectrum of **192**. The proton coupled ^{31}P NMR spectrum of **192** shows a doublet of multiplets at δ = –105.0 ppm ($^{1}J_{P,H}$ = 204.6 Hz) indicating the enhanced shielding effect of the triisopropylsilyl group as compared to the tert-butyldimethylsilyl moiety.

Syntheses of **191** and **192** include the isolation of such highly pyrophoric compounds as *tert*-butylphosphine and the corresponding lithiated phosphine **65**. The employment of borane protected phosphanes was envisaged, finally, with a view to their deprotection by amines.[141] The stability of phosphinoboranes towards different reactions conditions makes borane a versatile protecting reagent.[142]



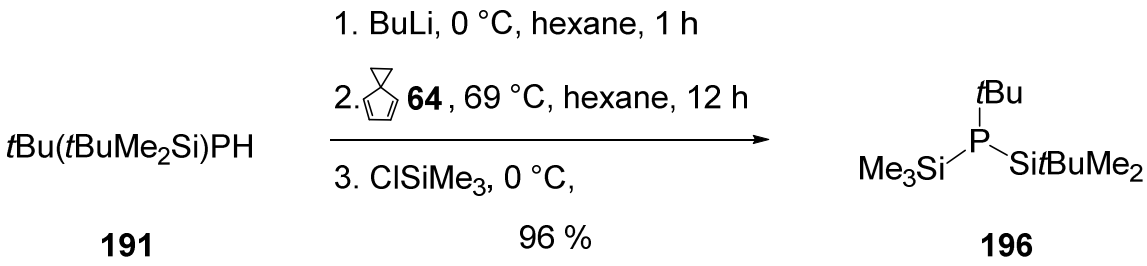
In this work, the borane protected silylphosphane **194** was obtained in 80 % yield by a sequence starting with deprotonation of *tert*-butylphosphane borane adduct (**193**)[143] with butyllithium[144] followed by addition of *tert*-butyldimethylchlorosilane. **194** is nonpyrophoric, but still sensitive to air and hydrolysis. Vacuum distillation of the crude product resulted in a partial dissociation of the borane moiety at elevated temperature (^{31}P NMR analysis). Consequently, the crude phosphane **194** was treated with neat diethyl amine at reflux and after filtration of $NHEt_2$ borane adduct through alumina **191** was obtained in 80 % yield. The ^{31}P NMR spectrum shows a doublet of multiplets at δ = –37.3 ppm ($^1J_{P,H}$ = 317.8 Hz) indicating the incorporation of the phosphorus lone pair into the coordination to borane. The difference between the coupling constants for the P–H bonds of the coordinated and not coordinated phosphanes being more than 180 Hz. These results are similar to those obtained for **142** and **143** (vide supra). Further, the ^{11}B NMR spectrum exhibits a doublet at δ = –37.3 ppm with $^1J_{P,B}$ = 31.4 Hz. The spin-spin coupling constant of the bond between the ^{31}P- and ^{11}B nuclei range from 10 to 180 Hz.[145]

Next, the isolation of the solvent free lithiated silylphosphane **195** was attempted. Treatment of **191** in hexane with 1.1 equiv. butyllithium did not induce the precipitation of the corresponding lithium salt even if a turbid solution was concentrated. The quench of the reaction mixture with trimethylsilyl chloride delivered the disilylated phosphane **196** in excellent yields as an air and hydrolysis sensitive colorless oil indicating that the deprotonation step was fully achieved.

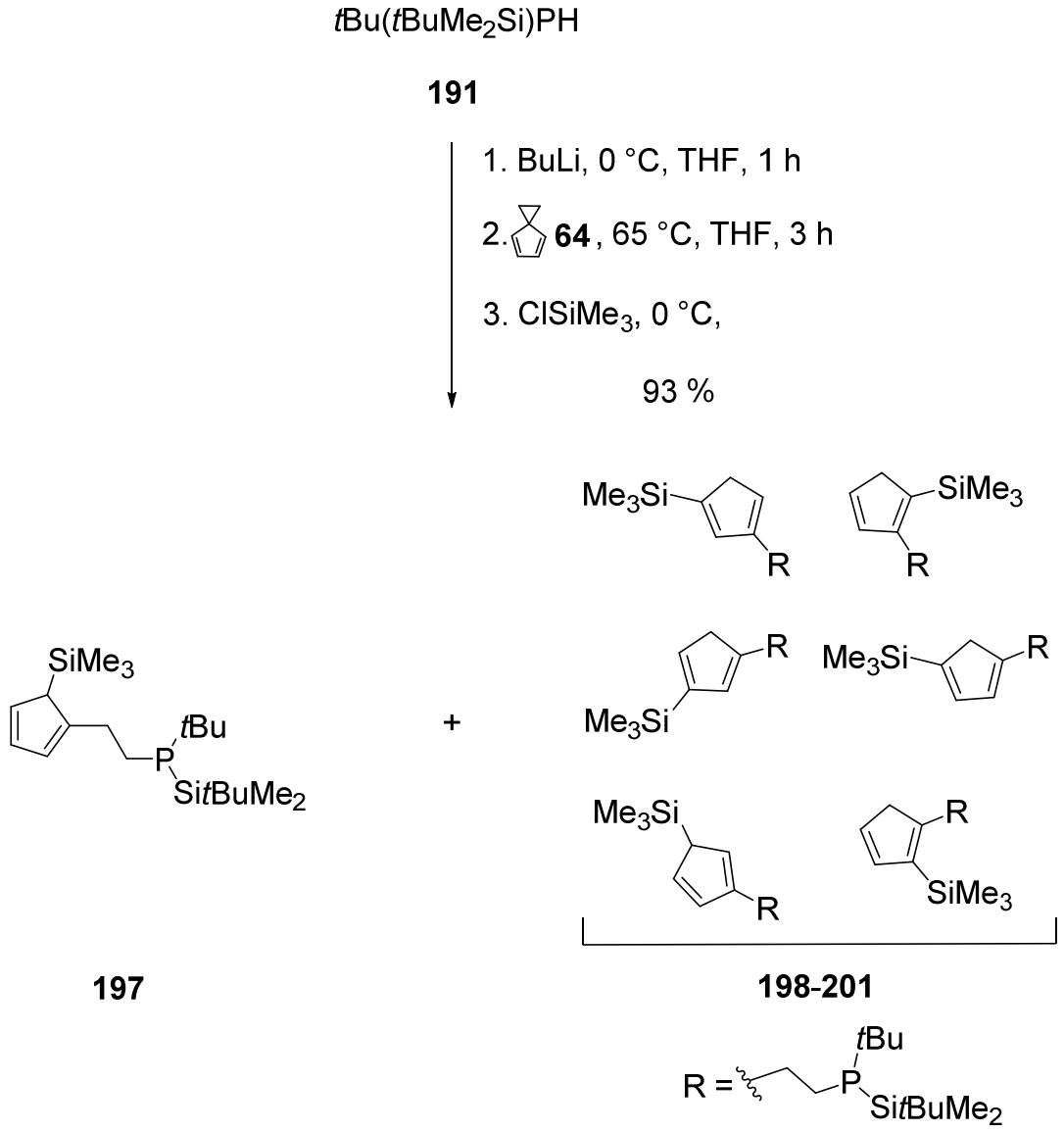


191 **195** **196**, 98 %

The ^{31}P NMR spectrum of **196** exhibits a resonance at δ = –114.6 ppm demonstrating the enhanced shielding effect of the additional silyl group bound to phosphorus as compared to the secondary silylphosphane **191** (δ = –95.3 ppm).



The corresponding reaction of **191** with **64** failed in hexane, resulting in the isolation of **196** in 96 % yield after quench with trimethylsilyl chloride, indicating that the nucleophilic ring opening reaction did not take in the noncoordinating solvent, presumably, due to its inability to affect aggregation.



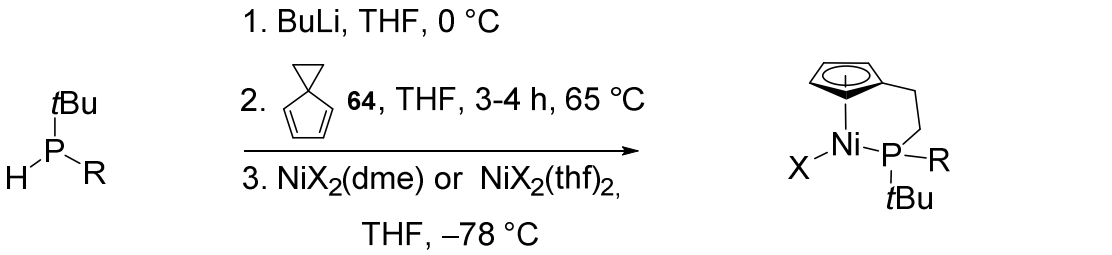
The change of the polarity of the solvent led to the silylphosphane functionalized silylcyclopentadiene derivatives **197**-**201** in 93 % crude yield as s mixture of regioisomers which could not be separated. In the ^{31}P NMR spectrum a signal for the main regioisomer **197** (δ = –53.9 ppm) and four signals for minor isomers **198**-**201** (δ = –54.1, –54.2, –54.2 and –54.3 ppm) with 7:1 (**198**-**201**, overall) ratio, respectively, were observed. According to 2D NMR experiments (HSQC, HMBC and H,H-COSY) the silylation took place mainly at the vinylic position.

Compounds **197**-**201** can be further applied in synthesis of the cyclopentadienyl chelate complexes under the cleavage of the trimethylsilyl group. It was reported earlier, that trimethylsilyl or tributylstannyl substituted cyclopentadienyl derivatives serve as convenient precursors in preparation of cyclopentadienyl metal complexes.[52,146]

Having shown that the silylphosphane **191** successfully opens the cyclopropyl ring in **64**, the new bidentate system was to be coordinated as a chelate to nickel.

2.5.2 Synthesis of Cyclopentadienyl Nickel(II) Complexes with Bulky Silylphosphane Substituted Chelating Tethers

Silylphosphanes **191** and **192** were deprotonated with butyllithium, and the intermediate lithium phosphides were treated *in situ* with **64** followed by the addition of the resulting reaction mixtures to the suspensions of nickel(II) halide complexes in THF. After repeated recrystallizations, the chelates **202**-**204** were obtained in 56, 75 and 53 % yields, respectively. Attempt at chromatographic purification resulted in the immediate decomposition of the chelates. Interestingly, the synthesis of **202** could only be achieved when $NiCl_2(thf)_2$ was used as the metal halide source. Complexes **202**-**204** are quite sensitive to air, with the chloro-derivative **202** decomposing faster in the air than **203** or **204**.

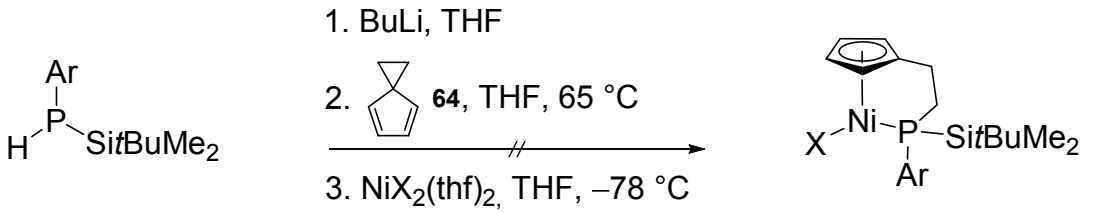


191: R = Si*t*BuMe$_2$
192: R = Si*i*Pr$_3$

202: X = Cl, R = Si*t*BuMe$_2$, 56 %
203: X = Br, R = Si*t*BuMe$_2$, 69 %
204: X = Br, R = Si*i*Pr$_3$, 53 %

In the ^{31}P NMR spectra of **202**-**204**, singlets at δ = 24.0 24.9, and 25.4 ppm, respectively, were observed, indicating a coordinated silylphosphane tether with nickel. The comparison with the data of the related chloro complexes **3** and **6** (*vide supra*), which show respective resonances around 90 ppm,[14,16] demonstrating a shielding effect of the silyl substituent as compared to the *tert*-butyl group. The ^{1}H NMR spectra of **202**-**204** exhibit each two multiplets for the CH_2-groups in the ethylene bridge as well as four multiplets assigned to the cyclopentadienyl group. The *tert*-butyl group bound to phosphorus appear each as a doublet with $^{3}J_{P,H}$ = 14.0, 14.4 and 14.0 Hz, respectively. For **202** and **203**, the signal for the *tert*-butyl group bound to silicon appears each as a singlet, whereas for the corresponding resonance of the *tert*-butyl bound to phosphorus each a doublet was observed. The isopropyl methyl groups in **204** show two different signals in the ^{1}H and ^{13}C NMR spectra, whereby for the free silylphosphane **192** the corresponding function was observed either as a doublet with $^{4}J_{P,H}$ = 5.0 Hz or as two singlets in the ^{1}H NMR spectrum. The ^{13}C NMR spectrum of **192** shows, however, a broad singlet. Presumably, the isopropyl methyl groups in **192** were not sufficiently different to be resolved by the NMR spectroscopy. Owing to the incorporation of the phosphanyl lone pair into the coordination to nickel, the signals in **204** could be resolved apart from each other. The HRMS measurements of **202**-**204** are in full agreement with the calculated values. The attempted recrystallization of **202**-**204** from different solvent systems did not resulted in crystals suitable for the X-ray analysis.

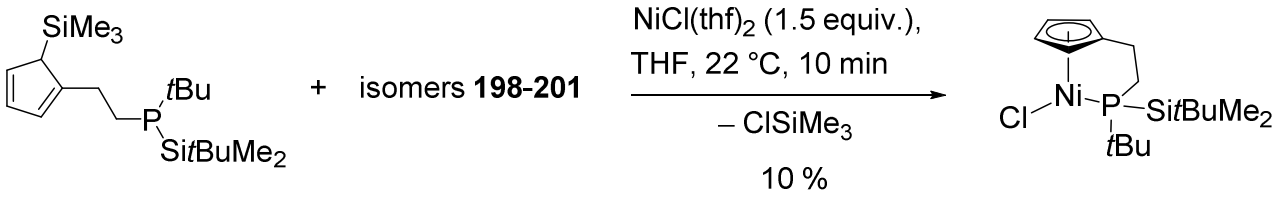
The corresponding reactions of silylated arylphosphanes **186** and **190** with nickel(II) halo complexes did not result in the expected chelates **205**-**208**, leading to complicated mixtures of compounds , which could not be identified by the spectroscopic and spectrometric analyses. Probably, an enhanced steric hindrance in **186** does not allow the phosphane moiety to coordinate to nickel, whereas the failed complexation of **190** to nickel is not fully clear. The electronic and steric effects have likely acted in concert. The phenyl substituted phosphane group is less bulky than the *tert*-butyl substituted phosphanyl function. Electronically, the phenyl group has both the negative inductive and the strong resonance effects. The *tert*-butyl group, on the other hand, has only the positive inductive effect.



186: Ar = Mes*
190: Ar = Ph

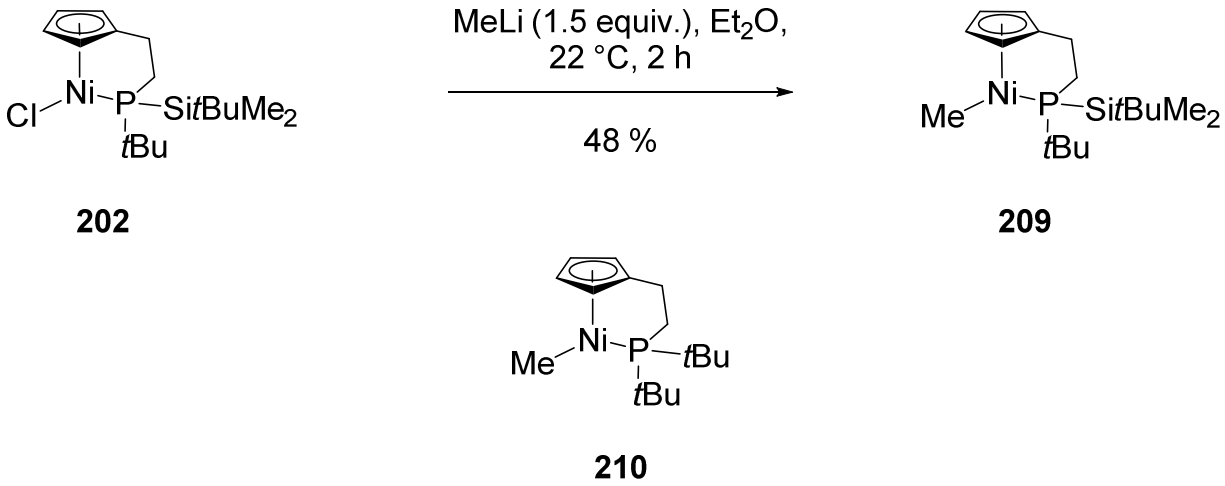
205: X = Cl, Ar = Mes*
206: X = Br, Ar = Mes*
207: X = Cl, Ar = Ph
208: X = Br, Ar = Ph

The silylphosphane functionalized silylcyclopentadiene derivatives **197**-**201** were subjected to a complexation reaction with $NiCl_2(thf)_2$. After stirring for 0.5 h, the color of the reaction mixture began to turn from red-violet into brown, indicating the decomposition of the formed complex **202** induced, presumably, by the subsequent reaction of the elaborated trimethylchlorosilane with **202**. The spectroscopic and spectrometric analyses of the crude reaction mixture did not give any evidence on the formation of **202**. Shorter reaction times led to lower yields of about 10 %. Thus, the one-pot reaction of secondary silylphosphanes with nickel halide complexes remains currently the most effective access to this new kind of chelates.



197 **202**

Cyclopentadienylalkylphosphane nickel halide chelates can undergo a variety of reactions with formations of nickel-carbon bonds.[14] Methylation of **202** with methyllithium was achieved in 48 % yield showing that the silylphosphane ligand moiety withstands these reaction conditions. However, the yield of **209** is somewhat lower that for the corresponding compound **210**[14] with two *tert*-butyl substituents at the phosphorus atom.

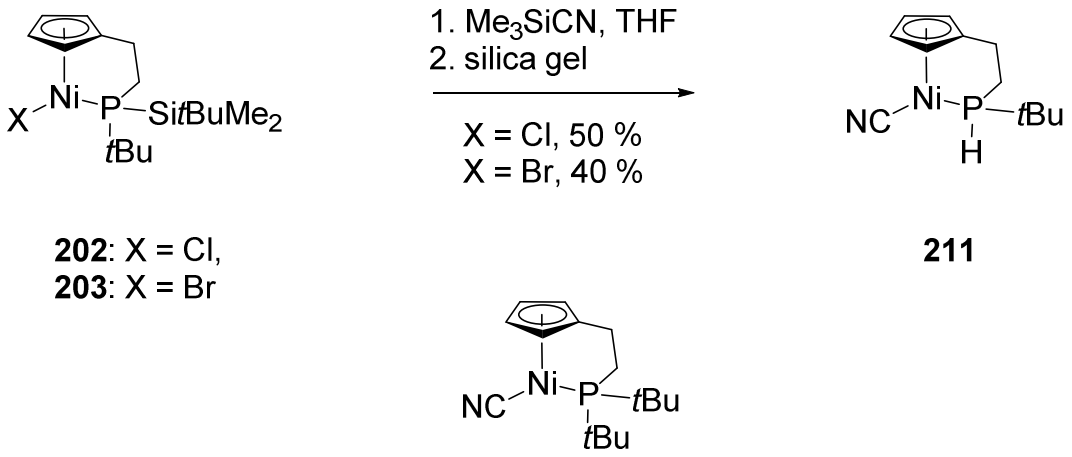


202 **209**

210

Crystallization from pentane at –30 °C afforded crystals not suitable for a crystallographic analysis. **209** is much more stable (no decomposition over 3 weeks at –18 °C) in the crystalline state than as a solid obtained by solvent evaporation. The significant spectroscopic features are the ^{1}H NMR absorption of the Ni-methyl protons at δ = –0.59 ppm and the respective ^{13}C NMR signal at δ = –42.3 ppm with coupling constants of $^{3}J_{P,H}$ = 4.6 Hz and $^{2}J_{P,C}$ = 19.5 Hz, respectively, proving the coordination of the phosphane ligand. In addition, the ^{31}P NMR spectrum shows a signal at δ = 16.5 ppm confirming the coordinated nature of the phosphane side chain to the nickel atom. The HRMS is in accord with the calculated value.

Substitution of the halide ligand in **202** or **203** by a cyano ligand was achieved by treatment with trimethylsilyl cyanide in THF followed by column chromatography at silica gel. However, in addition to the substitution in both cases a protiodesilylation of the phosphorus atom was observed resulting in the formation of complex **211** in 50 % and 40 % yield, respectively, as a green, air stable crystalline solid.



202: X = Cl,
203: X = Br

211

212

211 was fully characterized. In the proton coupled ^{31}P NMR spectrum a doublet of multiplets at δ = 56.8 ppm with $^{1}J_{P,H}$ = 342.4 Hz was observed. The ^{31}P NMR shift compares to a value of δ = 90.0 ppm for **212**[126] and reflects the usual difference in chemical shift between secondary and tertiary phosphanes.[147] The IR spectrum is characterized by a sharp P–H absorption at 2330 cm^{-1} and a strong C≡N absorption at 2107 cm^{-1}. The observed HRMS value is in accord with the calculated one.

Crystallization from hexane/ethyl acetate (1:1) at 0 °C afforded green crystals suitable for an X-ray crystal structure analysis. **211** crystallizes twinned in an orthorhombic crystal system with the space group $Pca2_1$ (Nr. 29). Attempted recrystallizations from other solvents failed. The unit cell of **211** contains two independent molecules. While **211a** (Figure 3) confirms the constitution assigned on the basis of spectroscopic and spectrometric data, **211b** (Figure 4) shows a disordered geometry at the *tert*-butylphosphane moiety.

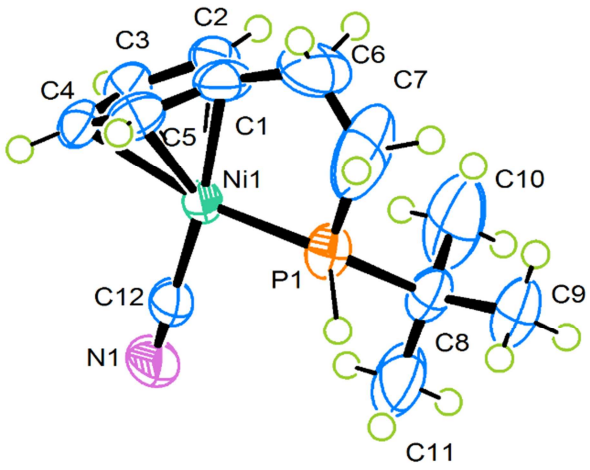


Figure 3. Structure of **211** in the crystal. Representation **211a** (50 % propability level). Selected bond lengths [pm] and angles [°]: Ni1–C1 202.6(6), Ni1–C2 212.8(6), Ni1–C3 213.6(5), Ni1–C4 212.0(5), Ni1–C5 211.7(5), Ni1–C12 185.6(6), Ni1–P1 214.3(2), C7–P1 181(1), C8–P1 183.6(6), C12–N1 115.1(8), P1–H1 141(5); Ni1–C12–N1 178.5(6), C12–Ni1–P1 101.3(2), H1–P1–Ni1 127(2), Ni1–P1–C7 102.8(4), Ni1–P1–C8 123.4(2), C7–P1–H1 103(2), C7–P1–C8 110.5(4), H1–P1–C8 89(2).

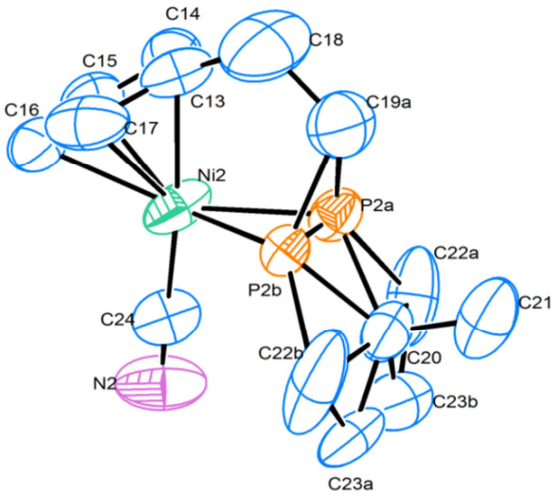
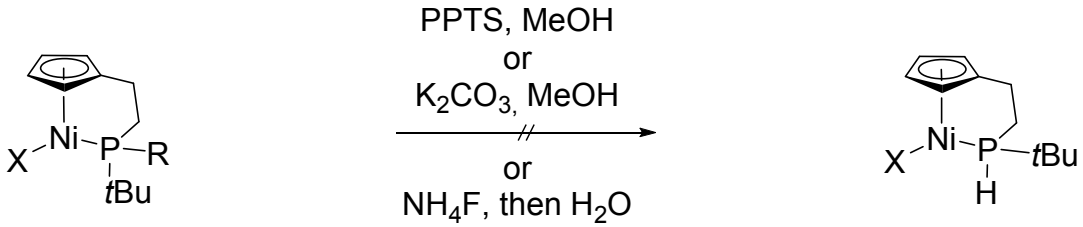


Figure 4. Structure of **211** in the crystal. Representation **211b** (50 % propability level, hydrogen atoms omitted for clarity). Selected bond lengths [pm], angles and torsions between planes [°]: Ni2–C13 204.6(3), Ni2–C14 211.4(8), Ni2–C15 209.0(6), Ni2–C16 208.5(8), Ni2–C17 211.7(2), Ni2–C24 183.6(1), Ni2–P2a 224.6(0), Ni2–P2b 208.1(5), C24–N2 114.4(8), C19a–P2a 174.9(1), C19a–P2b 189.2, P2a–P2b 112.3(9), C20–P2a 175.5(8), C20–P2b 179.5(8); Ni2–C24–N2, 179.4(2); C19a–P2a–P2b and P2a–P2b–Ni2, 106.9(9); P2a–P2b–Ni2 and Ni2–C24, 95.0(7).

