New Reactions of Cyclopentadienylnickel Chelates with Secondary Phosphane Tethers

Sandra Lauren Heinisch,[a] Irina Werner,[a] and Holger Butenschön*[a]

Dedicated to Professor Dr. K. Peter C. Vollhardt on the occasion of his 75th birthday
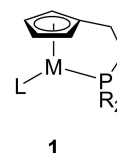
In continuation of our research in cyclopentadienylalkylphosphane nickel chelates with secondary phosphane tethers the first cationic representatives of this class of compounds are reported. These were obtained by reaction of the respective bromo complex with tris(4-trifluoromethylphenyl)phosphane as well as with a number of alkyl and aryl isonitriles in the presence of indium tribromide. This Lewis acid is crucial for the success of the reactions leading to the respective tetrabromoindate salts. The compounds were characterized spectroscopically, including rare $^{14}N,^{13}C$ couplings being observed. Finally, deprotonation experiments are reported, which provide some evidence for deprotonation taking place, although the expected phosphinidene chelates could not be isolated due to rapid decomposition.

Introduction