The structure **211a** shows that the cyclopentadienyl ligand is practically planar with C1 being only slightly closer to the nickel atom than the other cyclopentadienyl carbon atoms. The ethylene bridge shows the typical torsion causing a minimization of vicinal H,H interactions. The phosphorus atom has a distorted quasi tetrahedral environment with some angles significantly deviating from the tetrahedral angle: C8–P1–Ni1 123.4°, H1–P1–Ni1 127.0°, Ni1–P1–C8 123.4°, and H1–C1–P8 98.0°. This distortion is presumably due to the strain exerted by the ethylene bridge in combination with the large difference in steric bulk between the *tert*-butyl group and the hydrogen atom bound to phosphorus.

A DFT calculation[89] reproduced the measured structure. In **211** the HOMO energy is calculated to be –5.2 eV as compared to –5.1 eV in **212**, the calculated energies of the LUMO are –1.4 eV for **211** and –1.2 eV for **212**. In both compounds the HOMO shows a nodal plane corresponding to the quasi plane of symmetry defined by the cyano ligand, the nickel atom, the phosphorus atom C1, C6, and C7.

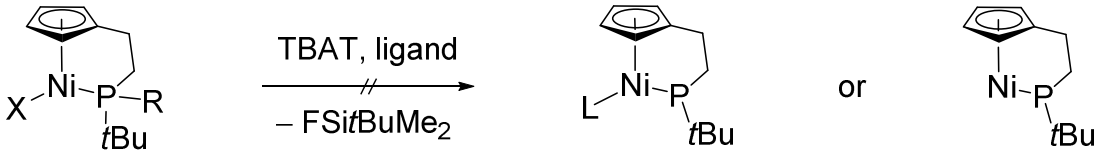
The formation of **211** represents only the second example of the protiodesilylation of a coordinated silylphosphane.[148] Attempts to protiodesilylation of complexes **202**-**204** *via* acidic and basic hydrolyses or by the reaction with tetrabutylammonium fluoride followed by the addition of water, failed, resulting in the decomposition of the starting complexes. The desired halo complexes **213** or **214** were not observed by the spectroscopic and spectrometric analyses of the crude reaction mixtures.



202: X = Cl, R = Si*t*BuMe$_2$,
203: X = Br, R = Si*t*BuMe$_2$,
204: X = Br, R = Si*i*Pr$_3$

213: X = Cl
214: X = Br

The chelates **202** and **203** were subjected to the desilylation reactions with TBAT (tetrabutylammonium triphenyldifluorosilicate)[149] in the presence of a variety of ligands under different reaction conditions. TBAT is anhydrous and nonhygroscopic as compared to NH_4F, which is difficult to dehydrate.[150] Neither the desired phosphido complex **215** nor its coordinatively unsaturated version **216** were observed according to the spectrometric analyses, even when the ligands were used in great excess. The spectroscopic analyses of the brownish oily products showed complicated mixtures of compounds which could not be identified.



202: X = Cl, R = Si*t*BuMe$_2$,
203: X = Br, R = Si*t*BuMe$_2$

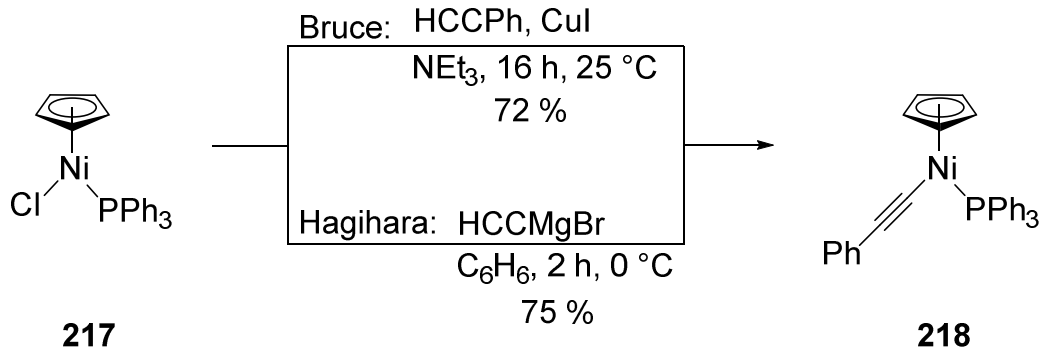
215 **216**

ligand: THF, acetonitrile, pyridine, PPh$_3$, 4-isocyanobenzonitrile

Next, further coupling reactions under the formation of nickel-carbon bonds were envisaged.

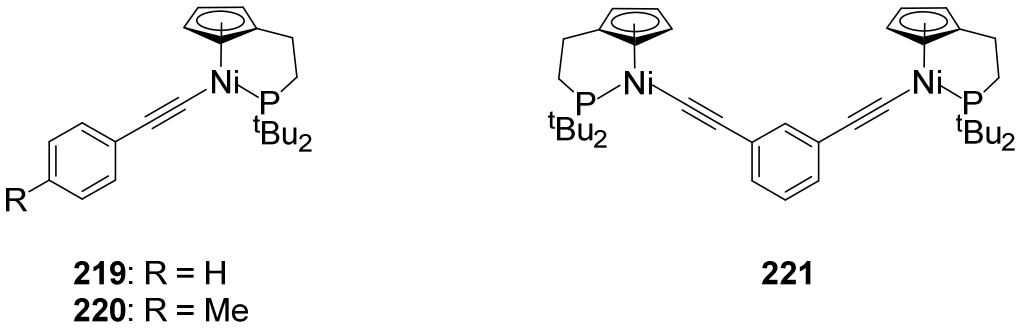
2.5.3 Bruce Coupling Reactions of the Nickel Chelate 203

In recent years, transition-metal *σ* alkynyl complexes have attracted much interest due to their potential use in nonlinear optics (NLO) and molecular wires. This area of research covers a great number of compounds ranging from monomeric units to polymers that contain as many as 10000 M–C≡C-linkages in a polymer chain.[151] The incorporation of the acetylide group into organometallic complexes and multi-metallic assemblies provides a facile pathway for electron delocalization between interacting metal centers.[152] Hagihara et al. reported the synthesis of the first cyclopentadienyl nickel complex **218** bearing a *σ* alkynyl ligand by treatment of the corresponding halide compound **217** with a Grignard reagent.[153] Bruce et al. developed successful routes for synthesis of nickel and other transition metals *σ* alkynyl complexes in the presence of organic amines with copper(I) halide as a catalyst.[154]



The first chelating cyclopentadienylalkylphosphane nickel *σ*-acetylide complexes **219**-**221** were reported by Butenschön et al. in 2007.[14] These chelates proved to be even more stable than their nonchelated analogues.

Further work of the group revealed a number of monomeric and polynuclear cyclopentadienylalkylphosphane nickel *σ*-acetylide complexes **219**-**221**, which in some cases could undergo several subsequent reactions.[126]

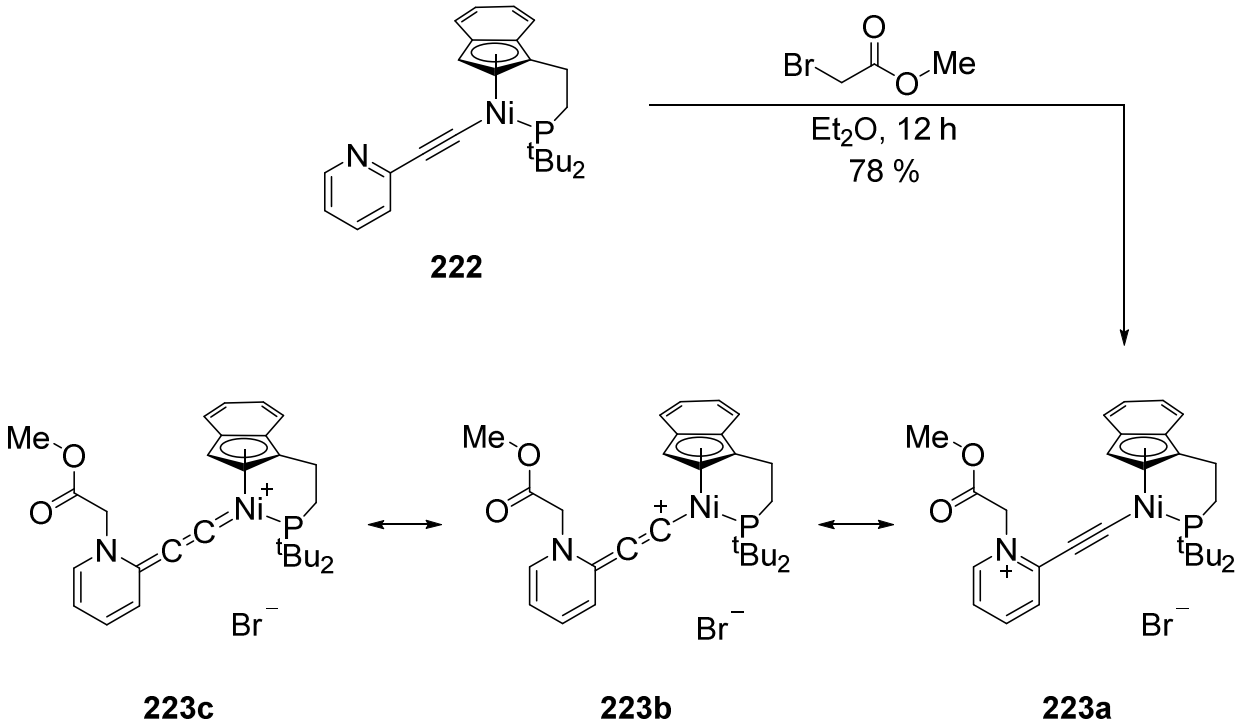


219: R = H
220: R = Me

221

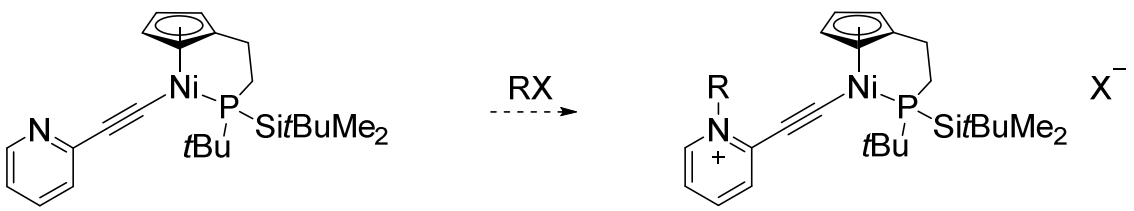
Among these compounds a heterocyclic representative, (2-pyridyl)ethynyl nickel indenyl chelate complex **223** deserves much attention. Treatment of complex **222** with methyl bromoacetate afforded the corresponding pyridinium salt **223**, which showed interesting spectroscopic data: a significantly higher ^{13}C NMR chemical shift ($\Delta\delta$ = 49.4 ppm) of the acetylide carbon in **223** clearly indicates a strong interaction between the positively charged pyridinium nitrogen atom and the acetylide carbon atom. The IR absorptions of the carbon-carbon triple bonds at 2083 cm^{-1} in **222** and at 2059 cm^{-1} in **223** are in accord with a weakened bond strength in the pyridinium de-

rivative **223**. On the basis of this spectroscopic information the authors proposed the resonance formulas **223a**-**223c**, pointing out a great contribution of the allenylidene formula **223c** to the phenomenon.[16]

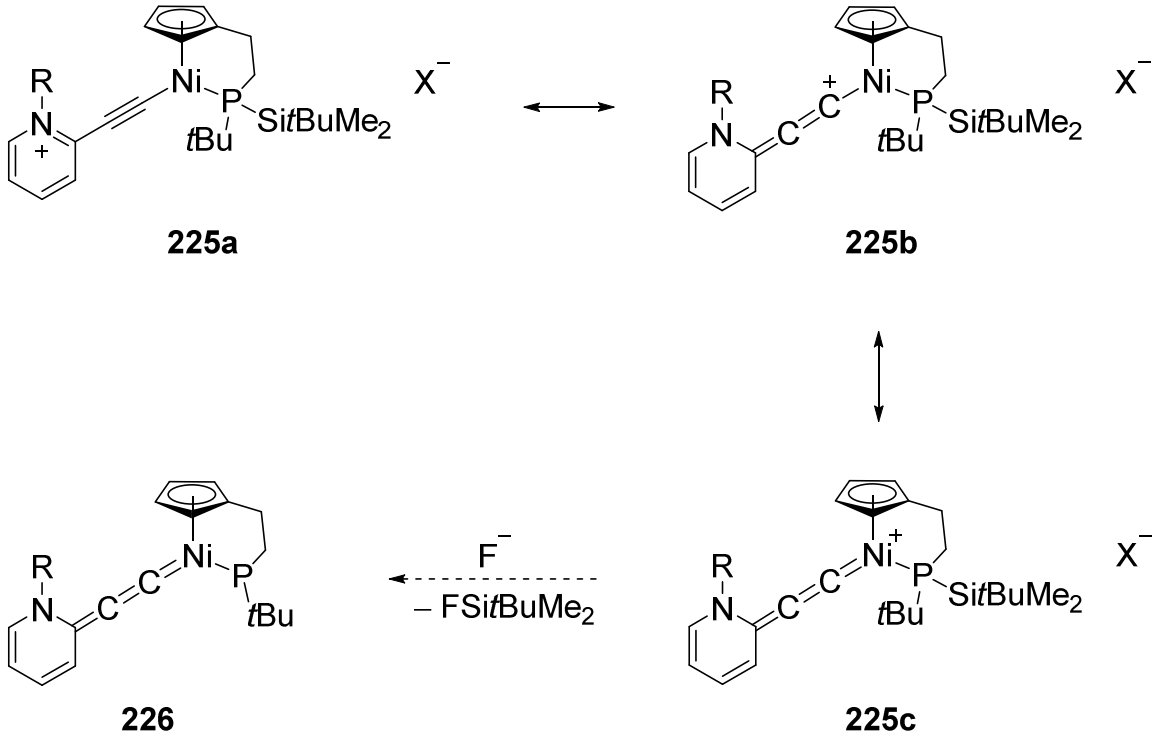


222 **223c** **223b** **223a**

Based on these results, the synthesis of the corresponding nickel complex **224** with a silylphosphane group in the tether was envisaged. The sequence of the quaternization of the pyridine nitrogen and the desilylation of the phosphane moiety is expected to lead to new neutral nickel phosphide complexes **226** bearing an allenylidene function *via* the corresponding cationic complexes **225**, which can be represented through the resonance formula **225a**-**225c**.



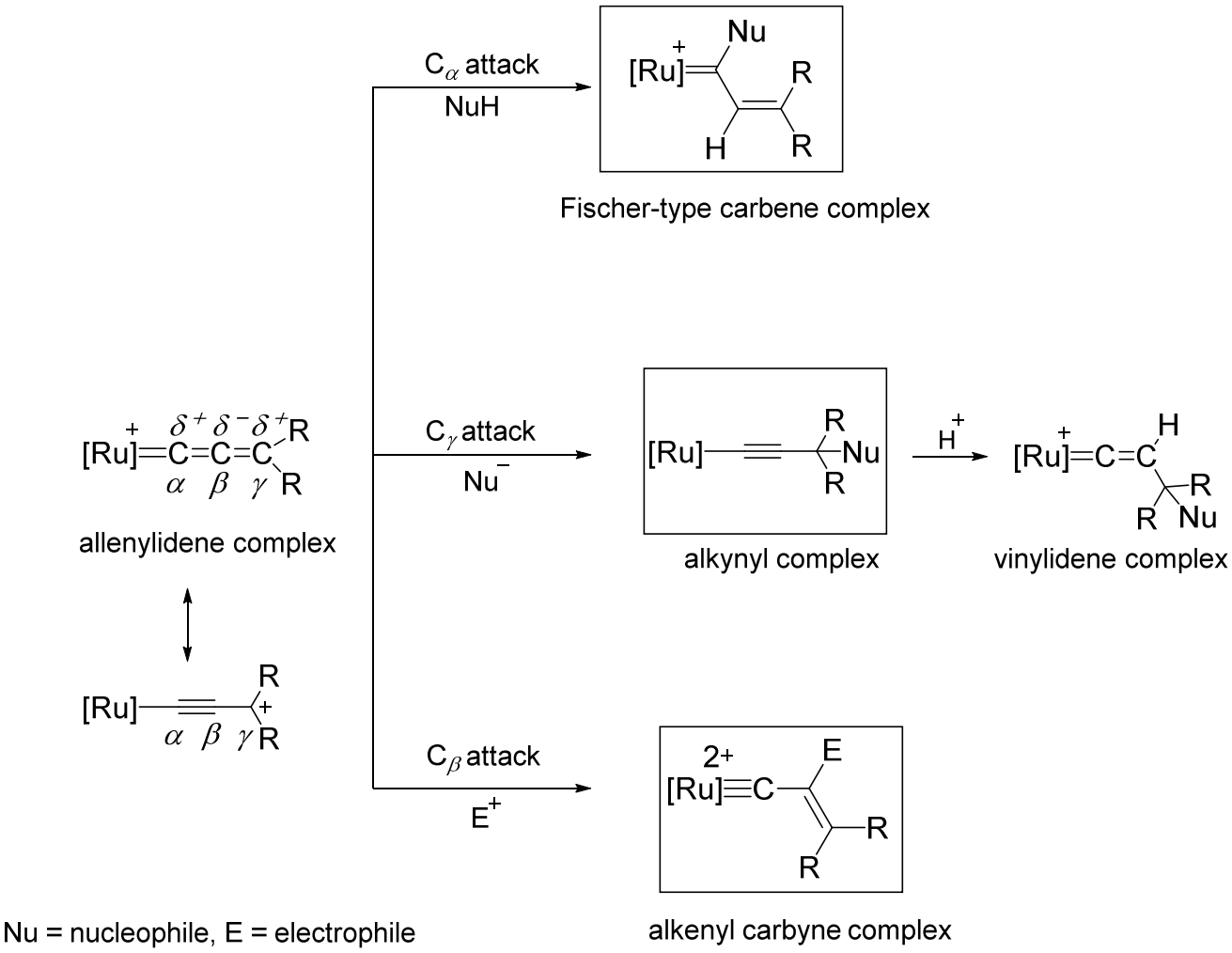
224 **225**



225a **225b** **225c** **226**

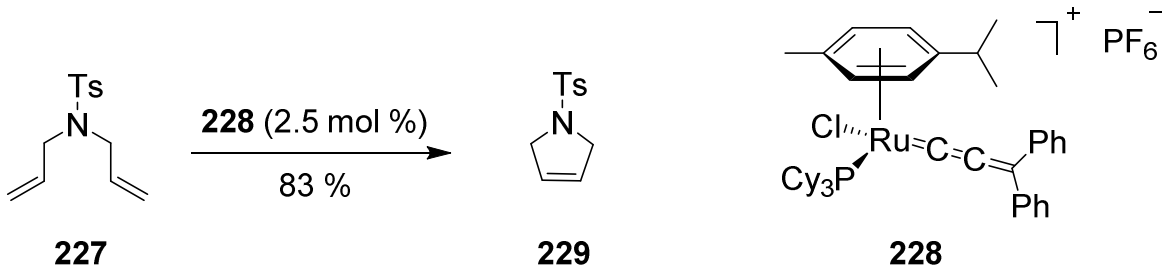
Metal allenylidene complexes are related to a class of metallacumulenes $L_nM(=C)_mCR_2$ with m = 2. Metallacumulenes possess *π*-conjugated $(=C)_m$ moieties, which allow electronic communication between metal centers and remote functional groups. Such compounds could be potentially useful as NLO materials and molecular wires.[155-157] While vinylidenes and allenylidenes of transition metals are quite common,[156,158] reports on the existence metallacumulenes with m = 3, 4 are very rare.[159] The longest isolated cumulenic chain $(CO)_5M(=C)_6C(NMe_2)_2$ (M = Cr, W) was recently synthesized by Fischer et al.[160]

According to theoretical studies, the regioselectivity of both nucleophilic and electrophilic additions to metal allenylidenes is frontier-orbital controlled with the LUMO mainly localized at the *α*-carbon atom and *γ*-carbon atom and the HOMO at the *β*-carbon atom. It has been found that the contributions of the *α*-carbon atom and *γ*-carbon atom to the LUMO are quite similar. Therefore, a nucleophile is expected to attack either the allenylidene *α*-carbon atom or *γ*-carbon atom to afford Fischer-type carbene or alkynyl complexes, respectively, whereas the addition of an electrophile to the *β*-carbon atom releases an alkenyl carbyne complex (Scheme 7).[156]



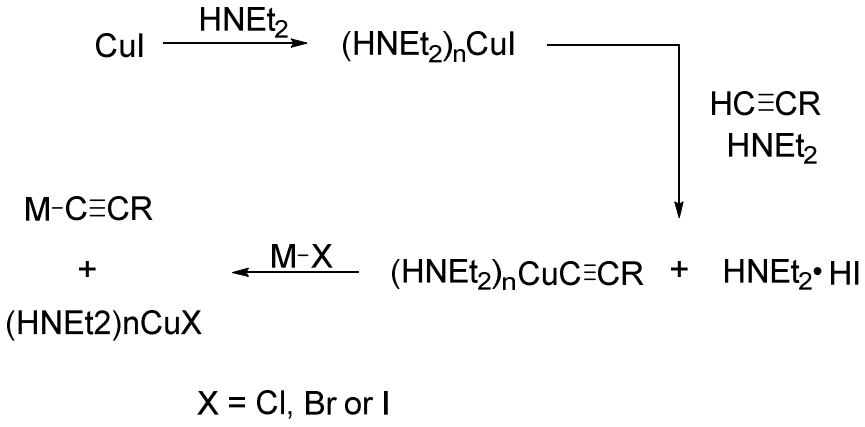
Scheme 7. Reactivity of allenylidene complexes.[156]

Only recently metal allenylidenes intermediates and complexes have emerged as catalyst precursors in alkene metathesis or catalyst intermediates in propargylation reactions.[161,162] The first catalytic application of allenylidene complexes in alkene metathesis was described in 1998 by Dixneuf, Fürstner et al.[163] As an illustrative example for RCM (Ring Closing Metathesis), using 2.5 mol % of ruthenium complex **228**, diene **227** was quantitatively converted into alkene **229**.



227 **229** **228**

Conventionally transition metal *σ*-acetylide complexes were prepared either by the reaction of metal halides with an alkynyl compound of an alkali metal,[164] magnesium,[153,165] or copper(I),[165] or by the direct dehydrohalogenation[166] in the reaction between metal halides and active acetylenes having electron-withdrawing substituents. In 1977, Sonogashira, Hagihara et al. developed a convenient method for the synthesis of *σ*-alkynyl complexes of transition metals.[167] The direct reaction of metal halides with terminal acetylene derivatives in the presence of catalytic amounts of copper(I) iodide in diethyl amine is usually carried out under mild reaction conditions, efficiently yielding metal *σ* alkynyl complexes (Scheme 8).

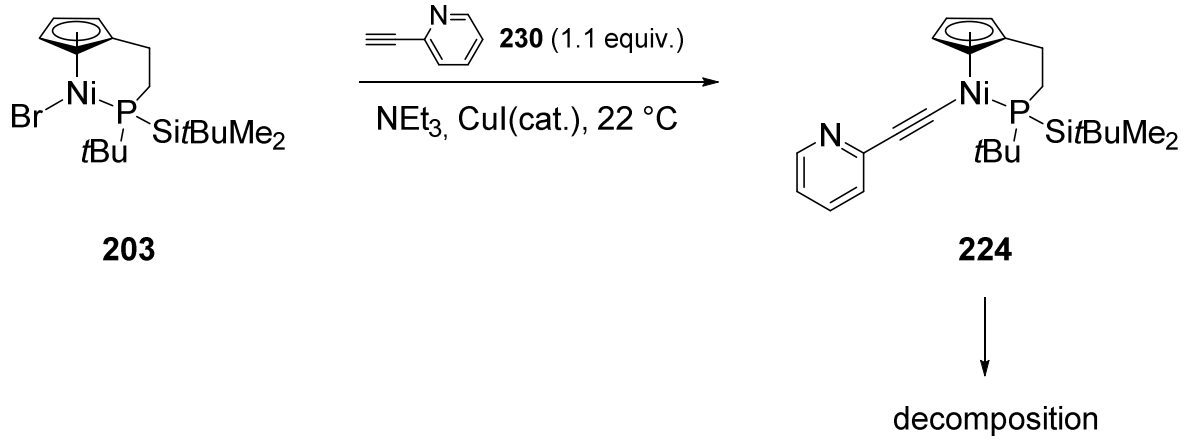


Scheme 8. Preparation of transition metal *σ* alkynyl complexes *via* copper(I) catalysed dehydrohalogenation.[167]

Bruce et al.[154] extended this methodology to the synthesis of cyclopentadienyl nickel *σ* alkynyl complexes. Butenschön et al.[16,126] followed this route in the preparation of

a great many of cyclopentadienyl nickel σ alkynyl chelate complexes. Humphrey et al.[168] applied the procedure for the synthesis of the nonchelated cyclopentadienylnickel σ-pyridylalkynyl complexes.

Analogously to the preparation of the chelate **222** (*vide supra*), **203** was treated with 2-ethynylpyridine (**230**)[169] in trimethylamine in the presence of a catalytic amount of copper(I) iodide, affording **224** as a green solid.

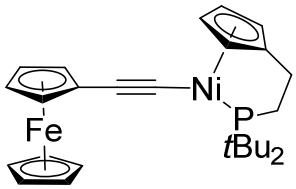


203 **224**

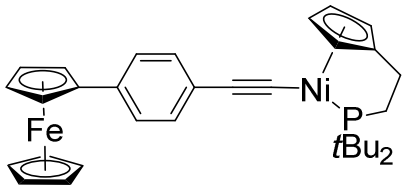
Unlike **222**, the silylphosphane functionalized complex **224** is unstable, decomposing gradually even at –30 °C under inert atmosphere. The decomposition in argonated solvents takes place even faster, so that only ^{1}H and ^{31}P NMR analyses were possible to carry out. The ^{31}P NMR spectrum of **224** exhibits a resonance at δ = 35.8 ppm which is shifted to lower fields as compared to **203** (δ = 24.9 ppm), due to the enhanced electron-withdrawing effect of the 2-ethynylpyridinyl group. The signals for the pyridine hydrogen atoms appear as multiplets in the ^{1}H NMR spectrum at δ = 6.86, 702-7.03, 7.35-7.39 and 8.34 ppm. These results are in accord with those reported for **222**.[16,126] Further conversions of **224** could not be performed, due to its instability.

It was interesting to study whether the change of the electronic properties of an alkynyl substituent would have influence on the stability of the alkynyl-nickel complexes. Therefore, the Bruce-coupling reactions with such electron-rich alkynes

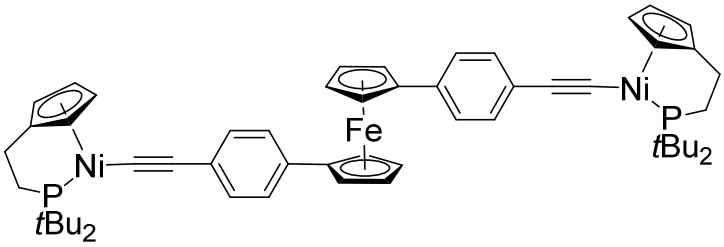
as ferrocenylalkynes were envisaged. Kohser et al. reported bi- and tri-metallic chelates **231**-**233**.[126]



231



232

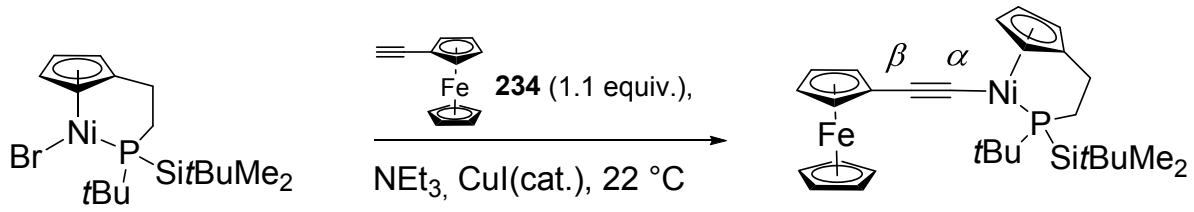


233

In particular, the ^{13}C NMR spectra are featured by the resonances for the alkynyl group which appear as doublets with $^{2}J_{P,C}$ = 34.1-34.7 Hz, assigned to the carbon atom next to nickel (*α*-carbon atom), and $^{3}J_{P,C}$ = 1.7-1.9 Hz, referred to the carbon atom bound to the ferrocenyl moiety (*β*-carbon atom).

The cyclovoltammetry of **231** and **233** showed each two different reversible waves at $E_{1/2}$ = –244 mV (Fe(II)-Fe(III) redox process), 219 mV (Ni(II)-Ni(III)) mV, and at $E_{1/2}$ = –457 mV (Fe(II)-Fe(III)), 215mV (Ni(II)-Ni(III)), respectively. However, for **232** only one redox process ($E_{1/2}$ = 25 mV) was indicated, due to the low oxidation potentials of the ferrocenyl and nickel moieties, which fall within the same range. Among these complexes, **233** shows the highest oxidation potential of the ferrocenyl group (ΔE = 605 mV), indicating an enhanced oxidation stability with an increasing substitution (the measured potentials refer to FcH/FcH^{+}).

In this work, the bimetallic complex **235** was obtained by the reaction of **203** with ethynylferrocene (**234**)[170] in 63 % yield. Compound **235**, if crystalline, is quite stable in the air. In the ^{1}H NMR spectrum the resonances of the hydrogen atoms of the unsubstituted ferrocenyl ring appear as a singlet at δ = 4.08 ppm, while two multiplets at δ = 3.91-3.92 and 4.12 ppm were assigned to the hydrogen atoms of the substituted ferrocenyl ring.



203 **235**

The ^{13}C NMR spectrum of **235** shows a doublet at δ = 82.7 ppm with $^{2}J_{P,C}$ = 30.9 Hz and a singlet at δ = 112.0 ppm which were assigned to α- and β-carbon atoms, respectively. These results are in accord with those reported for **231**.[126] The IR absorption for the alkyne moiety observed at 2093 cm^{-1} is shifted to higher wavenumbers as compared to **231**, demonstrating the enhanced positive inductive effect of the silyl substituent at the phosphorus group. The ^{31}P NMR spectrum exhibits a resonance at δ = 33.8 ppm confirming the coordination of the phosphane group to nickel.

The cyclovoltammetry of **235** (Figure 4) shows two quasi reversible waves at $E_{1/2}$ = –47.6 mV, indicating the Ni(II)-Ni(III) redox process, and at $E_{1/2}$ = 34.1 mV, which is assigned to the Fe(II)-Fe(III) redox process. Additionally, there is an irreversible wave at 153.0 mV due to an irreversible oxidation process, which could be assigned to the phosphane group. Remarkably, the oxidation potential of the ferrocenyl group in **235** (ΔE(**235**) = 78.5 mV) is much lower than that of the related compound **231** (ΔE(**231**) = 371.0 mV), indicating easier oxidizability of the ferrocene moiety, presumably, due to the enhanced electron donating effect of the silyl substituent at phosphorus. Similar observations were made for the difference between

the oxidation potentials of the nickel fragments in **231** (ΔE(**231**) = 168.0 mV) and in **235** (ΔE(**235**) = 6.3 mV).

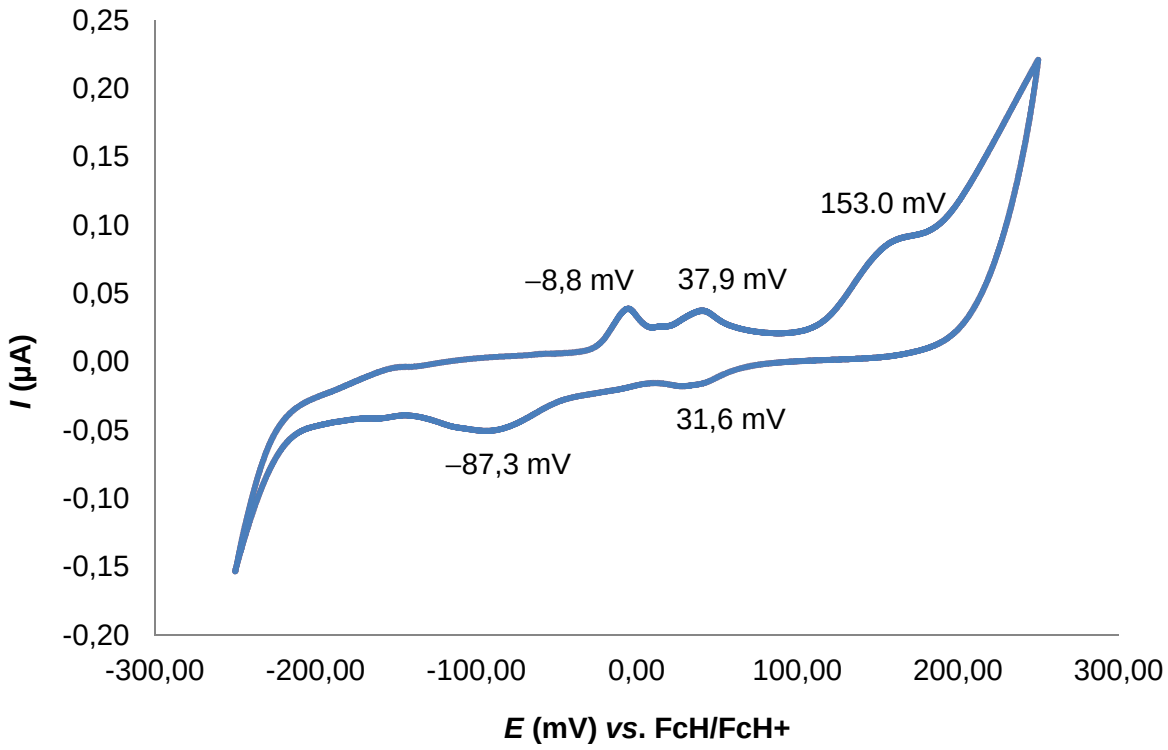
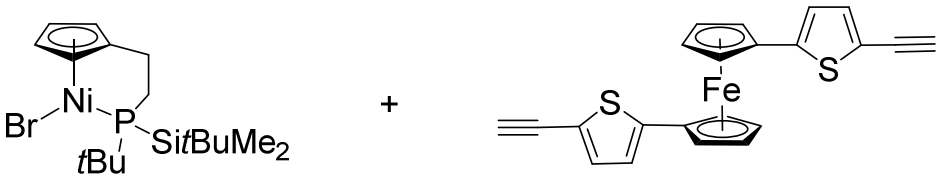


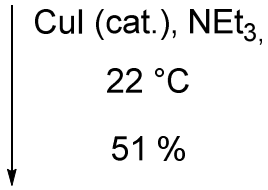
Figure 4. Cyclovoltammogram of **235**. Cyclovoltammetry data (potentials in mV *vs*. FcH/FcH^+, *v* = 100 mV/s, *T* = 22 °C, 2 mmol/L NBu_4PF_6, solvent dichloromethane).

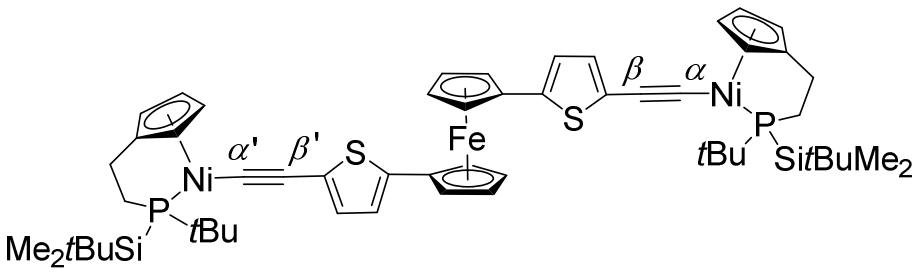
The corresponding reaction with of **203** with 1,1'-bis-(5-ethynyl-2-thienyl)ferrocene (**236**)[171] led to the trimetallic complex **237** in 51 % yield. **237** is less stable than **235**, being slowly decomposed at –30 °C even under protective atmosphere. However, in argonated solvents **237** is stable enough to be characterized by the ^{1}H, ^{13}C and ^{31}P NMR spectroscopy, which show only one set of signals, although the compound bears two stereogenic phosphorus atoms. As in the case referred to **114** (*vide supra*), the phenomenon can be explained by the insufficient difference between the hydrogen, carbon and phosphorus atoms in **237** to be resolved by NMR spectroscopy due to the remote position of the stereogenic phosphorus atoms.

In the ^{1}H NMR spectrum the resonances of the hydrogen atoms of the ferrocenyl ring appear as multiplets at δ = 4.06-4.07 and 4.27-4.28 ppm. To the CH-groups of the thiophenyl substituents the doublets at δ = 6.52 (d, $^{3}J_{H,H}$ = 3.6 Hz) and 6.56 (d, $^{3}J_{H,H}$ = 3.7 Hz) were assigned. All hydrogen resonances of the ferrocenyl and thiophenyl moieties are shifted to the higher fields in **237** as compared to the ferrocene **236**, presumably, due to the electron-donating effect of the nickel fragment. The ^{13}C NMR spectrum of **237** is featured by a doublet at δ = 98.5 ppm with $^{2}J_{P,C}$ = 30.8 Hz and a singlet at δ = 109.1 ppm which were assigned to α- and β-carbon atoms, respectively. The resonance of the α(α')-carbon atom in **237** is shifted to the lower fields, while the signal of the β(β')-carbon atom is slightly shifted to the higher field as compared to **235**. The IR absorption for the alkyne moiety observed at 2071 cm^{-1} is shifted to lower wavenumbers as compared to **235**, demonstrating the resonance effect of the thiophenyl group. The ^{31}P NMR spectrum exhibits a resonance at δ = 35.0 ppm confirming the coordination of the phosphane group to nickel.



203 **236**





237

Similar to **235**, the cyclovotammetry of **237** (Figure 5) shows two quasi reversible waves at $E_{1/2}$ = 54.1 mV, indicating the Ni(II)-Ni(III) redox process, and at $E_{1/2}$ = 32.3 mV, which is assigned to the Fe(II)-Fe(III) redox process. Additionally, there is an irreversible wave at 155.0 mV due to an irreversible oxidation, which could be assigned to the phosphane group. Moreover, there is a quasi-reversible process with the wave at $E_{1/2}$ = –166.5 mV, probably, due to the presence of sulfur.

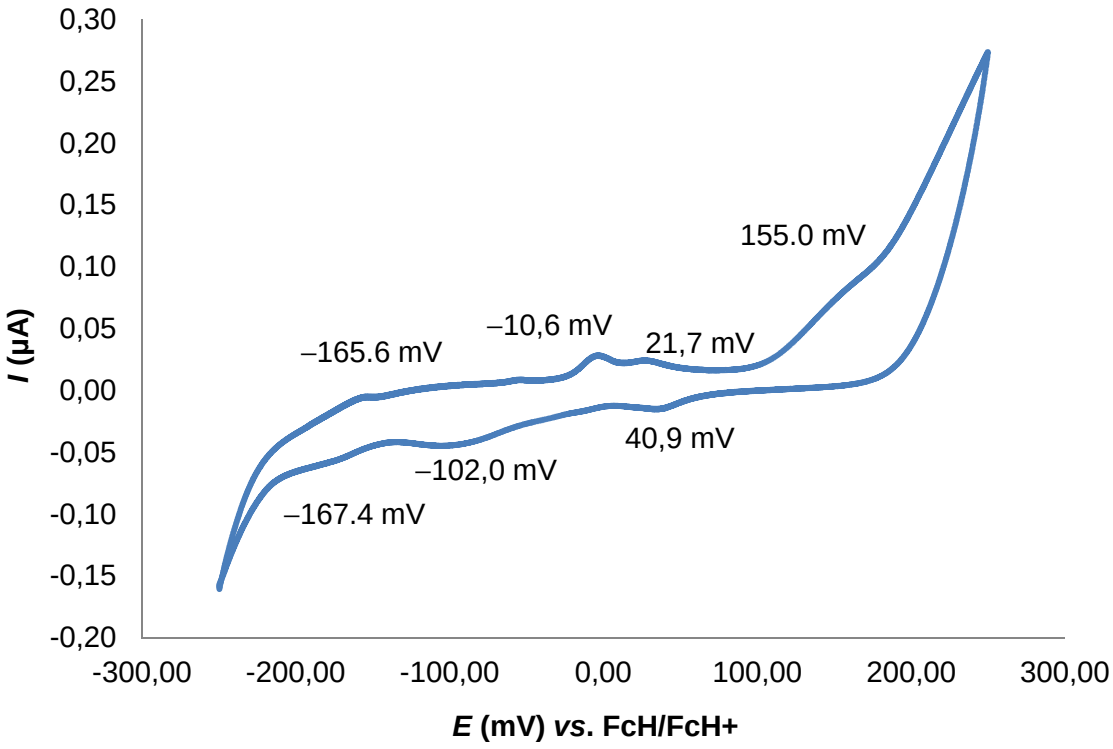


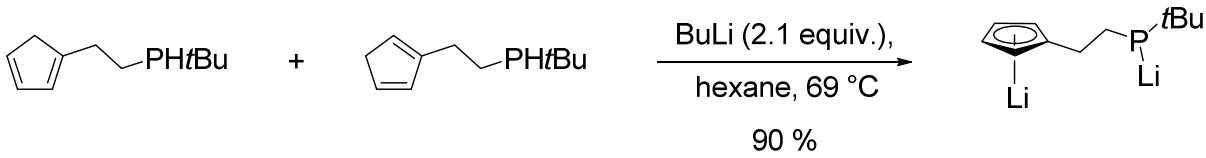
Figure 5. Cyclovoltammogram of **237**. Cyclovoltammetry data (potentials in mV *vs*. FcH/FcH^+, *v* = 100 mV/s, *T* = 22 °C, 2 mmol/L NBu_4PF_6, solvent dichloromethane).

The oxidation potential (ΔE_{237} = 78.5 mV) of the ferrocenyl group in **237** is slightly higher than that of **235** (ΔE = 13 mV). The same value was observed for the difference between the oxidation potentials of the nickel fragments in **237** (ΔE_{237} = 19.2 mV) and in **235**. These results resemble those, reported for **231** and **233**,[126] indicating an enhanced oxidation stability of the ferrocenyl and nickel fragments with an increasing substitution.

Alkynyl ferrocenes, such as **231**-**233**, **235** and **237**, can be potentially used as building blocks in the molecular electronics.[171,172]

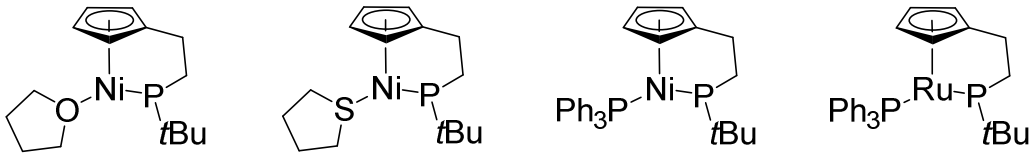
3. Summary and Outlook

In the scope of this work, two approaches to still unknown late-transition-metal cyclopentadienyl phosphido chelate complexes were attempted. The first method implied the reaction of the dilithiated ligand system **54** with a variety of late transition metal complexes. **54** was isolated as a highly pyrophoric compound by the double lithiation of new secondary phosphane functionalized cyclopentadiene ligand systems **66** and **67**, prepared from the reaction of the corresponding lithium phosphide with spiro[2.4]hepta-4,6-diene (**64**) in a nucleophilic cyclopropyl ring opening reaction.



66 **67** **54**

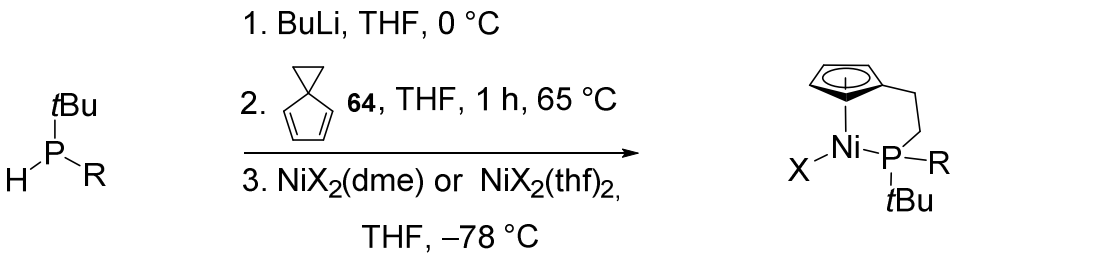
The corresponding phosphido complexes were observed by the spectrometric analyses of the crude reaction mixtures. The isolation as well as a full characterization of complexes **73**, **74**, **76** and **77** failed.



73 **74** **76** **77**

Further works using other ligands bound to a metal, capable of stabilizing reactive phosphido complexes, are needed.

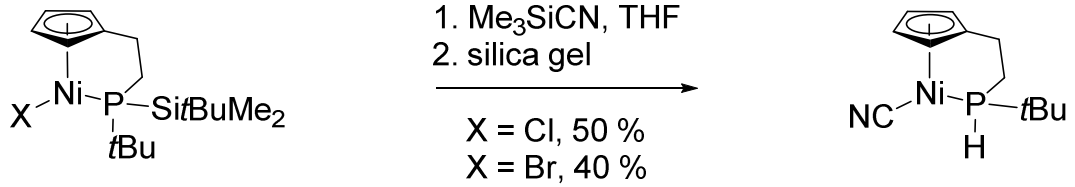
The second approach was based on the deprotonation or desilylation of the cyclopentadienyl complexes bearing a secondary phosphane or a silylphosphane functionalized tethers. The corresponding nickel compounds were prepared as the first late-transition-metal complexes of their kind. Silylphosphane substituted complexes **202**-**204** were synthesized from the corresponding new bulky secondary silylphosphanes **191** and **192**.



191: R = Si*t*BuMe$_2$
192: R = Si*i*Pr$_3$

202: X = Cl, R = Si*t*BuMe$_2$, 56 %
203: X = Br, R = Si*t*BuMe$_2$, 69 %
204: X = Br, R = Si*i*Pr$_3$, 53 %

The sequence of the ligand substitution reaction and a protiodesilylation of the phosphorus atoms in **202** and **203** led to the first secondary phosphane containing complex **211**. The crystal structure analysis confirmed the formation of **211**.



202: X = Cl,
203: X = Br

211

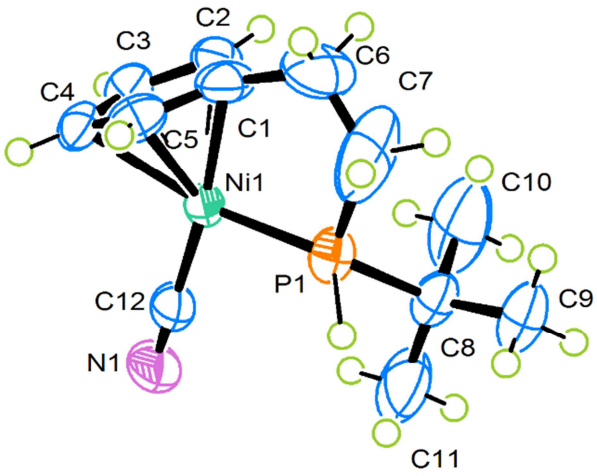
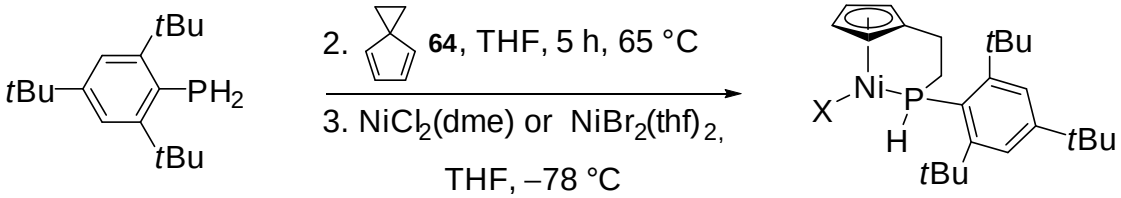


Figure 6. Structure of **211** in the crystal. Representation **211a** (50 % propability level, bond lengths and angles are listed in Figure 3).

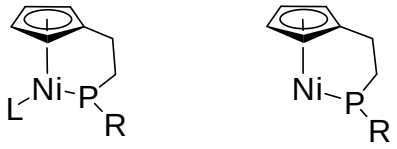
Bulky secondary phosphane containing complexes **142** and **143** were prepared from the corresponding bulky phosphane **111**, introducing a more direct route to this class of compounds.



111

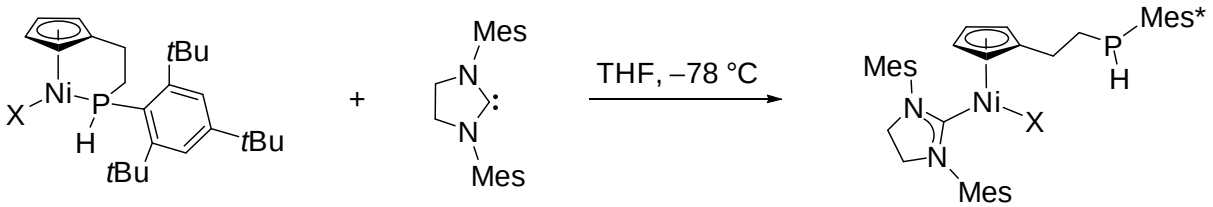
142: X = Cl, 48 %
143: X = Br, 69 %

The desilylation of the phosphane groups in **202**-**204** as well as the deprotonation of the P–H bonds in **142** and **143** in the presence a variety of ligands (THF, THT, pyridine, triphenylphosphane or 4-isocyanobenzonitrile) did not lead to the isolation and a full characterization of the desired phosphido complexes **H** or their unsaturated analogs **I**.



H **I**

In the reactions of **142** and **143** with SIMes (**161**) NHC functionalized complexes with fully dissociated phosphane tethers **162** and **163**, respectively, were obtained. The crystal structure analysis of **163** shows the sterically overcrowded environment at nickel center.



142: X = Cl
143: X = Br

161

162: X = Cl, 63 %
163: X = Br, 85 %

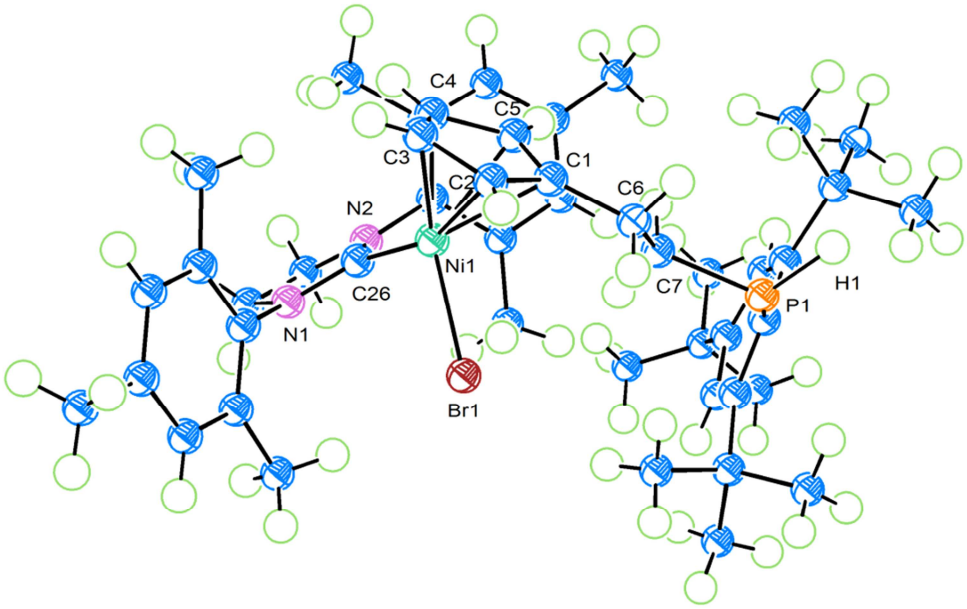
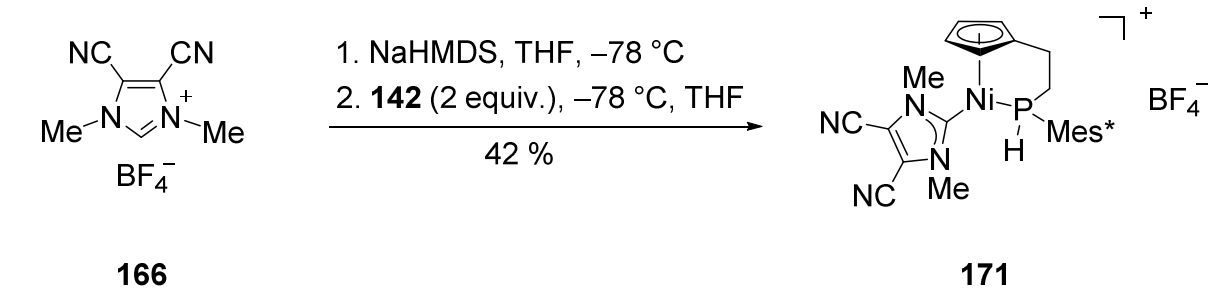
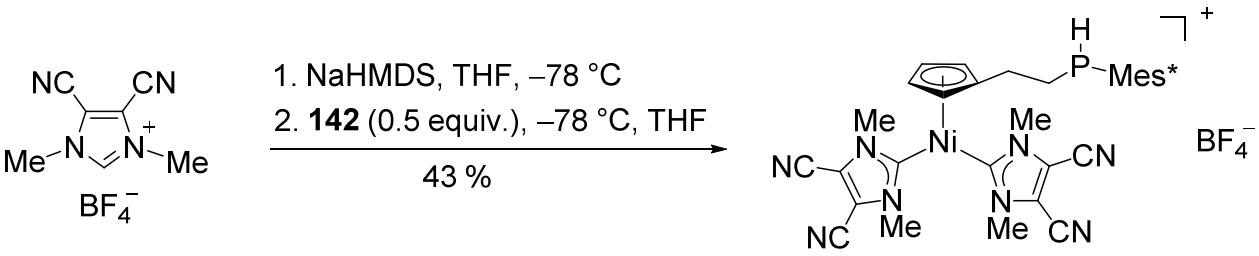


Figure 7. Crystal structure of **163** (views A-C, 50 % probability level). Key atoms are labeled (bond lengths and angles are listed in Figure 2).

The corresponding reactions of **142** with 0.5 or 2.0 equivalents of a less bulky and less electron-rich Im$(CF_3)_2$*N*Me_2-precursor **166** lead to the chelate **171** or the phosphane-dissociated compound **172**, respectively.

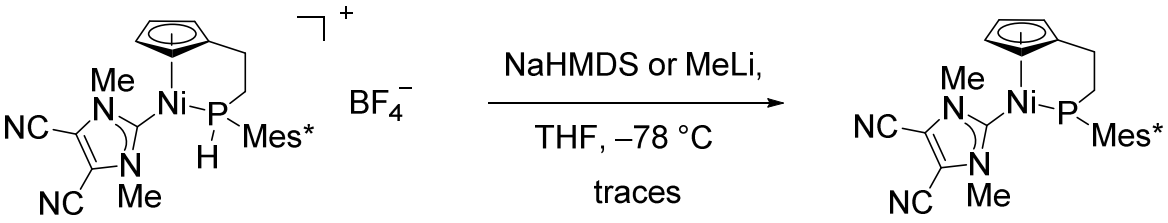


166 **171**



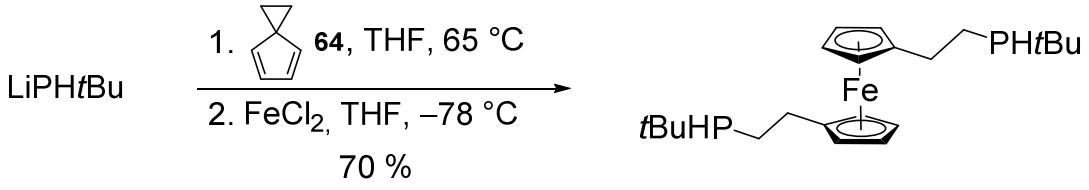
166 **172**

The deprotonation reactions of **171** with different bases did not result in the isolation and a full characterization of the expected phosphido compound **173**. The spectrometric analysis of the crude reaction mixture indicated, however, the formation of **173**.



171 **173**

Novel air-stable ferrocene derivative with secondary phosphane functionalized ethylene chains **114** was obtained by the reaction of lithium phosphide **65** with **64**. Related ferrocene derivatives with alkylidene spacers were previously reported by Hey-Hawkins et al.[92]



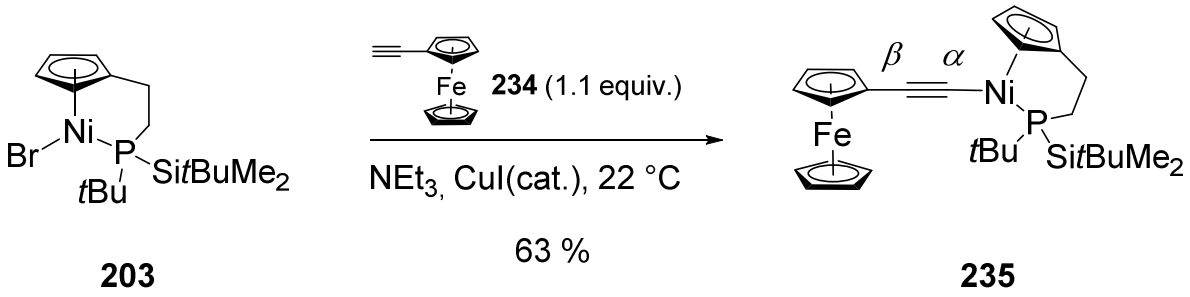
65 **114**

The first phospha-bridged [5.5]ferrocenophanes **123a** and **123b** were obtained as *cis*- and *trans*-isomers, respectively, by the dilithiation of **114** followed by treatment with 1,1'-di(2-bromoethyl)ferrocene (**137**).

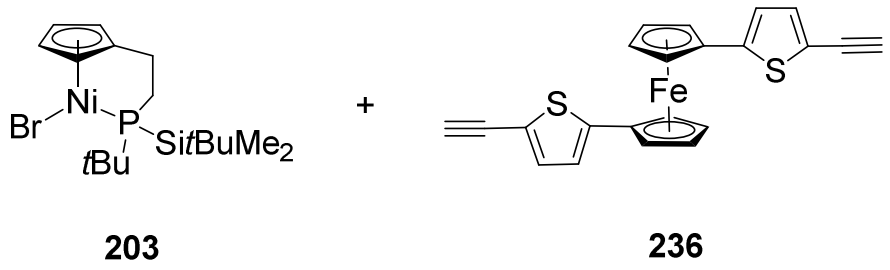
123a **123b**

Diphosphanes **114**, **123a** and **123b** might serve as the bidentate phosphine ligands in the complexation to transition metals.

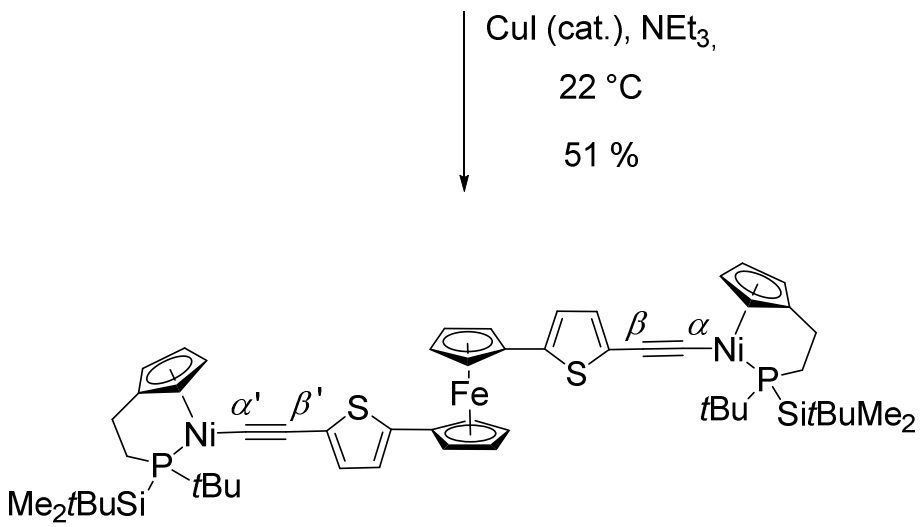
New alkynyl ferrocene derivatives **235** and **237** were obtained in Bruce-coupling reactions of **203** with alkynes **234** and **236**, respectively.



203 **235**



203 **236**



237

The cyclovoltammetry showed that **235** and **237** are easier oxidized than the related di-*tert*-butylphosphane substituted complexes **231** and **233**.

In summary, the isolation and the characterization of late-transition-metal cyclopentadienyl chelate complexes with a phosphido function could not be realized. However, their formation was observed by the spectrometric analyses, indicating that the complexes were formed, but, most probably, decomposed due to the reactive nature

of the metal-phosphido function. It will be interesting to investigate the catalytic properties of new silylphosphane and secondary phosphane functionalized complexes in the future.

Further, functionalization at the silylphosphane or secondary phosphane groups or at the carbon atoms in the tether *via* introduction of electron withdrawing alkyl or aryl substituents would be interesting in terms of investigation of the electronic fine tuning of the corresponding complexes.

4. Experimental Section

4.1 General Part

All operations involving air-sensitive organometallic compounds were carried out in an argon or nitrogen atmosphere, using standard vacline and Schlenk techniques. All glassware was flame-dried at reduced pressure and filled with a protective gas (repeated three times). Diethyl ether, 1,2-dimethoxyethane (DME), toluene, hexane and tetrahydrofuran (THF) were distilled from sodium benzophenone ketyl. Methylene chloride (DCM), acetonitrile (CH_3CN), ethyl acetate and triethylamine (Et_3N) were distilled from calcium hydride. Petroleum ether was distilled from calcium chloride. All chiral compounds were used in racemic form. Chemicals were either purchased and used as received or they were prepared according to literature procedures: LiPH*t*Bu (**65**),[72] spiro[2.4]hepta-4,6-diene (**64**),[174] *t*BuPCl$_2$ (**21**),[42] *t*BuPH$_2$BH$_3$ (**193**),[143] (2,4,6-tri-*tert*-butylphenyl)-phosphane (**111**),[111] 1,3-bis-(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene (**161**),[175] NiCl$_2$(thf)$_2$,[77] NiCl$_2$(py)$_2$,[78] RuCl$_2$(PPh$_3$)$_3$,[79] NiBr$_2$(thf)$_2$,[111] NiCl$_2$(dme),[176] NiBr$_2$(dme),[111] Fe(CO)$_4$I$_2$,[90] 1,3-dimethyl-4,5-dicyano-imidazolium tetrafluoroborate (**167**),[130] 1,1'-di-(2-bromoethyl)ferrocene (**137**),[109] (2,4,6-tri-*tert*-butylphenyl)(*tert*-butyldimethylsilyl)phosphane (**186**),[139] (*tert*-butyl-dimethylsilyl)phenylphosphane (**190**),[140] phenylphosphane,[177] 2-ethynylpyridine (**230**),[169] ethynylferrocene (**234**)[170] and 1,1'-bis-(5-ethynyl-2-thienyl)ferrocene (**236**).[171]

Preparative column chromatography was carried out by flash chromatography.[173] 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 a protective gas.

Thin layer chromatography (**TLC**) was performed using aluminium TLC plates coated with the silica gel 60F$_{24}$ (Merck) combined with the polygram® Alox N/UV$_{254}$ from Macherey-Nagel. The spots were visualized with the help of a UV-lamp (λ = 254 nm).

Infrared Spectra (**IR**) were recorded on a Perkin-Elmer FT 1710 spectrometer as golden gate attenuated total reflection (ATR). Signal intensities are abbreviated as s (strong), m (medium), w (weak) or br (broad).

High resolution mass spectra (**HRMS**) were recorded with the peak-matching method in Micromass GCT (TOF MS EI); ionization potential 70 eV, Micromass LCT spectrometer with Lock-Spray-Unit (ESI). All values are given in atomic units of mass per element charge (*m*/*z*).

^{1}H NMR spectra were measured using instruments Bruker WP 200 (200.1 MHz) and AVS 400 (400.1) at 25 °C. The chemical shifts refer to residual solvent signals of chloroform (δ = 7.26 ppm), benzene (δ = 7.06 ppm), THF (δ = 1.72, 3.58 ppm) and acetone (δ = 2.05 ppm) as internal standards.

^{13}C NMR spectra were measured using instruments Bruker WP 200 (50 MHz) and AVS 400 (100 MHz) at 25 °C. The chemical shifts refer to residual solvent signals of chloroform (δ = 77.16 ppm), benzene (δ = 128.06 ppm), THF (δ = 67.21, 25.31 ppm) and acetone (δ = 29.84, 206.26 ppm) as internal standards. Signal assignments in ^{13}C NMR spectra are based on DEPT, COSY, HMQC and HMBC measurements.

^{31}P NMR spectra were measured using an instrument Bruker AVS 400 (162 MHz). An aqueous solution of H_3PO_4 (85 %) was used as external reference.

^{11}B NMR spectra were measured using Bruker AVS 400 (128 MHz). A solution of BF_3 diethyl ether complex in Et_2O (15 %) was used as the external standard.

The multiplicity of the peaks are abbreviated as s = singlet, d = doublet, t = triplet, m = multiplet. The deuterated solvents $CDCl_3$, C_6D_6 and $(CD_3)_2CO$ were distilled under argon and used immediately. Atom numbering is arbitrary and does not correspond to the IUPAC.

Cyclovoltammetry was performed using Gamry Instruments Reference 600 potentiostat/galvanostat/ZRA with 0.1 mol/L tetrabutylammonium hexafluorophosphate electrolyte in dichloromethane at 22 °C, reference electrode Ag/Ag^+ in dichloromethane with 0.01 mol/L $AgNO_3$ and 0.1 mol/L tetrabutylammonium hexafluorophosphate. Electrode material for the working and counter electrode was platinum. The system

was calibrated with ferrocene/ferrocnium (FcH/FcH^+), and the measured potentials refer to FcH/FcH^+.

Combustion analyses were carried out for CHN Rapid (Heraeus) with acetanilide as standard. All values are given as mass percentages.

Melting points (**m**. **p**.) were determined with the Electrothermal IA 9200 Series Digital Melting Point Apparatus.

Inductively-Coupled-Plasma Mass Spectrometry (ICP-MS) measurements were performed on a XSeriesII from Thermo Fisher Scientific in the Institute of Inorganic Chemistry, Leibniz Universität Hannover (AK Analytik)

4.2 General Procedures

4.2.1 General Procedure for Reactions of 54 with Halo Complexes of Late Transition Metals (GPI)

At –78 °C a solution of **54** (1.0 equiv.) in THF was added dropwise to a suspension of nickel(II) or ruthenium(II) complexes (1.5 equiv.) in THF. The reaction mixture was slowly warmed to 22 °C and stirred for 2 h at this temperature. After solvent removal at reduced pressure the residue was taken up with dichloromethane and filtered through a 3 cm thick layer of Celite®. The crude products were analyzed by mass spectrometry.

4.2.2 General Procedure for the Syntheses of Cyclopentadienylethyl (2,4,6-Tri-*tert*-butylphenyl)phosphane Nickel Complexes 142 and 143 (GPII)

At –78 °C butyllithium (1.0 equiv., 2.5 M solution in hexane) was added to (2,4,6-tri-*tert*-butylphenyl)phosphane (**111**, 1.0 equiv.) in THF. After 0.5 h the reaction mixture was allowed to reach 22 °C and was stirred for 1 h at this temperature.

Spiro[2.4]hepta-4,6-diene (**64**, 1.1 equiv.) was added, and the reaction mixture was stirred at 65 °C for 5 h. After solvent removal at reduced pressure the residue was washed with hexane and dried in vacuum. The residue was dissolved in THF and slowly dropped to a cold suspension (–78 °C) of nickel(II) chloride or bromide THF or DME complexes (1.5 equiv.) in THF. The reaction mixture was slowly warmed to 22 °C and stirred for 2 h at this temperature. After solvent removal at reduced pressure the residue was taken up with toluene and filtered through a 3 cm thick layer of Celite®. The filtrate was concentrated, and the products were crystallized from toluene at –30 °C.

4.2.3 General Procedure for Reactions of 142 and 143 with *N*-heterocyclic Carbene SIMes (161) (GPIII)

At –78 °C SIMes (**161**, 1.0 equiv.) was added to **142** or **143** (1.0 equiv.) in THF. After 0.5 h the reaction mixture was allowed to reach 22 °C and was stirred for 2 h at this temperature. After solvent removal at reduced pressure the residue was taken up in diethyl ether and filtered through a 3 cm thick layer of Celite®. After solvent removal the crude products were purified by column chromatography.

4.2.4 General Procedure for the Syntheses of Cyclopentadienylethyl(silyl)-phosphane Nickel Complexes 202-204 (GPIV)

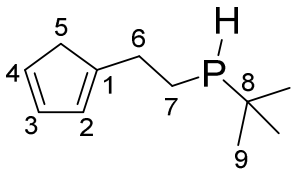
At 0 °C butyllithium (1.0 equiv., 2.5 M solution in hexane) was added to the silylphosphane (1.0 mmol) in THF. The resulting bright yellow solution was stirred for 1 h at 22 °C. Spiro[2.4]hepta-4,6-diene (**64**, 1.1 equiv.) was added, and the reaction mixture was stirred at 65 °C until it turned colorless (3-4 h). After the solvent removal at reduced pressure the residue was washed with hexane and dried in vacuum. The residue was dissolved in THF and slowly dropped into a cold suspension (–78 °C) of nickel(II) chloride or bromide THF or DME complexes (1.5 mmol) in THF. The reaction mixture was slowly warmed to 22 °C and stirred for 1-2 h. After solvent removal at reduced pressure the residue was taken up in boiling pentane and filtered through a frit covered with a 3 cm thick layer of Celite®. After solvent removal the products were recrystallized twice from pentane at –30 °C.

4.2.5 General Procedure for Bruce-coupling Reactions of 203 with Terminal Alkynes (GPV)

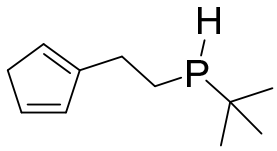
At 22 °C a terminal alkyne (1.1 equiv.) was added to a suspension of **203** (1.0 equiv.) and catalytic amount of copper(I) iodide in NEt_3. After stirring the reaction mixture for 3-15 h the solvent was removed at reduced pressure. The the residue was taken up in diethyl ether or in ethyl acetate and filtered through a 3 cm thick layer of Celite®. After solvent removal the crude products were purified by column chromatography.

4.3 Syntheses of Ligands

4.3.1 *tert*-Butyl(2-cyclopentadienylethyl)phosphanes 66 and 67



66



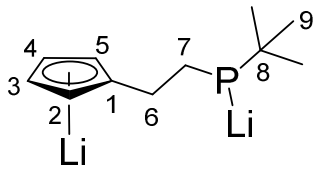
67

At 22 °C spiro[2.4]hepta-4,6-diene (**64**, 0.18 g, 1.9 mmol) was added to lithium *tert*-butyl phosphide (**65**, 0.17 g, 1.7 mmol) in THF (20 mL). After stirring at 65 °C for 1 h the solvent was removed at reduced pressure. The residue was washed with hexane (3 x 10 mL), and residual solvent was removed at reduced pressure. The residue was suspended in dichloromethane (10 mL) and treated with degassed water (10 mL). After 10 min of rapid stirring the layers were separated. The aqueous layer was extracted three times with dichloromethane (10 mL each), and the combined organic layers were dried over $MgSO_4$. The solution was filtered through a frit covered with a 3 cm thick layer of Celite®, and the solvent was removed at reduced pressure. The resulting pale yellow oil was taken up with hexane (30 mL) and filtered through a frit covered with a 1 cm thick layer of SiO_2. After solvent removal at reduced pressure the product was obtained as a mixture of two regioisomers **66** and **67** [1.1:1, 0.24 g, 1.3 mmol, 80 %, purity ≥ 80 % (^{31}P NMR)] as a colorless oil.

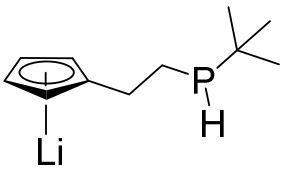
^{1}H NMR (400 MHz, $CDCl_3$, major isomer): δ = 1.15 (d, $^3J_{P,H}$ = 11.8 Hz, 9H, 9-H), 1.54-1.73 (m, 1H, 7-H), 1.96-2.08 (m, 1H, 7-H), 2.45-2.68 (m, 2H, 6-H), 2.90 (m, 2H, 5-H), 3.00 (dm, $^1J_{P,H}$ = 198.7 Hz, 1H, PH), 6.20 (m, 1H, 2-H), 6.25-6.27 (m, 1H, 3-H or 4-H), 6.41-6.47 (m, 1H, 3-H or 4-H) ppm. - ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 17.0 (d, $^2J_{P,C}$ = 14.0 Hz, C-7), 26.9 (d, $^1J_{P,C}$ = 6.1 Hz, C-8), 28.5 (d, $^1J_{P,C}$ = 15.1 Hz, C-6), 30.2 (d, $^2J_{P,C}$ = 12.1 Hz, C-9), 41.3 (s, C-5), 126.7 (d, $^4J_{P,C}$ = 0.3 Hz, C-2), 130.8 (s,

C-3 or C-4), 132.5 (s, C-3 or C-4), 149.9 (d, $^{3}J_{P,C}$ = 10.3 Hz, C-1) ppm. - ^{31}P NMR (162 MHz, $CDCl_3$): δ = –23.9 (major isomer), –23.7 ppm (minor isomer).

4.3.2 Dilithio (2-*tert*-Butylphosphidoethyl)cyclopentadienyl (54) and Lithio (2-*tert*-Butylphosphanylethyl)cyclopentadienyl (72)



54



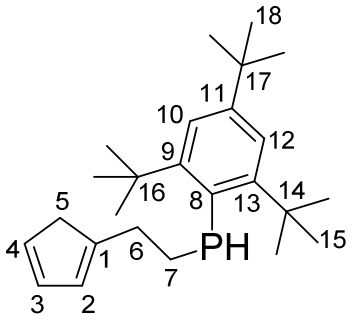
72

At 22 °C butyllithium (0.9 mL, 2.3 mmol, 2.5 M solution in hexane) was added to the mixture of **66** and **67** (0.2 g, 1.1 mmol) in hexane (40 mL). The resulting suspension was stirred for 2 h at 69 °C. The suspension was filtered through a frit and the residue was washed with hexane (3 x 10 mL). **54** [0.19 g, 0.9 mmol, 90 %, purity ≥ 80 % (^{31}P NMR)] and **72** were obtained in a 9:1 ratio as a light yellow, pyrophoric solid.

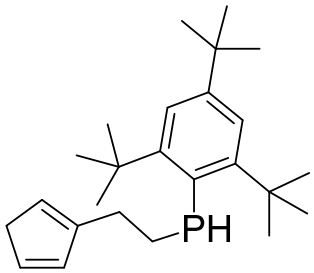
54: ^{1}H NMR (400 MHz, THF-d_8): δ = 1.08 (d, $^{3}J_{P,H}$ = 7.7 Hz, 9H, 9-H), 2.01-2.04 (m, 2H, 7-H), 2.55-2.61 (m, 2H, 6-H), 5.37-5.38 (m, 2H, 2-H or 3-H or 4-H or 5-H), 5.51-5.52 (m, 2H, 2-H or 3-H or 4-H or 5-H) ppm. - ^{13}C NMR (100.6 MHz, THF-d_8): δ = 26.7 (d, $^{1}J_{P,C}$ = 25.6 Hz, C-7), 27.7(d, $^{1}J_{P,C}$ = 21.5 Hz, C-8), 31.2 (d, $^{2}J_{P,C}$ = 10.1 Hz, C-6), 35.7 (d, $^{2}J_{P,C}$ = 11.8 Hz, C-9), 102.3 (s, C-2 or C-3 or C-4 or C-5), 102.8 (s, C-2 or C-3 or C-4 or C-5), 121.8 (d, $^{3}J_{P,C}$ = 4.0 Hz, C-1) ppm. - ^{31}P NMR (162 MHz, THF-d_8): δ = –47.8 ppm.

72: ^{31}P NMR (162 MHz, THF-d_8): δ = –23.8 ($^{1}J_{P,H}$ = 191.6 Hz) ppm.

4.3.3 2,4,6-Tri-*tert*-butyl(2-cyclopentadienylethyl)phosphanes 139 and 140



139



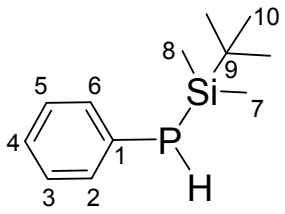
140

At –78 °C butyllithium (0.5 mL, 1.3 mmol, 2.5 M solution in hexane) was added to (2,4,6-tri-*tert*-butylphenyl)phosphane (**111**, 0.38 g, 1.3 mmol) in THF (50 mL). After 0.5 h the reaction mixture was allowed to reach 22 °C and stirred for 1 h at this temperature. Spiro[2.4]hepta-4,6-diene (**64**, 0.13 g, 1.4 mmol) was added, and the reaction mixture was stirred at 65 °C for 5 h. After solvent removal at reduced pressure the residue was washed with hexane (3 x 20 mL) and dried in vacuum. The residue was suspended in dichloromethane (20 mL) and treated with degassed water (20 mL). After 15 min of rapid stirring the layers were separated. The aqueous layer was extracted three times with CH_2Cl_2 (20 mL each), and the combined organic layers were dried over $MgSO_4$. The solution was filtered through a 3 cm thick layer of Celite®, and the solvent was removed at reduced pressure. The resulting pale yellow oil was taken up with hexane (30 mL) and filtered through a 1 cm thick layer of SiO_2. After solvent removal at reduced pressure regioisomers **139** and **140** [1.4:1 (^{31}P NMR), 0.33 g, 0.9 mmol, 69 %] were obtained as colorless solids (m. p. 84-85 °C).

^{1}H NMR (400 MHz, $CDCl_3$, major isomer): δ = 1.31 (s, 9H, 18-H), 1.58 (s, 18H, 15-H), 1.51-1.64 (m, 1H, 7-H), 1.78-1.90 (m, 1H, 7-H), 2.28-2.42 (m, 1H, 6-H), 2.45-2.59 (m, 1H, 6-H), 2.83 (m, 2H, 5-H), 4.83 (dm, 1H, $^1J_{P,H}$ = 221.5 Hz, PH), 6.12 (m, 1H, 2-H or 3-H or 4-H), 6.21-6.23 (m, 1H, 2-H or 3-H or 4-H), 6.37-6.39 (m, 1H, 2-H or 3-H or 4-H), 7.38 (m, 2H, 10-H and 12-H). - ^{31}C NMR (100.6 MHz, $CDCl_3$, major isomer):

δ = 27.2 (d, $^{2}J_{P,C}$ = 12.4 Hz, C-6), 28.7 (d, $^{1}J_{P,C}$ = 15.9 Hz, C-7), 31.4 (s, C-18), 33.7 (d, $^{4}J_{P,H}$ = 6.9 Hz, C-15), 35.0 (s, C-17), 38.5 (s, C-13 or C-14), 41.3 (s, C-5), 122.1 (s, C-10 or C-12), 122.2 (s, C-10 or C-12), 126.6 (s, C-2 or C-3 or C-4), 130.8 (s, C-2 or C-3 or C-4), 133.1 (d, $^{1}J_{P,C}$ = 7.6 Hz, C-8), 134.5 (s, C-2 or C-3 or C-4), 149.1 (s, C-11), 149.8 (d, $^{3}J_{P,C}$ = 11.5 Hz, C-1), 154.5 (s, C-9 or C-13), 154.6 (s, C-9 or C-13). - ^{31}P NMR (162 MHz, $CDCl_3$): δ = –72.6 (dm, $^{1}J_{P,H}$ = 221.5 Hz, minor isomer), –72.4 (dm, $^{1}J_{P,H}$ = 221.0 Hz, major isomer) ppm. - IR: $\tilde{\nu}$ = 2950 (vs), 2868 (s), 2388 (m, PH), 1591 (s, $CH_{arom.}$), 1528 (w), 1475 (m), 1393 (s), 1360 (vs, *t*Bu), 1281 (w), 1236 (m), 1213 (s), 1128 (w), 1005 (m), 975 (w), 947 (m), 927 (m), 896 (s, Cp), 878 (s, Cp), 849 (w), 811 (m), 756 (s), 727 (m), 683 (s), 649 (m) cm^{-1}. - HRMS (ESI, acetonitrile): calcd. for $C_{25}H_{40}P$ 371.2868; found 371.2872.

4.3.4 Phenyl(*tert*-butyldimethylsilyl)phosphane (190)[140]

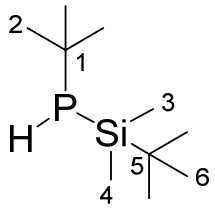


190

At –78 °C butyllithium (4.3 mL, 10.9 mmol, 2.5 M in hexane) was added to phenylphosphane (**189**, 1.2 g, 10.9 mmol) in THF (40 mL). The resulting solution was stirred for 1 h at 22 °C. At –78 °C *tert*-butyldimethylsilyl chloride (1.63 g, 10.9 mmol) in THF (30 mL) was added dropwise, and the resulting reaction mixture was stirred for 12 h at 22 °C. After solvent removal at reduced pressure the residue was taken up in hexane (60 mL) and filtered through a frit covered with a 3 cm thick layer of Celite®. After solvent removal at reduced pressure the product was isolated by distillation at 10^{-2} mbar/100-101 °C to give **190** (2.17 g, 9.7 mmol, 89 %) as a pyrophoric colorless oil.

^{1}H NMR (400 MHz, C_6D_6): δ = 0.00-0.02 (m, 6H, 8-H or 7-H), 0.91 (d, $^{4}J_{P,H}$ = 0.5 Hz, 9H, 10-H), 3.32 (d, $^{1}J_{P,H}$ = 201.9 Hz, 1H, PH), 6.98-7.04 (m, 3H, 3-H, 4-H, 5-H), 7.28-7.32 (m, 2H, 1-H, 6-H) ppm. - ^{13}C NMR (100.6 MHz, C_6D_6): δ = –5.1 (d, $^{2}J_{P,C}$ = 13.9 Hz, C-7 or C-8), –4.3 (s, C-7 or C-8), 18.3 (d, $^{2}J_{P,C}$ = 9.3 Hz, C-9), 26.9 (d, $^{3}J_{P,C}$ = 2.5 Hz, C-10), 126.8 (s, C-4), 128.6 (d, $^{3}J_{P,C}$ = 6.1 Hz, C-3 or C-5), 133.5 (d, $^{1}J_{P,C}$ = 16.1 Hz, C-1), 134.4 (d, $^{2}J_{P,C}$ = 14.6 Hz, C-2 or C-6) ppm. - ^{31}P NMR (162 MHz, C_6D_6): δ = –130.3 ppm.

4.3.5 *tert*-Butyl(*tert*-butyldimethylsilyl)phosphane (191)



191

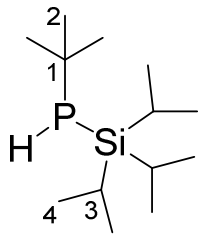
Variant 1. At 0 °C *tert*-butyldimethylsilyl chloride (1.01 g, 6.7 mmol) in THF (30 mL) was slowly added to lithium *tert*-butylphosphide (**65**, 0.64 g, 6.7 mmol) in THF (100 mL). The reaction mixture was warmed to 22 °C and stirred for 12 h at this temperature. After solvent removal at reduced pressure the residue was taken up in 60 mL of hexane and filtered through a frit covered with a 3 cm thick layer of Celite®. After solvent removal at reduced pressure the product was isolated by distillation at 10^{-2} mbar/50-51 °C to give **191** (1.10 g, 5.4 mmol, 81 %) as a pyrophoric colourless oil.

Variant 2. **194** (0.90 g, 4.1 mmol) was dissolved in diethylamine (40 mL), and the reaction mixture was stirred at 55 °C for 12 h. After solvent removal at reduced pressure the residue was taken up in hexane (50 mL) and filtered through a frit covered with a 5 cm thick layer of alumina. After solvent removal at reduced pressure the

product was isolated by distillation at 10^{-2} mbar/50-51 °C to give of **191** (0.67 g, 3.2 mmol, 80 %) as a colorless oil.

^{1}H NMR (400 MHz, C_6D_6): δ = 0.21 (d, $^{4}J_{P,H}$ = 6.6 Hz, 3H, 3-H or 4-H), 0.22 (d, $^{4}J_{P,H}$ = 3.1 Hz, 3H, 3-H or 4-H), 0.95 (s, 9H, 6-H), 1.21 (d, $^{3}J_{P,H}$ = 12.1 Hz, 9H, 2-H), 2.44 (d, $^{1}J_{P,H}$ = 194.6 Hz, 1H, PH) ppm. - ^{13}C NMR (100.6 MHz, C_6D_6): δ = –3.1 (d, $^{3}J_{P,C}$ = 12.3 Hz, C-3 or C-4), –1.3 (s, C-3 or C-4), 18.3 (d, $^{2}J_{P,C}$ = 11.7 Hz, C-5), 26.4 (d, $^{3}J_{P,C}$ = 3.0 Hz, C-6), 27.7 (d, $^{1}J_{P,C}$ = 11.5 Hz, C-1), 34.3 (d, $^{2}J_{P,C}$ = 12.0 Hz, C-2) ppm. - ^{31}P NMR (162 MHz, C_6D_6): δ = –95.3 ppm.

4.3.6 *tert*-Butyl(triisopropylsilyl)phosphane (192)



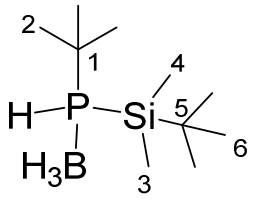
192

At 22 °C a solution of triisopropylsilyl chloride (0.96 g, 5.0 mmol) in THF (30 mL) was slowly added to the solution of lithium *tert*-butylphosphide (**65**) (0.48 g, 5.0 mmol) in THF (100 mL). The reaction mixture was stirred at 65 °C for 6 h. After solvent removal at reduced pressure the residue was taken up in hexane (60 mL) and filtered through a frit covered with a 3 cm thick layer of Celite®. After solvent removal at reduced pressure the product was isolated by distillation at 10^{-2} mbar/63-64 °C to give **192** (0.96 g, 3.9 mmol, 78 %) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.05-1.14 (m, 1H, 3-H), 1.13 (d, $^{4}J_{P,H}$ = 5.0 Hz, 18H, 4-H), 1.20-1.31 (m, 2H, 3-H), 1.29 (d, $^{3}J_{P,H}$ = 12.5 Hz, 9H, 2-H), 2.54 (d, $^{1}J_{P,H}$ = 204.8 Hz, 1H, PH) ppm. - ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 13.2 (d, $^{2}J_{P,C}$ = 8.6 Hz, C-3),

19.6 (br s, C-4), 27.9 (d, $^{1}J_{P,C}$ = 11.5 Hz, C-1), 34.7 (d, $^{2}J_{P,C}$ = 11.6 Hz, C-2) ppm. - ^{31}P NMR (162 MHz, $CDCl_3$): δ = –105.0 (dm, $^{1}J_{P,H}$ = 204.6 Hz, PH) ppm.

4.3.7 *tert*-Butyl(*tert*-butyldimethylsilyl)phosphane Borane adduct (194)

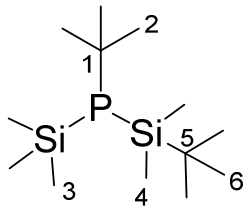


194

At 0 °C butyllithium (6.4 mL, 16.0 mmol, 2.5 M in hexane) was added to *tert*-butylphosphinoborane (**193**, 1.67 g, 16.0 mmol) in THF (40 mL). The resulting solution was stirred for 1 h at 22 °C. At 0 °C *tert*-butyldimethylsilyl chloride (2.41 g, 16.0 mmol) in THF (30 mL) was added dropwise, and the resulting reaction mixture was stirred for 12 h at 22 °C. After solvent removal at reduced pressure the residue was taken up in hexane (100 mL) and filtered through a frit covered with a 3 cm thick layer of Celite®. The solvent was removed at reduced pressure affording **194** [2.79 g, 12.7 mmol, 80 %, purity ≥ 95 % (^{31}P NMR)] as a colorless oil. Vacuum distillation of the crude **194** resulted in a partial dissociation of the borane moiety at the elevated temperature (10^{-2} mbar/72-73 °C).

^{1}H NMR (400 MHz, C_6D_6): δ = 0.03 (d, $^{4}J_{P,H}$ = 4.4 Hz, 3H, 3-H or 4-H), 0.21 (d, $^{4}J_{P,H}$ = 6.0 Hz, 3H, 3-H or 4-H), 0.89 (s, 9H, 6-H), 1.06 (d, $^{3}J_{P,H}$ = 14.3 Hz, 9H, 2-H), 1.60 (br m, 3H, BH_3), 3.42 (dq, $^{1}J_{P,H}$ = 321.2 Hz, $^{3}J_{H,H}$ = 7.7 Hz, 1H, PH) ppm. ^{13}C NMR (100.6 MHz, C_6D_6): δ = –4.8 (d, $^{3}J_{P,C}$ = 11.3 Hz, C-3 or C-4), –3.1 (d, $^{3}J_{P,C}$ = 4.4 Hz, C-3 or C-4), 18.5 (d, $^{2}J_{P,C}$ = 7.1 Hz, C-5), 26.8 (d, $^{3}J_{P,C}$ = 0.9 Hz, C-6), 28.3 (d, $^{1}J_{P,C}$ = 25.5 Hz, C-1), 29.6 (d, $^{2}J_{P,C}$ = 2.5 Hz, C-2) ppm. - ^{31}P NMR (162 MHz, C_6D_6): δ = –37.3 (dm, $^{1}J_{P,H}$ = 317.8 Hz) ppm. - ^{11}B NMR (128 MHz, C_6D_6): δ = –39.5 (d, $^{1}J_{P,B}$ = 31.4 Hz) ppm.

4.3.8 *tert*-Butyl(*tert*-butyldimethylsilyl)(trimethylsilyl)phosphane (196)

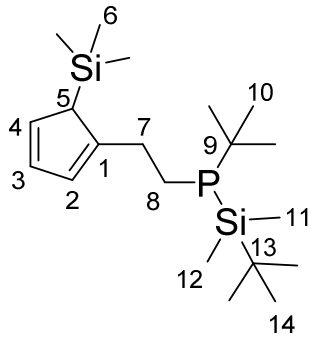


196

At 0 °C butyllithium (0.9 mL, 2.4 mmol, 2.5 M in hexane) was added to **191** (0.5 g, 2.4 mmol) in hexane (40 mL). The resulting solution was stirred for 1 h at 22 °C. At 0 °C trimethylsilyl chloride (0.27 g, 2.5 mmol) in hexane (10 mL) was added dropwise, and the resulting reaction mixture was stirred for 12 h at 22 °C. After solvent removal at reduced pressure the residue was taken up in hexane (60 mL) and filtered through a frit covered with a 3 cm thick layer of Celite®. The solvent was removed at reduced pressure affording **196** [0.65 g, 2.3 mmol, 98 %, purity ≥ 95 % (^{31}P NMR)] as a colorless oil.

^{1}H NMR (400 MHz, C_6D_6): δ = 0.28 (d, $^{4}J_{P,H}$ = 1.9 Hz, 6H, 4-H), 0.34 (d, $^{3}J_{P,H}$ = 4.2 Hz, 9H, 3-H), 1.04 (s, 9H, 6-H), 1.32 (d, $^{3}J_{P,H}$ = 12.6 Hz, 9H, 2-H) ppm. - ^{13}C NMR (100.6 MHz, C_6D_6): δ = –0.7 (s, C-4), 4.3 (d ,$^{2}J_{P,C}$ = 12.4 Hz, C-3), 19.0 ($^{2}J_{P,C}$ = 19.9 Hz, C-2), 27.4 (d, $^{3}J_{P,C}$ = 3.8 Hz, C-6), 30.9 (d, $^{1}J_{P,C}$ = 14.6 Hz, C-1), 35.4 (d, $^{2}J_{P,C}$ = 11.1 Hz, C-2) ppm. - ^{31}P NMR: (162 MHz, C_6D_6): δ = –114.6 ppm.

4.3.9 tert-Butyl(tert-butyldimethylsilyl)[2-(trimethylsilyl)cyclopentadienylethyl]-phosphanes 197-201



197

\+ isomers **198-201**

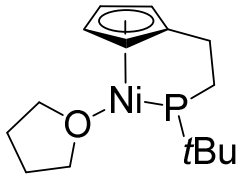
At 0 °C butyllithium (0.6 mL, 1.4 mmol, 2.5 M solution in hexane) was added to **191** (0.3 g, 1.4 mmol) in THF (40 mL). The resulting solution was stirred for 1 h at 22 °C. Spiro[2.4]hepta-4,6-diene (**64**, 0.13 g, 1.4 mmol) was added, and the reaction mixture was stirred at 65 °C for 3 h. After solvent removal at reduced pressure the residue was washed with hexane (3 x 10 mL) and dried in vacuum. The residue was dissolved in THF (30 mL). At 0 °C trimethylsilyl chloride (0.1 g, 1.4 mmol) in THF (10 mL) was added dropwise, and the resulting reaction mixture was stirred for 12 h at 22 °C. After solvent removal at reduced pressure the residue was taken up in hexane (60 mL) and filtered through a frit covered with a 3 cm thick layer of Celite®. The solvent was removed at reduced pressure affording **197**-**201** [0.48 g, 1.3 mmol, 93 %, purity ≥ 80 % (^{31}P NMR), mixture of five regioisomers [1.00 (**197**):0.1 (**198**-**201**)] as colorless oils.

197 (major isomer): ^{1}H NMR (400 MHz, $CDCl_3$, isomer): δ = –0.04 (s, 9H, 6-H), 0.15 (m, 3H, 11-H or 12-H), 0.25 (d, $^{3}J_{P,H}$ = 2.7 Hz, 3H, 11-H or 12-H), 0.96 (s, 9H, 14-H), 1.19 (d, $^{3}J_{P,H}$ = 12.0 Hz, 9H, 10-H), 1.75 (m, 2H, 7-H), 2.61 (m, 2H, 8-H), 3.26 (s, 1H, 5-H), 6.05 (m, 1H, 2-H or 3-H or 4-H), 6.44-6.47(m, 2H, 2-H or/and 3-H or/and 4-H) ppm. - ^{13}C NMR (100.6 MHz, $CDCl_3$, major isomer): δ = –5.3 (s, C-11 or C-12), –2.8 (s, C-6), –1.8 (s, C-11 or C-12), 18.6 (d, $^{2}J_{P,C}$ = 15.7 Hz, C-13), 20.3 (d, $^{1}J_{P,C}$ = 18.5 Hz, C-8), 27.2 (d, $^{3}J_{P,C}$ = 3.8 Hz, C-14), 29.5 (d, $^{1}J_{P,C}$ = 13.9 Hz, C-9), 31.1 (d, $^{2}J_{P,C}$ =

12.4 Hz, C-10), 32.5 (d, $^{2}J_{P,C}$ = 26.9 Hz, C-7), 51.1 (s, C-5), 126.7 (s, C-2 or C-3 or C-4), 131.9 (s, C-2 or C-3 or C-4), 134.1 (s, C-2 or C-3 or C-4), 146.7 (d, $^{3}J_{P,C}$ = 15.9 Hz, C-1) ppm. - ^{31}P NMR (162 MHz, $CDCl_3$): δ = –54.32, –54.23, –54.20, –54.16, –53.9 (major isomer) ppm.

4.4 Attempted Reactions of 54 towards Cyclopentadienyl Phosphido Chelate Complexes

4.4.1 {[2-(*tert*-Butylphosphido)ethyl]cyclopentadienyl}(tetrahydrofuran)-nickel(II) (73)

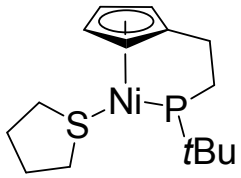


73

GPI: From a solution of **54** (0.03 g, 0.1 mmol) in THF (30 mL) and a suspension of $NiCl_2(thf)_2$ (0.04 g, 0.1 mmol) in THF (50 mL). After work up, traces of **73**.

HRMS (ESI, acetonitrile): calcd. for $C_{15}H_{25}NiOP$ [M^++Na]: 333.0894; found 333.0898.

4.4.2 {[2-(*tert*-Butylphosphido)ethyl]cyclopentadienyl}(tetrahydrothiophene)-nickel(II) (74)

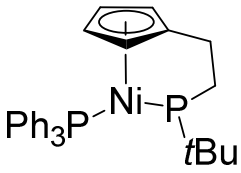


74

GPI: From a solution of **54** (0.04 g, 0.1 mmol) in THF (30 mL) and a suspension of $NiCl_2$ (0.02 g, 0.2 mmol) in THT (0.17 g, 2.0 mmol) and THF (50 mL). After work up, traces of **74**.

HRMS (ESI, methanol): calcd. for $C_{15}H_{25}NiSP$ $[M^+ + H]$: 327.0846; found 327.0856.

4.4.3 {[2-(*tert*-Butylphosphido)ethyl]cyclopentadienyl}(triphenylphospnane)-nickel(II) (76)



76

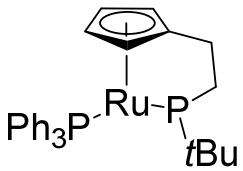
Variant 1 (GPI). From a solution of **54** (0.04 g, 0.1 mmol) in THF (40 mL) and a suspension of $NiCl_2(PPh_3)_2$ (0.06 g, 0.1 mmol) THF (60 mL). After work up, traces of **76**.

Variant 2. At 22 °C spiro[2.4]hepta-4,6-diene (**64**, 0.06 g, 0.6 mmol) was added to lithium *tert*-butyl phosphide (**65**, 0.06 g, 0.6 mmol) in THF (20 mL). After stirring at 65 °C for 1 h the solvent was removed at reduced pressure. The residue was washed

with hexane (3 x 10 mL), and residual solvent was removed at reduced pressure. The residue was dissolved in THF (20 mL) and slowly dropped into a cold suspension (–78 °C) of $NiCl_2(PPh_3)_2$ (0.59 g, 0.9 mmol) in THF (100 mL). The reaction mixture was slowly warmed to 22 °C and stirred for 2 h. After solvent removal at reduced pressure the residue was taken up dichloromethane and filtered through a frit covered with a 3 cm thick layer of Celite®. **76** was obtained in traces.

HRMS (ESI, methanol): calcd. for $C_{29}H_{32}NiP_2$ [M^++H]: 501.1411; found 501.1415.

4.4.4 {[2-(*tert*-Butylphosphido)ethyl]cyclopentadienyl}(triphenylphospnane)-ruthenium(II) (77)



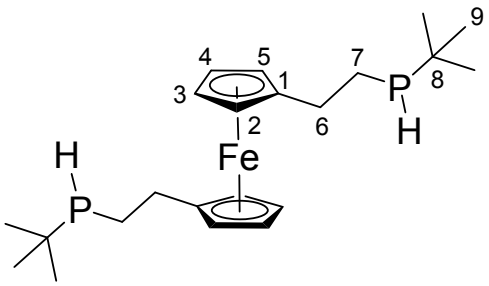
77

Variant 1 (GPI). From a solution of **54** (0.03 g, 0.1 mmol) in THF (40 mL) and a suspension of $RuCl_2(PPh_3)_3$ (0.10 g, 0.1 mmol) THF (80 mL). After work up, traces of **77**.

Variant 2. At 22 °C spiro[2.4]hepta-4,6-diene (**64**, 0.05 g, 0.6 mmol) was added to lithium *tert*-butyl phosphide (**65**, 0.06 g, 0.6 mmol) in THF (20 mL). After stirring at 65 °C for 1 h the solvent was removed at reduced pressure. The residue was washed with hexane (3 x 10 mL), and residual solvent was removed at reduced pressure. The residue was dissolved in THF (20 mL) and slowly dropped into a cold suspension (–78 °C) of $RuCl_2(PPh_3)_3$ (0.59 g, 0.9 mmol) in THF (100 mL). The reaction mixture was slowly warmed to 22 °C and stirred for 2 h. After solvent removal at reduced pressure the residue was taken up dichloromethane and filtered through a frit covered with a 3 cm thick layer of Celite®. **77** was obtained in traces.

HRMS (ESI, methanol): calcd. for $C_{29}H_{32}P_2Ru$ [M^++H]: 545.1101; found 545.1102.

4.5 1,1'-Di[(2-*tert*-butylphosphanyl)ethyl]ferrocene (114)



114

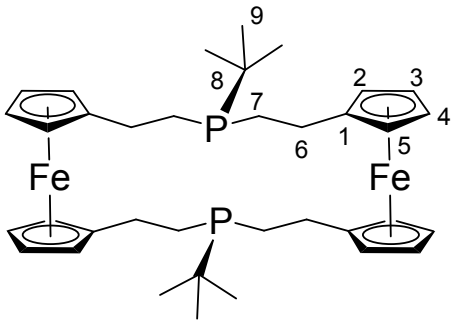
Variant 1. At 22 °C spiro[2.4]hepta-4,6-diene (**64**, 0.56 g, 6.1 mmol) was added to lithium *tert*-butylphosphide (**65**, 0.53 g, 5.6 mmol) in THF (60 mL). After stirring at 65 °C for 1 h the solvent was removed at reduced pressure. The residue was washed with hexane (3 x 20 mL), and the solvent was removed at reduced pressure. The residue was dissolved in THF (40 mL) and slowly added dropwise to a cold suspension (–78 °C) of anhydrous iron(II) chloride (0.35 g, 2.8 mmol) in THF (300 mL). The reaction mixture was slowly warmed to 22 °C and stirred for 12 h. After solvent removal at reduced pressure the residue was taken up in hexane (100 mL) and filtered through a frit covered with a 3 cm thick layer of Celite®. After solvent removal at reduced pressure and purification of the residue by column chromatography (2 x 30 cm, SiO_2, PE) *rac*-**114** (0.86 g, 2.0 mmol, 70 %) was isolated as a yellow solid (m. p. 64-65 °C, dec.).

Variant 2. At 22 °C spiro[2.4]hepta-4,6-diene (**64**, 0.5 g, 5.3 mmol) was added to lithium *tert*-butylphosphide (**65**, 0.45 g, 4.8 mmol) in THF (60 mL). After stirring at 65 °C for 1 h the solvent was removed at reduced pressure. The residue was washed with hexane (3 x 20 mL), and the solvent was removed at reduced pressure. The residue was dissolved in THF (40 mL) and slowly added dropwise to a cold suspension (–78 °C) of anhydrous $Fe(CO)_4I_2$ (2.23 g, 5.3 mmol) in THF (500 mL). The reaction

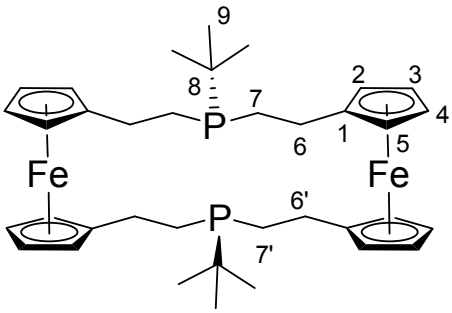
mixture was slowly warmed to 22 °C and stirred for 12 h. After solvent removal at reduced pressure the residue was taken up in hexane (100 mL) and filtered through a frit covered with a 3 cm thick layer of Celite®. After solvent removal at reduced pressure and purification of the residue by column chromatography (2 x 30 cm, SiO_2, PE) *rac*-**114** (0.67 g, 1.6 mmol, 34 %) was isolated as a yellow solid (m. p. 64-65 °C, dec.).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.14 (d, $^3J_{P,H}$ = 11.7 Hz, 18H, 9-H), 1.50-1.61 (m, 2H, 7-H), 1.92-2.03 (m, 2H, 7-H), 2.36-2.46 (m, 2H, 6-H), 2.51-2.61 (m, 2H, 6-H), 3.00 (dm, $^1J_{P,H}$ = 198.8 Hz, 2H, PH), 4.02 (m, 8H, 2-H, 3-H, 4-H, 5-H) ppm. - ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 19.7 (d, $^1J_{P,C}$ = 14.4 Hz, C-7), 27.0 (d, $^1J_{P,C}$ = 6.1 Hz, C-8), 28.3 (d, $^2J_{P,C}$ = 15.5 Hz, C-6), 30.2 (d, $^2J_{P,C}$ = 12.2 Hz, C-9), 68.0 (s, C-2 or C-3 or C-4 or C-5), 68.1 (s, C-2 or C-3 or C-4 or C-5), 68.6 (s, C-2 or C-3 or C-4 or C-5), 68.7 (s, C-2 or C-3 or C-4 or C-5), 89.8 (d, $^3J_{P,C}$ = 12.3 Hz, C-1) ppm. - ^{31}P NMR (162 MHz, $CDCl_3$): δ = –23.6 (dm, $^1J_{P,H}$ = 199.2 Hz, PH) ppm. - IR: $\tilde{\nu}$ = 2945 (m), 2857 (m), 2262 (s, PH), 1461 (s), 1441 (m), 1362 (s, *t*Bu), 1225 (m), 1198 (m), 1106 (m), 1038 (s), 1021 (s), 975 (s), 919 (m), 866 (m), 842 (m), 816 (vs, Cp), 796 (s), 768 (s), 657 (m) cm^{-1}. - HRMS (TOF MS EI^+): calcd. for $C_{22}H_{36}FeP_2$ 418.1642; found 418.1646. - Elemental analysis: calcd. (%) for $C_{22}H_{36}FeP_2$ C 63.16, H 8.69; found C 63.33, H 9.07.

4.6 1,16-Di-*tert*-butyl-1,16-diphospha[5.5]ferrocenophanes (*cis*-123a and *trans*-123b)



123a



123b

At –78 °C butyllithium (1.4 mL, 3.4 mmol, 2.5 M solution in hexane) was added to **114** (0.71 g, 1.7 mmol) in THF (300 mL). The resulting solution was stirred for 1 h at 22 °C. A solution of **137** (0.68 g, 1.7 mmol) in THF (200 mL) was added, and the reaction mixture was stirred at 65 °C for 3 h. After solvent removal at reduced pressure the residue was taken up in dichloromethane (100 mL) and filtered through a frit covered with a 3 cm thick layer of Celite®. The solvent was removed at reduced pressure and the residue was washed with ethyl acetate (3 x 50 mL) affording **123a** and **123b** [0.38 g, 0.6 mmol, 35 %, mixture of two isomers (1.0:1.1) (^{31}P NMR)] as a light yellow solid (m. p. 235-236 °C, dec.). Crystallization from dichloromethane/ethyl acetate (2:1) at –30 °C afforded, presumably, **123b** [light yellow solid, purity ≥ 95 % (^{31}P NMR)]. The mother liquor was concentrated at reduced pressure and washed with diethyl ether (3 x 30 mL) affording, most probably, **123a** [light yellow solid, purity ≥ 95 % (^{31}P NMR)].

123a (minor isomer): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.97 (d, $^{3}J_{P,H}$ = 11.4 Hz, 18H, 9-H), 1.48-1.62 (m, 8H, 7-H), 2.46-2.64 (m, 8H, 6-H), 3.99-4.09 (m, 16H, 2-H, 3-H, 4-H, 5-H) ppm. - ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 27.4 (d, $^{2}J_{P,C}$ = 12.8 Hz, C-9), 27.8 (d, $^{1}J_{P,C}$ = 9.3 Hz, C-8), 28.2 (d, $^{2}J_{P,C}$ = 2.6 Hz, C-6), 28.4 (d, $^{1}J_{P,C}$ = 5.2 Hz, C-7),

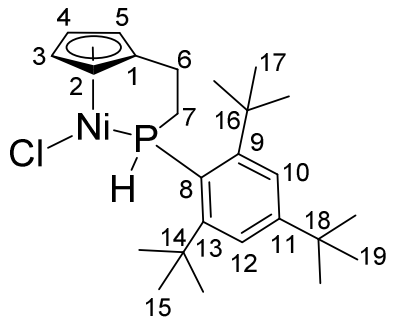
67.4 (s, C-2 or C-3 or C-4 or C-5), 67.6 (s, C-2 or C-3 or C-4 or C-5), 68.4 (s, C-2 or C-3 or C-4 or C-5), 69.2 (s, C-2 or C-3 or C-4 or C-5), 90.5 (d, $^{3}J_{P,C}$ = 16.0 Hz, C-1) ppm. - ^{31}P NMR (162 MHz, $CDCl_3$): δ = 0.9 ppm.

123b (major isomer): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.97 (d, $^{3}J_{P,H}$ = 11.4 Hz, 18H, 9-H), 1.53-1.60 (m, 8H, 7(7')-H), 2.53-2.66 (m, 8H, 6(6')-H), 3.92-4.12 (m, 16H, 2-H, 3-H, 4-H, 5-H) ppm. - ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 27.5 (d, $^{2}J_{P,C}$ = 12.5 Hz, C-9), 27.9 (s, C-6 or C-6' or C-7 or C-7'), 27.9 (s, C-8), 28.0 (s, C-6 or C-6' or C-7 or C-7'), 28.5 (s, C-6 or C-6' or C-7 or C-7'), 28.7 (s, C-6 or C-6' or C-7 or C-7'), 67.4 (s, C-2 or C-3 or C-4 or C-5), 67.7 (s, C-2 or C-3 or C-4 or C-5), 68.5 (s, C-2 or C-3 or C-4 or C-5), 69.9 (s, C-2 or C-3 or C-4 or C-5), 90.3 (d, $^{3}J_{P,C}$ = 14.7 Hz, C-1) ppm. - ^{31}P NMR (162 MHz, $CDCl_3$): δ = 0.8 ppm.

123a and **123b**: IR: $\tilde{\nu}$ = 3087 (m), 2936 (m), 2896 (m), 2860 (m), 1629 (m), 1468 (m), 1442 (m), 1361 (m, *t*Bu), 1314 (w), 1227 (w), 1132 (vs), 1087 (vs), 1039 (s), 1020 (s), 951 (w), 925 (m), 852 (w), 803 (s, Cp), 796 (s), 782 (w), 741 (w), 673 (w), 622 (w) cm^{-1}. - HRMS (ESI, acetonitrile): calcd. for $C_{36}H_{50}Fe_2P_2$ [M^++H]: 657.2165; found 657.2166.

4.7 Direct Synthesis of Nickel(II) Cyclopentadienylcomplexes with Secondary Phosphane Tethers

4.7.1 {[2-(2,4,6-Tri-*tert*-butylphenylphosphanyl)ethyl]cyclopentadienyl}chloro-nickel(II) (142)



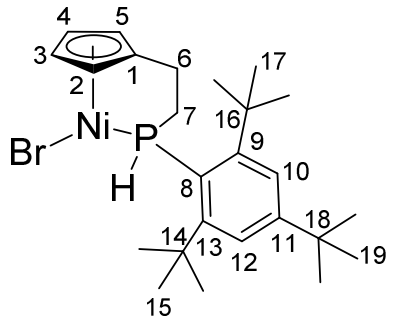
142

GP(II): To **111** (1.39 g, 5.0 mmol) in THF (150 mL) butyllithium (2.0 mL, 5.0 mmol, 2.5 M solution in hexane) was added at –78 °C. After stirring, **64** (0.51 g, 5.5 mmol) was added at 22 °C. After solvent removal and washing with hexane (3 x 20 mL) the residue was dissolved in THF (50 mL) and added to a suspension of $NiCl_2$(dme) (1.65 g, 7.5 mmol) in THF (400 mL). After work up and recrystallization, **142** (1.11g, 2.4 mmol, 48 %) as a red-purple solid (m. p. 174-175 °C, dec.).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.27-1.30 (m, 2H, 6-H), 1.27 (s, 9H, 19-H), 1.69 (s, 9H, 15-H or 17-H), 1.86 (s, 9H, 15-H or 17-H), 2.11-2.14 (m, 1H, 7-H), 2.39-2.50 (m, 1H, 7-H), 5.10-5.12 (m, 1H, 2-H or 3-H or 4-H or 5-H), 5.51-5.53 (m, 1H, 2-H or 3-H or 4-H or 5-H), 5.64-5.66 (m, 1H, 2-H or 3-H or 4-H or 5-H), 5.64-5.66 (m, 0.5H, PH), 5.74-5.75 (m 1H, 2-H or 3-H or 4-H or 5-H), 6.50 (m, 0.5H, PH), 7.34 (s, 1H, 10-H or 12-H), 7.38 (s, 1H, 10-H or 12-H). - ^{31}C NMR (100.6 MHz, $CDCl_3$): δ = 23.1 (s, C-6), 31.1 (s, C-19), 34.4 (s, C-15 or C-17), 34.8 (s, C-15 or C-17), 34.9 (s, C-18), 38.7 (s, C-14 or C-16), 39.8 (s, C-14 or C-16), 42.3 (br s, C-7), 94.7 (s, C-2 or C-3 or C-4 or C-5), 96.0 (s, C-1), 99.6 (s, C-2 or C-3 or C-4 or C-5), 101.4 (s, C-2 or C-3 or C-4 or

C-5), 101.7 (s, C-2 or C-3 or C-4 or C-5), 118.9 (br s, C-8), 123.1 (s, C-10 or C-12), 125.0 (s, C-10 or C-12), 151.9 (s, C-11), 156.8 (s, C-9 or C-13), 157.2 (s, C-9 or C-13). - ^{31}P NMR (162 MHz, $CDCl_3$): δ = 0.8 (dm, $^1J_{P,H}$ = 343.8 Hz) ppm. - IR: $\tilde{\nu}$ = 2961 (vs), 2868 (m), 2348 (br, w, PH), 1593 (m, $CH_{arom.}$), 1531 (w), 1459 (m), 1441 (m), 1392 (m), 1361 (s, *t*Bu), 1237 (m), 1211 (m), 1186 (w), 1126 (m), 1050 (m), 1007 (m), 987 (w), 919 (s), 865 (vs, Cp), 781 (vs), 750 (s), 750 (w), 687 (m), 649 (w), 613 (vs) cm^{-1}. - HRMS (TOF MS EI^+): calcd. for $C_{25}H_{38}ClNiP$ 462.1753; found 462.1753.

4.7.2 {[2-(2,4,6-Tri-*tert*-butylphenylphosphanyl)ethyl]cyclopentadienyl}bromo-nickel(II) (143)



143

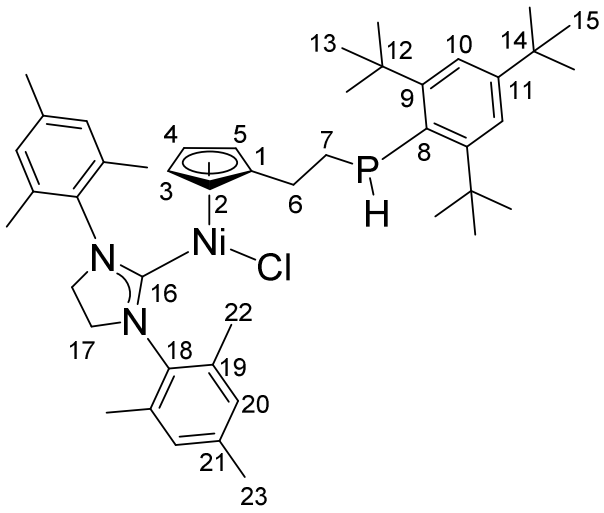
GP(II): To **111** (0.89 g, 3.2 mmol) in THF (100 mL) butyllithium (1.3 mL, 3.2 mmol, 2.5 M solution in hexane) was added at −78 °C. After stirring, **64** (0.32 g, 3.5 mmol) was added at 22 °C. After solvent removal and washing with hexane (3 x 20 mL) the residue was dissolved in THF (30 mL) and added to a suspension of $NiBr_2(thf)_2$ (1.74 g, 4.8 mmol) in THF (500 mL). After work up and recrystallization, **143** (1.14 g, 2.2 mmol, 69 %) as a red-purple solid (m. p. 107-108 °C, dec.).

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.18-1.41 (m, 2H, 6-H), 1.27 (s, 9H, 19-H), 1.69 (s, 9H, 15-H or 17-H), 1.84 (s, 9H, 15-H or 17-H), 2.18 (m, 1H, 7-H), 2.36-2.52 (m, 1H, 7-H), 5.13 (m, 1H, 2-H or 3-H or 4-H or 5-H), 5.55 (m, 1H, 2-H or 3-H or 4-H or 5-H),

5.72-5.74 (m, 1H, 2-H or 3-H or 4-H or 5-H), 5.82-5.84 (m 1H, 2-H or 3-H or 4-H or 5-H), 6.16 (dm, 1H, $^{1}J_{P,H}$ = 349.1 Hz, PH), 7.34 (s, 1H, 10-H or 12-H), 7.38 (s, 1H, 10-H or 12-H). - ^{31}C NMR (100.6 MHz, $CDCl_3$): δ = 23.3 (s, C-6), 31.1 (s, C-19), 34.6 (s, C-15 or C-17), 34.9 (s, C-15 or C-17), 35.1 (s, C-18), 38.8 (s, C-14 or C-16), 39.9 (s, C-14 or C-16), 43.0 (d, $^{1}J_{P,C}$ = 24.6 Hz, C-7), 93.5 (s, C-2 or C-3 or C-4 or C-5), 99.0 (s, C-2 or C-3 or C-4 or C-5), 99.6 (s, C-1), 100.2 (s, C-2 or C-3 or C-4 or C-5), 101.2 (s, C-2 or C-3 or C-4 or C-5), 119.4 (d, $^{1}J_{P,C}$ = 9.5 Hz, C-8), 123.1 (s, C-10 or C-12), 125.1 (s, C-10 or C-12), 151.0 (s, C-11), 156.8 (s, C-9 or C-13), 157.2 (s, C-9 or C-13). - ^{31}P NMR (162 MHz, $CDCl_3$): δ = –5.7 (dm, $^{1}J_{P,H}$ = 349.9 Hz) ppm. - IR: $\tilde{\nu}$ = 2959 (s), 2357 (m, PH), 1593 (m, $CH_{arom.}$), 1440 (m), 1359 (s, *t*Bu), 1186 (m), 1007 (m), 920 (m), 863 (vs, Cp), 781 (vs), 749 (s), 685 (s), 614 (vs) cm^{-1}. - HRMS (TOF MS EI^{+}): calcd. for $C_{25}H_{38}BrNiP$ 506.1248; found 506.1251. - Elemental analysis: calcd. (%) for $C_{25}H_{38}BrNiP$ C 59.08, H 7.55; found C 58.88, H 7.79.

4.8 Reactions of 142 and 143 with *N*-heterocyclic Carbenes

4.8.1 {[2-(2,4,6-Tri-*tert*-butylphenylphosphanyl)ethyl]cyclopentadienyl}-[1,3-bis-(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene]-chloronickel(II) (162)



162

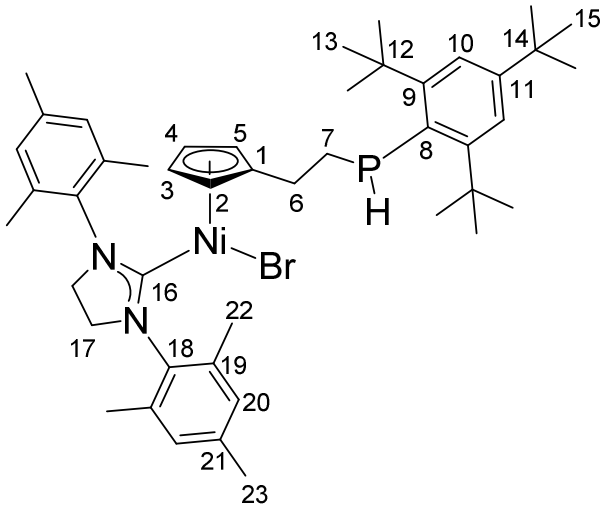
Variant 1 (GPIII). A solution of SIMes (**161**, 0.34 g, 1.1 mmol) in THF (20 mL) was added to a solution of **142** (0.5 g, 1.1 mmol) in THF (200 mL). After work up and purification by column chromatography [2 x 20 cm, SiO_2, PE/ethyl acetate, (8:2)] **162** (0.53 g, 0.7 mmol, 63 %) was isolated as a red solid (m. p. 158-159 °C, dec.).

Variant 2. At –78 °C butyllithium (0.3 mL, 0.7 mmol, 2.5 M solution in hexane) was added to (2,4,6-tri-*tert*-butylphenyl)phosphane (**111**, 0.20 g, 0.7 mmol) in THF (50 mL). After 0.5 h the reaction mixture was allowed to reach 22 °C and stirred for 1 h at this temperature. Spiro[2.4]hepta-4,6-diene (**64**, 0.07 g, 0.8 mmol) was added, and the reaction mixture was stirred at 65 °C for 5 h. After solvent removal at reduced pressure the residue was washed with hexane (3 x 20 mL) and dried in vacuum. The residue was dissolved in THF and slowly dropped to a cold suspension (–78 °C) of

$NiCl_2$(dme) (0.23 g, 1.0 mmol) in THF (200 mL). The reaction mixture was slowly warmed to 22 °C and stirred for 1 h at this temperature. A solution of SIMes (**161**, 0.34 g, 1.1 mmol) in THF (20 mL) was added to the reaction mixture at –78 °C and stirred for 1 h at 22 °C. After solvent removal at reduced pressure the residue was taken up in diethyl ether and filtered through a 3 cm thick layer of Celite®. After solvent removal the crude product was purified by column chromatography [2 x 20 cm, SiO_2, PE/ethyl acetate, (8:2)] **162** (0.23 g, 0.3 mmol, 47 %) was isolated as a red solid (m. p. 64-65 °C, dec.).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.19-1.44 (m, 2H, 6-H), 1.32 (s, 9H, 15-H), 1.44-1.65 (m, 2H, 7-H), 1.53 (s, 9H, 13-H), 2.31 (s, 6H, 23-H), 2.32 (s, 12H, 22-H), 3.87 (s, 4H, 17-H), 4.22-4.25 (m, 3H, 2-H or/and 3-H or/and 4-H or/and 5-H), 4.34 (m, 2-H or 3-H or 4-H or 5-H), 4.69 (dm, 1H, $^1J_{P,H}$ = 221.7 Hz, PH), 6.92 (d, 4H J = 13.4 Hz, 20-H), 7.40 (d, 1H, $^4J_{P,H}$ = 1.9 Hz, 10-H). - ^{31}C NMR (100.6 MHz, $CDCl_3$): δ = 18.7 (br s, C-23), 21.3 (s, C-22), 25.2 (d, $^1J_{P,C}$ = 17.5 Hz, C-7), 25.7 (d, $^2J_{P,C}$ = 11.7 Hz, C-6), 31.5 (s, C-15), 33.7 (d, $^4J_{P,C}$ = 6.9 Hz, C-13), 35.0 (s, C-14), 38.5 (s, C-12), 51.0 (s, C-17), 82.1 (s, C-2 or C-3 or C-4 or C-5), 83.7 (s, C-2 or C-3 or C-4 or C-5), 97.4 (s, C-2 or C-3 or C-4 or C-5), 97.5 (s, C-2 or C-3 or C-4 or C-5), 116.2 (d, $^3J_{P,C}$ = 13.8 Hz, C-1), 122.1 (d, $^3J_{P,C}$ = 3.9 Hz, C-10), 129.5 (s, C-20), 134.1 (d, J = 29.6 Hz, C-18), 136.9 (br s, C-21), 137.1 (s, C-19), 138.1 (s, C-9), 148.8 (s, C-11), 154.6 (d, $^2J_{P,C}$ = 7.6 Hz, C-9), 202.7 (s, C-16). - ^{31}P NMR (162 MHz, $CDCl_3$): δ = –73.1 (dm, $^1J_{P,H}$ = 221.7 Hz) ppm. - IR: $\tilde{\nu}$ = 2954 (m), 2915 (m), 2870 (m), 2405 (m, PH), 1590 (m, $CH_{arom.}$), 1483 (s), 1432 (s), 1361 (m, *t*Bu), 1290 (m), 1263 (vs), 1214 (w), 1126 (w), 1058 (w), 999 (w), 922 (w), 878 (w), 855 (w), 809 (w), 755 (m), 650 (w), 625 (w) cm^{-1}.- ICP-MS (qualitative): positive for ^{35}Cl.

4.8.2 {[2-(2,4,6-Tri-*tert*-butylphenylphosphanyl)ethyl]cyclopentadienyl}-[1,3-bis-(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene]-bromonickel(II) (163)



163

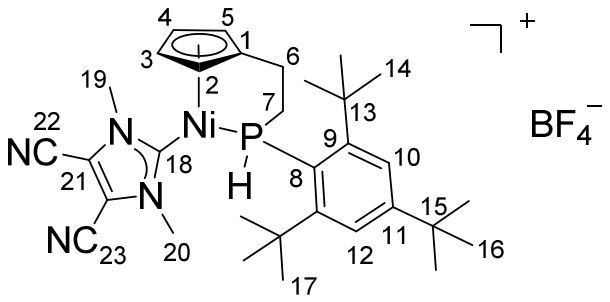
GPIII: A solution of SIMes (**161**, 0.20 g, 0.6 mmol) in THF (20 mL) was added to a solution of **143** (0.15 g, 0.6 mmol) in THF (200 mL). After work up and purification by column chromatography [2 x 20 cm, SiO_2, PE/ethyl acetate, (8:2)] **163** (0.41 g, 0.5 mmol, 85 %) was isolated as a red solid (m. p. 157-158 °C, dec.).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.16-1.43 (m, 2H, 6-H), 1.32 (s, 9H, 15-H), 1.48-1.68 (m, 2H, 7-H), 1.53 (s, 9H, 13-H), 2.32 (s, 6H, 23-H), 2.33 (s, 12H, 22-H), 3.86 (s, 4H, 17-H), 4.22-4.25 (m, 3H, 2-H or/and 3-H or/and 4-H or/and 5-H), 4.34 (m, 2-H or 3-H or 4-H or 5-H), 4.68 (dm, 1H, $^1J_{P,H}$ = 222.1 Hz, PH), 6.93 (d, 4H J = 14.0 Hz, 20-H), 7.40 (d, 1H, $^4J_{P,H}$ = 1.7 Hz, 10-H). - ^{31}C NMR (100.6 MHz, $CDCl_3$): δ = 18.7 (br s, C-23), 21.3 (s, C-22), 25.2 (d, $^1J_{P,C}$ = 17.4 Hz, C-7), 25.7 (d, $^2J_{P,C}$ = 11.6 Hz, C-6), 31.5 (s, C-15), 33.7 (d, $^4J_{P,C}$ = 7.0 Hz, C-13), 35.1 (s, C-14), 38.4 (s, C-12), 51.0 (s, C-17), 82.1 (s, C-2 or C-3 or C-4 or C-5), 83.7 (s, C-2 or C-3 or C-4 or C-5), 97.4 (s, C-2 or C-3 or C-4 or C-5), 97.4 (s, C-2 or C-3 or C-4 or C-5), 116.3 (d, $^3J_{P,C}$ = 14.0 Hz, C-1), 122.1 (d, $^3J_{P,C}$ = 3.9 Hz, C-10), 129.5 (s, C-20), 134.2 (d, J = 29.6 Hz, C-18), 137.0

(br s, C-21), 137.1 (s, C-19), 138.1 (s, C-9), 148.7 (s, C-11), 154.6 (d, $^{2}J_{P,C}$ = 7.5 Hz, C-9), 202.7 (s, C-16). - ^{31}P NMR (162 MHz, $CDCl_3$): δ = –73.0 (dm, $^{1}J_{P,H}$ = 222.1 Hz) ppm. - IR: $\tilde{\nu}$ = 2953 (s), 2913 (m), 2869 (m), 2394 (m, PH), 1591 (w, $CH_{arom.}$), 1483 (s), 1432 (s), 1361 (m, *t*Bu), 1290 (m), 1263 (s), 1263 (vs), 1213 (w), 1185 (w), 1126 (w), 1058 (w), 1031 (w), 922 (w), 878 (w), 853 (m), 792 (w), 755 (m), 650 (w), 625 (w) cm^{-1}.

Crystal structure analysis of 163: Single crystals of **163** were obtained by slow evaporation from ethyl acetate at 22 °C. Empirical formula $C_{46}H_{64}BrN_2NiP$, formula weight 814.58 g/mol, crystal system monoclinic, space group $P2_1/c$, unit cell dimensions a = 9.9936(12), b = 20.069(3), c = 25.157(4) Å, α = 90°, β= 90°, γ = 90°, V = 5045.5(13) $Å^3$, Z = 4, $d_{calc.}$ = 1.072 g/cm^3, μ = 1.236 mm^{-1}, crystal size 0.20 x 0.20 x 0.60 mm, F (000) = 1728, T = 202 K, Cu-K_α radiation (λ = 1.54187 Å), θ-range 1.30 to 25.17°, reflections collected/unique 98267/9014 [R(int) = 0.2320], completeness of data θ = 25.17 (99.7 %), index ranges –11≤ h ≤ 11, –23≤ k ≤ 24, –29 ≤ l ≤ 30, numerical absorption correction, no extinction correction, direct methods, full-matrix least-squares refinement on F^2, goodness-of-fit on F^2 = 1.047, R_1=0.0891 (I >2σ_I), wR_2 (I >2σ_I) = 0.2750, R_1 (all data) = 0.1658, wR_2 (all data) = 0.3284, final difference electron density 1.272 and –1.444 $eÅ^{-3}$.

4.8.3 {[2-(2,4,6-Tri-*tert*-butylphenylphosphanyl)ethyl]cyclopentadienyl}-(1,3-dimethyl-4,5-dicyanoimidazol-2-ylidene)nickel(II)-tetrafluoroborate (171)



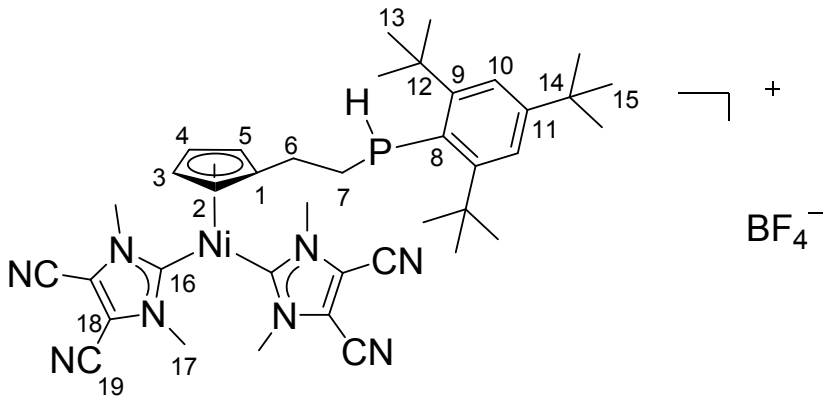
171

At –78 °C NaHMDS (0.4 mL, 0.4 mmol, 1.0 M solution in THF) was added to a suspension of **166** (0.09 g, 0.4 mmol) in THF (30 mL). After stirring for 1 h at this temperature, the reaction mixture was slowly added to a cold solution (–78 °C) of **142** (0.37 g, 0.8 mmol) in THF (250 mL). After 1 h the reaction mixture was allowed to reach 22 °C and stirred for 2 h at this temperature. After solvent removal at reduced pressure the residue was taken up with dichloromethane and filtered through a 3 cm thick layer of Celite®. After solvent removal the residue was washed with ethyl acetate (5 x 20 mL) and dried in vacuum. **171** [0.05 g, 0.17 mmol, 42 %, purity ≥ 90 % (^{1}H NMR)] was obtained as a green solid (m. p. 231-232 °C, dec.).

^{1}H NMR (400 MHz, acetone-d_6): δ = 1.29 (s, 9H, 16-H), 1.59 (br s, 9H, 14-H or 17-H), 1.68 (br s, 9H, 14-H or 17-H), 1.93-2.21 (m, 2H, 6-H), 2.68-2.75 (m, 1H, 7-H), 3.04-3.17 (m, 1H, 7-H), 4.25 (br s, 3H, 19-H or 20-H), 4.31 (br s, 3H, 19-H or 20-H), 5.26-5.27 (m, 1H, 2-H or 3-H or 4-H or 5-H), 5.87-5.88 (m, 1H, 2-H or 3-H or 4-H or 5-H), 6.13-6.14 (m, 1H, 2-H or 3-H or 4-H or 5-H), 6.36-6.37 (m, 1H, 2-H or 3-H or 4-H or 5-H), 6.68 (ddd, 1H, $^1J_{P,H}$ = 353.3 Hz, $^2J_{C,H}$ = 11.7 Hz, $^3J_{C,H}$ = 4.0 Hz, PH), 7.46 (s, 1H, 10-H or 12-H), 7.47 (s, 1H, 10-H or 12-H). - ^{31}C NMR (100.6 MHz, acetone-d_6): δ = 23.6 (d, $^2J_{P,C}$ = 5.3 Hz, C-6), 31.1 (s, C-16), 34.0 (br s, C-14 or C-17), 34.6 (br s, C-14 or C-17), 35.5 (s, C-15), 39.3 (br s, C-13), 40.2 (br s, C-19 or C-20), 40.6 (br s, C-

19 or C-20), 47.0 (d, $^{1}J_{P,C}$ = 29.3 Hz, C-7), 89.2 (d, $^{4}J_{P,C}$ = 6.7 Hz, C-2 or C-5), 96.7 (d, $^{4}J_{P,C}$ = 2 Hz, C-2 or C-5), 99.2 (s, C-3 or C-4), 102.3 (s, C-3 or C-4), 107.7 (s, C-21), 116.1 (d, $^{3}J_{P,C}$ = 10.1 Hz, C-1), 117.8 (d, $^{1}J_{P,C}$ = 10.1 Hz, C-8), 121.2 (s, C-22 or C-23), 121.5 (s, C-22 or C-23), 124.5 (br s, C-10 or C-12), 125.3 (br s, C-10 or C-12), 153.5 (d, $^{4}J_{P,C}$ = 3.5 Hz, C-11), 157.6 (br s, C-9), 182.1 (d, $^{1}J_{P,C}$ = 14.7 Hz, C-18).- ^{31}P NMR (162 MHz, acetone-d_6): δ = –10.6 (dm, $^{1}J_{P,H}$ = 353.3 Hz; dm, $^{1}J_{P,H}$ = 363.0 Hz) ppm. - IR: $\tilde{\nu}$ = 2963 (m), 2241 (m, C≡N), 1589 (w, $CH_{arom.}$), 1526 (w), 1466 (m), 1445 (m), 1389 (m), 1363 (m, *t*Bu), 1284 (w), 1213 (w), 1051 (vs), 1036 (vs), 897 (w), 865 (m), 829 (w), 752 (w), 675 (w), 618 (w) cm^{-1}. - HRMS (ESI, acetonitrile): calcd. for $C_{32}H_{44}N_4NiP$ [M^+]: 573.2657; found 573.2654.

4.8.4 {[2-(2,4,6-Tri-*tert*-butylphenylphosphanyl)ethyl]cyclopentadienyl}-[bis-(1,3-dimethyl-4,5-dicyanoimidazol-2-ylidene)]nickel(II)-tetrafluoroborate (172)



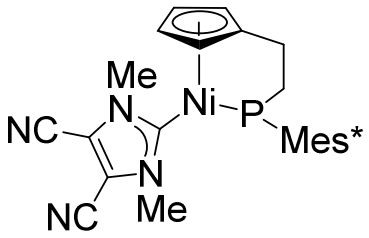
172

At –78 °C NaHMDS (0.8 mL, 0.8 mmol, 1.0 M solution in THF) was added to a suspension of **166** (0.18 g, 0.8 mmol) in THF (30 mL). After stirring for 1 h at this temperature, the reaction mixture was slowly added to a cold solution (–78 °C) of **142** (0.20 g, 0.4 mmol) in THF (250 mL). After 1 h the reaction mixture was allowed to reach 22 °C and stirred for 2 h at this temperature. After solvent removal at reduced pressure the residue was taken up with dichloromethane and filtered through a 3 cm

thick layer of Celite®. After solvent removal the residue was washed with ethyl acetate (5 x 20 mL) and dried in vacuum. **172** (0.13 g, 0.17 mmol, 43 %) was obtained as a green solid (m. p. 220-222 °C, dec.).

^{1}H NMR (400 MHz, acetone-d_6): δ = 1.29 (s, 9H, 15-H), 1.39-1.51 (m, 2H, 6-H), 1.51 (s, 18H, 13-H), 1.67-1.78 (m, 1H, 7-H), 1.67-1.78 (m, 1H, 7-H), 1.92-2.08 (m, 1H, 7-H), 4.35 (s, 17-H), 4.73 (dm, $^{1}J_{P,H}$ = 219.6 Hz, PH), 5.47-5.49 (m, 1H, 2-H or 3-H or 4-H or 5-H), 5.54-5.56 (m, 1H, 2-H or 3-H or 4-H or 5-H), 5.98-6.00 (m, 1H, 2-H or 3-H or 4-H or 5-H), 7.42 (d, 2H, $^{4}J_{P,H}$ = 2.0 Hz, 10-H). - ^{31}C NMR (100.6 MHz, acetone-d_6): δ = 26.5 (d, $^{1}J_{P,C}$ = 16.5 Hz, C-7), 29.1 (d, $^{1}J_{P,C}$ = 14.1 Hz, C-6), 31.5 (s, C-15), 33.8 (d, $^{3}J_{P,C}$ = 7.1 Hz, C-13), 35.5 (s, C-12), 38.9 (s, C-14), 40.1 (s, C-17), 91.5 (s, C-2 or C-3 or C-4 or C-5), 92.2 (s, C-2 or C-3 or C-4 or C-5), 96.4 (s, C-2 or C-3 or C-4 or C-5), 96.6 (s, C-2 or C-3 or C-4 or C-5), 107.8 (s, C-18), 113.4 (d, $^{3}J_{P,C}$ = 10.0 Hz, C-1), 117.9 (s, C-19), 122.9 (d, $^{3}J_{P,C}$ = 4.1 Hz, C-10), 133.5 (d, $^{1}J_{P,C}$ = 28.9 Hz, C-8), 150.0 (s, C-11), 155.2 (d, $^{2}J_{P,C}$ = 7.8 Hz, C-9), 180.0 (s, C-16). - ^{31}P NMR (162 MHz, acetone-d_6): δ = –74.4 (dm, $^{1}J_{P,H}$ = 219.6 Hz) ppm. - IR: $\tilde{\nu}$ = 2955 (m), 2869 (w), 2392 (br w, PH), 2242 (m, C≡N), 1593 (w, $CH_{arom.}$), 1531 (w), 1446 (s), 1389 (s), 1361 (s, *t*Bu), 1283 (w), 1236 (w), 1213 (w), 1051 (vs), 897 (m), 879 (w), 823 (m), 755 (w), 691 (w), 618 (w) cm^{-1}. - HRMS (ESI, acetonitrile): calcd. for $C_{39}H_{50}N_8NiP$ [M^+]: 719.3250; found 719.3250.

4.9 Deprotonation Reactions of 171



173

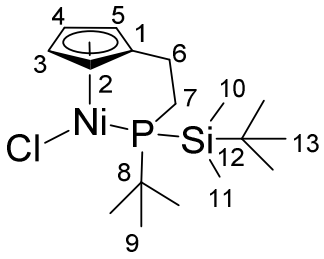
Variant 1. At –78 °C NaHMDS (0.1 mL, 0.1 mmol, 1.0 M solution in THF) was added to a suspension of **171** (0.03 g, 0.1 mmol) in THF (30 mL). After stirring for 1 h at this temperature, the reaction mixture was as allowed to reach 22 °C and stirred for 1 h at this temperature. After solvent removal at reduced pressure the residue was taken up with dichloromethane and filtered through a 3 cm thick layer of Celite®. **173** was obtained in traces.

Variant 2. At –78 °C butyllithium (0.1 mL, 0.1 mmol, 2.5 M solution in hexane) was added to a suspension of **171** (0.03 g, 0.1 mmol) in THF (30 mL). After stirring for 1 h at this temperature, the reaction mixture was as allowed to reach 22 °C and stirred for 1 h at this temperature. After solvent removal at reduced pressure the residue was taken up with dichloromethane and filtered through a 3 cm thick layer of Celite®. **173** was obtained in traces.

HRMS (ESI, acetonitrile): calcd. for $C_{32}H_{44}N_4NiP$ $[M^+ + H]$: 573.2657; found 573.2657.

4.10 Syntheses of Nickel(II) Cyclopentadienylcomplexes with Silylphosphane Tethers

4.10.1 {2-[(*tert*-Butyl)(*tert*-butyldimethylsilyl)phosphanyl]ethyl}-(cyclopentadienyl)chloronickel(II) (202)



202

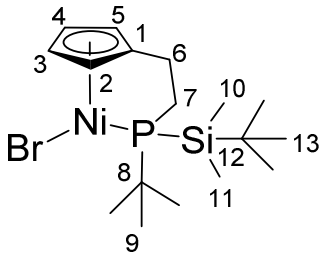
Variant 1 (**GPIV**). *tert*-Butyl(*tert*-butyldimethylsilyl)phosphane (**191**, 0.51 g, 2.5 mmol), spiro[2.4]hepta-4,6-diene (**64**, 0.25 g, 2.7 mmol), $NiCl_2(thf)_2$ (1.02 g, 3.7 mmol) in THF (400 mL). **202** (0.54 g, 1.4 mmol, 56 %) as red-purple small crystals (m. p. 102-103 °C, dec.).

Variant 2. At 22 °C a solution of **197**-**201** (0.05 g, 0.1 mmol) in THF (20 mL) was slowly added to a suspension of $NiCl_2(thf)_2$ (0.04 g, 0.2 mmol) in THF (100 mL). The reaction mixture was stirred at this temperature for 10 min. After solvent removal at reduced pressure the residue was taken up in boiling pentane and filtered through a frit covered with a 3 cm thick layer of Celite®. After solvent removal the crude product was recrystallized twice from pentane at –30 °C. **202** (0.01 g, 0.02 mmol, 10 %) as red-purple small crystals (m. p. 102-103 °C, dec.).

^{1}H NMR (400 MHz, C_6D_6): δ = 0.34 (d, $^3J_{P,H}$ = 3.6 Hz, 3H, 10-H or 11-H), 0.53 (d, $^3J_{P,H}$ = 4.8 Hz, 3H, 10-H or 11-H), 0.86-1.02 (m, 2H, 6-H), 1.09 (s, 9H, 13-H), 1.36 (d, $^3J_{P,H}$ = 14.0 Hz, 9H, 9-H), 1.46-1.65 (m, 2H, 7-H), 5.41 (m, 2H, 2-H or/and 3H or/and

4-H or/and 5-H), 5.52-5.53 (m, 1H, 2-H or 3H or 4-H or 5-H), 5.66-5.68 (m, 1H, 2-H or 3H or 4-H or 5-H) ppm. - ^{13}C NMR (100.6 MHz, C_6D_6): δ = –3.3 (d, $^3J_{P,C}$ = 7.3 Hz, C-10 or C-11), –1.9 = (d, $^3J_{P,C}$ = 10.8 Hz, C-10 or C-11), 20.5 (d, $^2J_{P,C}$ = 3.7 Hz, C-12), 26.3 (s, C-6), 28.2 (s, C-13), 30.3 (s, C-9), 32.2 ($^1J_{P,C}$ = 13.1 Hz, C-8), 34.1 (d, $^1J_{P,C}$ = 16.7 Hz, C-7), 95.9 (d, $^3J_{P,C}$ = 6.1 Hz, C-1), 97.0 (s, C-2 or C-3 or C-4 or C-5), 97.3 (d, $^4J_{P,C}$ = 5.5 Hz, C-2 or C-5), 97.8 (s, C-2 or C-3 or C-4 or C-5), 98.8 (s, C-2 or C-3 or C-4 or C-5) ppm. - ^{31}P NMR (162 MHz, C_6D_6): δ = 24.0 ppm. - IR: $\tilde{\nu}$ = 2930 (s), 2894 (s), 2859 (s), 1458 (s), 1414 (m), 1391 (m), 1358 (s, *t*Bu), 1248 (s, *t*Bu), 1168 (m), 1096 (w), 1058 (m), 1041 (m), 1007 (s), 932 (m), 841 (s, Cp), 811 (vs, Cp), 780 (s), 693 (m), 670 (m), 609 (m) cm^{-1}. - HRMS (TOF MS EI$^+$): calcd for $C_{17}H_{32}ClNiPSi$ 388.1053; found 388.1049. - Elemental analysis: calcd. (%) for $C_{17}H_{32}ClNiPSi$ C 52.39, H 8.29; found C 51.63, H 8.56.

4.10.2 {2-[(*tert*-Butyl)(*tert*-butyldimethylsilyl)phosphanyl]ethyl}-(cyclopentadienyl)bromonickel(II) (203)

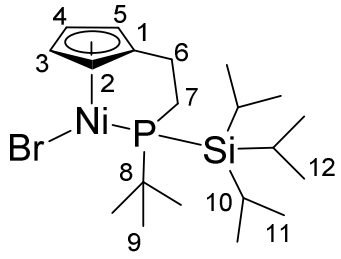


203

Variant 1 (GPIV). *tert*-Butyl(*tert*-butyldimethylsilyl)phosphane (**191**, 0.72 g, 3.5 mmol), 0.35 g of spiro[2.4]hepta-4,6-diene (**64**, 0.35 g, 3.8 mmol), $NiBr_2(thf)_2$ (1.90 g, 5.2 mmol) in THF (500 mL). **203** (1.12 g, 2.6 mmol, 75 %) as red-purple small crystals (m. p. 103-104 °C, dec.).

^{1}H NMR (400 MHz, C_6D_6): δ = 0.37 (d, $^{3}J_{P,H}$ = 4.9 Hz, 3H, 10-H or 11-H), 0.56 (d, $^{3}J_{P,H}$ = 6.2 Hz, 3H, 10-H or 11-H), 0.93-1.18 (m, 2H, 6-H), 1.06 (s, 9H, 13-H), 1.36 (d, $^{3}J_{P,H}$ = 14.0 Hz, 9H, 9-H), 1.53-1.74 (m, 2H, 7-H), 5.38 (m, 2H, 2-H or/and 3H or/and 4-H or/and 5-H), 5.58 (m, 1H, 2-H or 3H or 4-H or 5-H), 5.71 (m, 1H, 2-H or 3H or 4-H or 5-H) ppm. ^{13}C NMR (100.6 MHz, C_6D_6): δ = –2.9 (d, $^{3}J_{P,C}$ = 7.8 Hz, C-10 or C-11), –1.6 = (d, $^{3}J_{P,C}$ = 12.0 Hz, C-10 or C-11), 20.6 (d, $^{2}J_{P,C}$ = 4.7 Hz, C-12), 26.3 (d, $^{3}J_{P,C}$ = 1.2 Hz, C-6), 28.3 (s, C-13), 30.5 (d, $^{2}J_{P,C}$ = 3.2 Hz, C-9), 32.4 (d, $^{1}J_{P,C}$ = 13.6 Hz, C-8), 34.9 (d, $^{1}J_{P,C}$ = 17.0 Hz, C-7), 96.5 (s, C-2 or C-3 or C-4 or C-5), 96.6 (s, C-2 or C-3 or C-4 or C-5), 97.4 (s, C-2 or C-3 or C-4 or C-5), 97.7 (d, $^{4}J_{P,C}$ = 2.6 Hz, C-2 or C-5), 99.8 (d, $^{3}J_{P,C}$ = 7.6 Hz, C-1), ppm. - ^{31}P NMR (162 MHz, C_6D_6): δ = 24.8 ppm. - IR: $\tilde{\nu}$ = 2930 (s), 2895 (s), 2860 (s), 1457 (s), 1414 (w), 1391 (w), 1358 (s, *t*Bu), 1247 (s, *t*Bu), 1177 (w), 1096 (w), 1058 (w), 1041 (w), 1008 (m), 932 (m), 840 (s, Cp), 810 (vs, Cp), 782 (s), 771 (s), 692 (w), 669 (m), 610 (m) cm^{-1}. - HRMS (TOF MS EI^{+}): calcd. for $C_{17}H_{32}BrNiPSi$ 432.0548; found 432.0543. - Elemental analysis: calcd. (%) for $C_{17}H_{32}BrNiPSi$ C 47.03, H 7.44; found C 46.77, H 7.61.

4.10.3 {2-[(*tert*-Butyl)(triisopropylsilyl)phosphanyl]ethyl}(cyclopentadienyl)-bromonickel(II) (204)

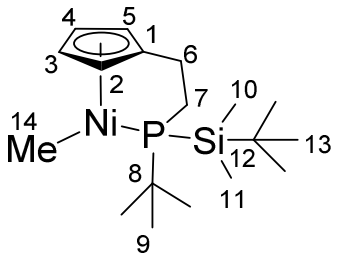


204

GPIV: *tert*-Butyl(triisopropylsilyl)phosphane (**192**, 0.23 g, 0.93 mmol)), spiro[2.4]hepta-4,6-diene (**64**, 0.09 g, 1.0 mmol), $NiBr_2(thf)_2$ (0.61 g, 1.4 mmol) in THF (160 mL). **204** (0.23 g, 0.49 mmol, 53 %) as red-purple small crystals (m. p. 120-121 °C, dec.).

^{1}H NMR (400 MHz, C_6D_6): δ = 0.91-1.22 (m, 2H, 6-H), 1.23 (d, $^{3}J_{P,H}$ = 7.4 Hz, 9H, 11-H or 12-H), 1.30 (d, $^{3}J_{P,H}$ = 7.4 Hz, 9H, 11-H or 12-H), 1.41 (d, $^{3}J_{P,H}$ = 14.0 Hz, 9H, 9-H), 1.51-1.61 (m, 3H, 10-H), 1.61-1.69 (m, 1H, 7-H), 1.75-1.84 (m, 1H, 7-H), 5.32 (m, 1H, 2-H or 3-H or 4-H or 5-H), 5.40 (m, 1H, 2-H or 3-H or 4-H or 5-H), 5.52-5.53 (m, 1H, 2-H or 3-H or 4-H or 5-H), 5.77-5.79 (m, 1H, 2-H or 3-H or 4-H or 5-H) ppm. - ^{13}C NMR (100.6 MHz, C_6D_6): δ = 14.1 (d, $^{2}J_{P,C}$ = 7.4 Hz, C-10), 20.2 (s, C-11 or C-12), 20.4 (s, C-11 or C-12), 26.8 (C-6), 30.8 (d, $^{2}J_{P,C}$ = 3.0 Hz, C-9), 33.3 (d, $^{1}J_{P,C}$ = 11.3 Hz, C-8), 36.2 (d, $^{1}J_{P,C}$ = 15.4 Hz, C-7), 96.9 (s, C-3 or C-4), 97.2 (d, $^{4}J_{P,C}$ = 5.6 Hz, C-2 or C-5), 97.4 (d, $^{4}J_{P,C}$ = 2.8 Hz, C-2 or C-5), 98.9 (s, C-3 or C-4), 100.0 (d, $^{3}J_{P,C}$ = 7.7 Hz, C-1). - ^{31}P NMR (162 MHz, C_6D_6): δ = 25.2 ppm. - IR: $\tilde{\nu}$ = 2920 (s), 2866 (s), 1456 (s), 1392 (w), 1357 (m), 1239 (w), 1172 (m), 1057 (m), 1005 (m), 929 (m), 875 (s), 821 (s, Cp), 783 (vs), 764 (s), 654 (s), 609 (m) cm^{-1}. - HRMS (TOF MS EI^{+}): calcd. for $C_{20}H_{38}BrNiPSi$ 474.1017; found 474.1012.

4.10.4 {2-[(*tert*-Butyl)(*tert*-butyldimethylsilyl)phosphanyl]ethyl}-(cyclopentadienyl)methylnickel(II) (209)



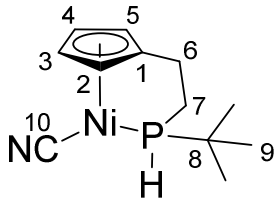
209

At 22 °C methyllithium (1.8 mL, 3.0 mmol, 1.6 M in Et_2O) was added to **202** (0.79 g, 2.0 mmol) in diethyl ether (100 mL). The resulting green reaction mixture was stirred for 2 h at this temperature. After solvent removal at reduced pressure the residue was taken up in pentane (50 mL) and filtered through a frit covered with a 3 cm thick layer of Celite®. The filtrate was concentrated and the product was crystallized from

pentane at –30 °C. **209** (0.36 g, 0.9 mmol, 48 %) was isolated as small green crystals (m. p. 78-79 °C, dec.).

^{1}H NMR (400 MHz, C_6D_6): δ = –0.59 (d, $^{3}J_{P,H}$ = 4.6 Hz, 3H, 14-H), 0.1 (d, $^{3}J_{P,H}$ = 4.1 Hz, 3H, 10-H or 11-H), 0.29 (d, $^{3}J_{P,H}$ = 5.1 Hz, 3H, 10-H or 11-H), 1.10 (s, 9H, 13-H), 1.13 (d, $^{3}J_{P,H}$ = 13.6 Hz, 9H, 9-H), 1.66-1.80 (m, 2H, 6-H), 1.96-2.05 (m, 1H, 7-H), 2.01-2.19 (m, 1H, 7-H), 5.14 (m, 1H, 2-H or 3-H or 4-H or 5-H), 5.34-5.35 (m, 1H, 2-H or 3-H or 4-H or 5-H), 5.60 (m, 1H, 2-H or 3-H or 4-H or 5-H), 5.91-5.92 (m, 1H, 2-H or 3-H or 4-H or 5-H) ppm. - ^{13}C NMR (100.6 MHz, C_6D_6): δ = –42.3 (d, $^{2}J_{P,C}$ = 19.5 Hz, C-14), –3.7 = (d, $^{3}J_{P,C}$ = 6.3 Hz, C-10 or C-11), –2.4 = (d, $^{3}J_{P,C}$ = 10.0 Hz, C-10 or C-11), 20.3 (d, $^{2}J_{P,C}$ = 7.0 Hz, C-12), 26.0 (d, $^{2}J_{P,C}$ = 2.6 Hz, C-6), 27.9 (s, C-13), 30.2 (d, $^{2}J_{P,C}$ = 4.6 Hz, C-9), 32.8 ($^{1}J_{P,C}$ = 13.3 Hz, C-8), 41.0 (d, $^{1}J_{P,C}$ = 16.0 Hz, C-7), 87.9 (d, $^{4}J_{P,C}$ = 5.3 Hz, C-2 or C-5), 89.9 (d, $^{4}J_{P,C}$ = 5.9 Hz, C-2 or C-5), 93.7 (s, C-3 or C-4), 95.6 (s, C-3 or C-4), 107.8 (d, $^{3}J_{P,C}$ = 8.1 Hz, C-1) ppm. - ^{31}P NMR (162 MHz, C_6D_6): δ = 16.5 ppm. - IR: $\tilde{\nu}$ = 2935 (m), 2891 (m), 2855 (m), 1461 (m), 1388 (m), 1363 (m, *t*Bu), 1251 (m, *t*Bu), 1181 (w), 1127 (s), 1046 (w), 1023 (m), 927 (w), 836 (s, Cp), 808 (vs, Cp), 777 (vs), 765 (s), 696 (w), 661 (m), 615 (m) cm^{-1}. - HRMS (TOF MS EI^{+}): calcd. for $C_{18}H_{35}NiPSi$ 368.1599; found 368.1595.

4.11 {2-[(*tert*-Butylphosphanyl)ethyl]cyclopentadienyl}cyanonickel(II) (211)



211

Variant 1. At 22 °C trimethylsilylcyanide (0.06 g, 0.6 mmol) was added to **202** (0.19 g, 0.5 mmol) in THF (30 mL). The resulting green reaction mixture was stirred for 4 h at this temperature. After solvent removal at reduced pressure the residue was puri-

fied by column chromatography (2 x 30 cm, SiO_2, ethyl acetate). The solution was concentrated, and the product was crystallized from hexane/ethyl acetate (1:1) at 0 °C. **211** (0.27 g, 1.0 mmol, 50 %), green crystals (m. p. 108-109 °C, dec.).

Variant 2. At 22 °C trimethylsilylcyanide (0.60 g, 6.0 mmol) was added to **203** (0.62 g, 3.0 mmol) in THF (50 mL). The resulting green reaction mixture was stirred for 5 h at this temperature. After solvent removal at reduced pressure the residue was purified by column chromatography (2 x 30 cm, SiO_2, ethyl acetate). The solution was concentrated, and the product was crystallized from hexane/ethyl acetate (1:1) at 0 °C. **211** (0.32 g, 1.2 mmol, 40 %).

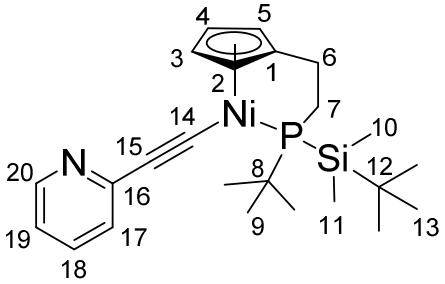
^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.33 (d, $^3J_{P,H}$ = 16.5 Hz, 9H, 9-H), 1.85-2.06 (m, 2H, 6-H), 2.03-2.05 (m, 1H, 7-H), 2.63-2.74 (m, 1H, 7-H), 4.70 (dm, $^1J_{P,H}$ = 342.4 Hz, 1H, PH), 5.50-5.52 (m, 1H, 2-H or 3-H or 4-H or 5-H), 5.57-5.61 (m, 2H, 2-H or/and 3-H or/and 4-H or/and 5-H), 5.65 (m, 1H, 2-H or 3-H or 4-H or 5-H) ppm. - ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 24.5 (d, $^2J_{P,C}$ = 3.6 Hz, C-6), 27.8 (d, $^2J_{P,C}$ = 3.9 Hz, C-9), 29.3 (d, $^1J_{P,C}$ = 27.3 Hz, C-8), 36.7 (d, $^1J_{P,C}$ = 26.2 Hz, C-7), 92.2 (d, $^4J_{P,C}$ = 5.2 Hz, C-2 or C-3 or C-4 or C-5), 92.7 (d, $^5J_{P,C}$ = 1.6 Hz, C-2 or C-3 or C-4 or C-5), 93.8 (d, $^4J_{P,C}$ = 4.7 Hz, C-2 or C-3 or C-4 or C-5), 95.4 (d, $^5J_{P,C}$ = 1.7 Hz, C-2 or C-3 or C-4 or C-5), 111.0 (d, $^3J_{P,C}$ = 8.9 Hz, C-1), 125.7 (d, $^2J_{P,C}$ = 24.4 Hz, C-10) ppm. - ^{31}P NMR (162 MHz, $CDCl_3$): δ = 56.7 (dm, $^1J_{P,H}$ = 342.1 Hz, PH) ppm. - IR: $\tilde{\nu}$ = 3073 (m), 2952 (m, -CH_3, -CH_2-), 2865 (m, -CH_3, -CH_2-), 2330 (m, PH), 2107 (vs, C≡N), 1463 (s), 1414 (w), 1396 (w), 1358 (m, *t*Bu), 1309 (w), 1276 (w), 1194 (m), 1171 (m), 1104 (w), 1068 (w), 1048 (w), 1018 (m), 979 (m), 942 (w), 873 (m), 846 (vs, Cp), 801 (vs, Cp), 687 (m), 655 (w), 627 (m) cm^{-1}. - HRMS (TOF MS EI$^+$): calcd. for $C_{12}H_{18}NNiP$ 265.0530; found 265.0526. - Elemental analysis: calcd. (%) for $C_{12}H_{18}NNiP$ C 54.19, H 6.83, N 5.26; found C 54.09, H 7.01, N 5.54.

Crystal structure analysis of 211: Single crystals of **211** were obtained by crystallization from hexane/ethyl acetate (1:1) at 0 °C. Empirical formula $C_{12}H_{12}NNiP$, formula weight 259.90 g/mol, crystal system orthorhombic, space group $Pca2_1$, unit cell dimensions *a* = 12.5336(1), *b* = 16.6769(1), *c* = 12.3516(1) Å, α = 90°, β = 90°, γ = 90°, *V* = 2581.75(3) Å^3, *Z* = 8, $d_{calc.}$ = 1.337 g/cm^3, µ = 3.068 mm^{-1}, crystal size 0.27 x

0.25 x 0.11 mm, *F* (000) = 1072, Bruker KAPPA APEX II CCD diffractometer, *T* = 193 K, Cu-K_α radiation (λ = 1.54187 Å), θ-range 2.65 to 65.85°, reflections collected/unique 30288/325 [*R*(int) = 0.0591], completeness of data θ = 65.85 (96.0%), index ranges –12≤ *h* ≤ 14, –18≤ *k* ≤ 19, –14 ≤ *l* ≤ 14, numerical absorption correction, no extinction correction, direct methods, full-matrix least-squares refinement on F^2, two independent molecules per asymmetric unit, inversion twin (fractions 0.6/0.4), goodness-of-fit on F^2 = 1.066, R_1=0.0573 ($I > 2\sigma_I$), wR_2 ($I > 2\sigma_I$) = 0.1652, R_1 (all data) = 0.0593, wR_2 (all data) = 0.1678, final difference electron density 0.820 and –0.326 eÅ^{-3}; CCDC 1011721.

4.12 Bruce-coupling Reactions of 203 with Terminal Alkynes

4.12.1 {[2-(*tert*-Butyl)(*tert*-butyldimethylsilyl)phosphanyl)ethyl]-cyclopentadienyl}[2-(2-pyridyl)ethynyl]nickel(II) (224)

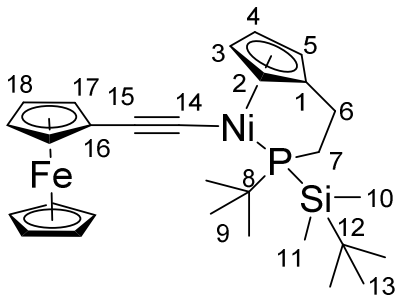


224

GPV: From **230** (0.07 g, 0.7 mmol) in NEt_3 (10 mL), **203** (0.26 g, 0.6 mmol) in NEt_3 (50 mL) and CuI (5 mg). After stirring the reaction mixture for 3 h the solvent was removed at reduced pressure. After work up with diethyl ether, and purification by column chromatography [2 x 30 cm, SiO_2, PE/ethyl acetate, (7:3)] **124** was isolated as a green solid contaminated with brown oil (purity ≥ 90 % (^{31}P NMR). Repeated purification procedures resulted in decomposition.

^{1}H NMR (400 MHz, C_6D_6): δ = 0.51 (d, $^{3}J_{P,H}$ = 5.4 Hz, 3H, 10-H or 11-H), 0.61 (d, $^{3}J_{P,H}$ = 6.4 Hz, 3H, 10-H or 11-H), 1.17 (s, 9H, 13-H),1.48 (d, $^{3}J_{P,H}$ = 134.8 Hz, 9H, 9-H), 1.90-2.13 (m, 2H, 6-H), 2.48-2.62 (m, 2H, 7-H), 5.49 (m, 1H, 2-H or 3-H or 4-H or 5-H), 5.54 (m, 2H, 2-H or/and 3-H or/and 4-H or/and 5-H), 5.76-5.77 (m, 1H, 2-H or 3-H or 4-H or 5-H), 6.86 (m, 1H, 17-H or 18-H or 19-H), 7.02-7.03 (m, 1H, 17-H or 18-H or 19-H), 7.35-7.39 (m, 1H, 17-H or 18-H or 19-H), 8.34 (m, 1H, 20-H) ppm. - ^{31}P NMR (162 MHz, $CDCl_3$): δ = 35.8 ppm.

4.12.2 {[2-(*tert*-Butyl(*tert*-butyldimethylsilyl)phosphanyl)ethyl]-cyclopentadienyl}[2-(ferrocenyl)ethynyl]nickel(II) (235)



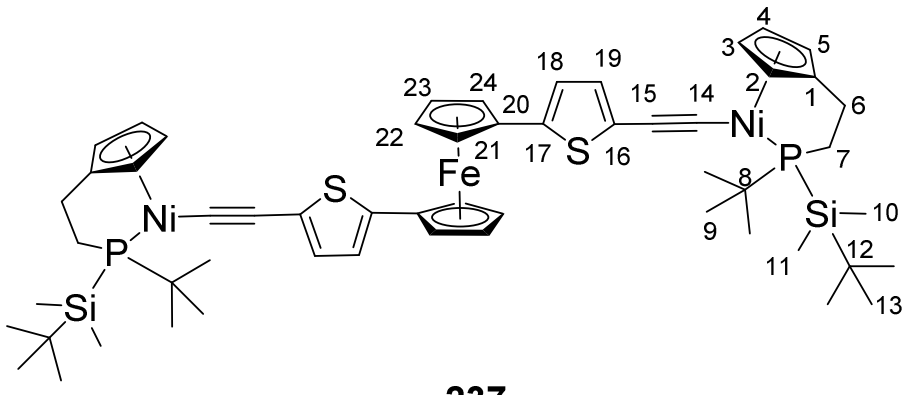
235

GPV: From **234** (0.14 g, 0.7 mmol) in NEt_3 (10 mL), **203** (0.20 g, 0.7 mmol) in NEt_3 (50 mL) and CuI (5 mg). After stirring the reaction mixture for 12 h the solvent was removed at reduced pressure. After work up with diethyl ether and purification by column chromatography (2 x 40 cm, SiO_2, PE) **235** (0.25g, 0.43 mmol, 63 %) as a brown solid (m. p. 114-116 °C, dec.).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.55 (d, $^{3}J_{P,H}$ = 5.2 Hz, 3H, 10-H or 11-H), 0.66 (d, $^{3}J_{P,H}$ = 6.4 Hz, 3H, 10-H or 11-H), 1.22 (s, 9H, 13-H), 1.49 (d, $^{3}J_{P,H}$ = 14.6 Hz, 9H, 9-H), 1.87-2.09 (m, 2H, 6-H), 2.46-2.60 (m, 2H, 7-H), 3.91-3.92 (m, 2H, 17-H or 18-H), 4.08 (s, 5H, Cp'), 4.12 (m, 4H, 17-H or 18-H), 5.44-5.45 (m, 1H, 2-H or 3-H or 4-H or 5-H), 5.51-5.52 (m, 2H, 2-H or/and 3-H or/and 4-H or/and 5-H), 5.79-5.80 (m, 1H,

2-H or 3-H or 4-H or 5-H) ppm. - ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = –3.1 (d, $^3J_{P,C}$ = 8.1 Hz, C-10 or C-11), –1.7 = (d, $^3J_{P,C}$ = 11.8 Hz, C-10 or C-11), 20.7 (d, $^2J_{P,C}$ = 5.3 Hz, C-13), 26.5 (s, C-6), 28.3 (s, C-12), 30.6 (d, $^2J_{P,C}$ = 3.7 Hz, C-9), 32.9 ($^1J_{P,C}$ = 14.7 Hz, C-8), 38.5 (d, $^1J_{P,C}$ = 15.4 Hz, C-7), 66.4 (d, $^1J_{C,H}$ = 2.4 Hz, C-17 or C-18), 69.2 (s, Cp'), 70.4 (d, $^1J_{C,H}$ = 4.7 Hz, C-17 or C-18), 73.8 (s, C-16), 82.7 (d, $^2J_{P,C}$ = 30.9 Hz, C-14), 91.9 (d, $^4J_{P,C}$ = 4.5 Hz, C-2 or C-3 or C-4 or C-5), 92.2 (d, $^4J_{P,C}$ = 5.8 Hz, C-2 or C-3 or C-4 or C-5), 94.3 (d, $^4J_{P,C}$ = 1.4 Hz, C-2 or C-3 or C-4 or C-5), 95.5 (s, C-3 or C-4), 107.6 (d, $^3J_{P,C}$ = 7.8 Hz, C-1), 112.0 (s, C-15) ppm. - ^{31}P NMR (162 MHz, $CDCl_3$): δ = 33.8 ppm. - IR: $\tilde{\nu}$ = 3096 (w), 2956 (m, -CH_3, -CH_2-), 2856 (m, -CH_3, -CH_2-), 2093 (s, C≡C), 14611 (m), 1447 (m), 1411 (w), 1356 (w), 1308 (w), 1247 (m), 1226 (w), 1202 (w), 1167 (w), 1105 (w), 1037 (w), 1020 (w), 1001 (m), 926 (w), 905 (w), 838 (m), 803 (vs, Cp), 783 (vs), 763 (s), 676 (w), 661 (m), 619 (m) cm^{-1}. - HRMS (ESI, acetonitrile): calcd. for $C_{29}H_{41}FeNiPSi$ 562.1418; found 562.1420.

4.12.3 1,1'-Bis{4-[2-(*tert*-butyl(*tert*-butyldimethylsilyl)phosphanyl)ethyl)-cyclopentadienylnickel(II)ethynyl]thiophenyl}ferrocene (237)



237

GPV: From **236** (0.84 g, 0.2 mmol) in NEt_3 (10 mL), **203** (0.15 g, 0.4 mmol) in NEt_3 (50 mL) and CuI (5 mg). After stirring the reaction mixture for 15 h the solvent was removed at reduced pressure. After work up with diethyl ether, and purification by column chromatography [2 x 40 cm, SiO_2, PE/ethyl acetate (1:1)] **237** (0.21g, 0.11 mmol, 51 %) as a brown solid (m. p. 92-93 °C, dec.).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.51 (d, $^{3}J_{P,H}$ = 5.2 Hz, 6H, 10-H or 11-H), 0.62 (d, $^{3}J_{P,H}$ = 3.6 Hz, 6H, 10-H or 11-H), 1.20 (s, 18H, 13-H), 1.49 (d, $^{3}J_{P,H}$ = 14.7 Hz, 18H, 9-H), 1.92-2.13 (m, 4H, 6-H), 2.49-2.62 (m, 4H, 7-H), 4.06-4.07 (m, 4H, 21-H, 24-H or 22-H, 23-H), 4.27-4.28 (m, 4H, 21-H, 24-H or 22-H, 23-H), 5.48 (m, 2H, 2-H or 3-H or 4-H or 5-H), 5.56 (m, 4H, 2-H or/and 3-H or/and 4-H or/and 5-H), 5.80-5.81 (m, 2H, 2-H or 3-H or 4-H or 5-H), 6.52 (d, $^{1}J_{H,H}$ = 3.6 Hz, 2H, 18-H or 19-H), 6.56 (d, $^{1}J_{H,H}$ = 3.7 Hz, 2H, 18-H or 19-H) ppm. - ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = –3.2 (d, $^{3}J_{P,C}$ = 8.0 Hz, C-10 or C-11), –1.8 = (d, $^{3}J_{P,C}$ = 11.8 Hz, C-10 or C-11), 20.7 (d, $^{2}J_{P,C}$ = 5.3 Hz, C-12), 26.6 (d, $^{3}J_{P,C}$ = 1.6 Hz, C-6), 28.3 (s, C-13), 30.5 (d, $^{2}J_{P,C}$ = 3.8 Hz, C-9), 33.1 ($^{1}J_{P,C}$ = 14.6 Hz, C-8), 38.7 (d, $^{1}J_{P,C}$ = 15.1 Hz, C-7), 68.3 (s, C-21, C-24 or C-22, C-23), 70.7 (s, C-21, C-24 or C-22, C-23), 81.8 (s, C-20), 91.6 (d, $^{4}J_{P,C}$ = 4.2 Hz, C-2 or C-3 or C-4 or C-5), 92.1 (d, $^{4}J_{P,C}$ = 5.6 Hz, C-2 or C-3 or C-4 or C-5), 94.4 (d, $^{4}J_{P,C}$ = 1.8 Hz, C-2 or C-3 or C-4 or C-5), 95.6 (d, $^{4}J_{P,C}$ = 1.6 Hz, C-2 or C-3 or C-4 or C-5), 98.5 (d, $^{1}J_{P,C}$ = 30.8 Hz, C-14), 108.4 (d, $^{3}J_{P,C}$ = 8.0 Hz, C-1), 109.1 (s, C-15), 121.6 (s, C-18 or C-19), 127.5 (s, C-16 or C-17), 127.7 (s, C-18 or C-19), 137.9 (s, C-16 or C-17) ppm. - ^{31}P NMR (162 MHz, $CDCl_3$): δ = 35.0 ppm. - IR: $\tilde{\nu}$ = 2952 (m, -CH_3, -CH_2-), 2853 (m, -CH_3, -CH_2-), 2363 (s), 2342 (s), 2070 (s, C≡C), 1460 (m), 1357 (w, *t*Bu), 1258 (m), 1022 (m, *t*Bu), 787 (s, Cp), 669 (m), 618 (m) cm^{-1}. - HRMS (ESI, acetonitrile): calcd. for $C_{56}H_{76}FeNi_2P_2S_2Si_2$ 1102.2459; found 1102.2460.

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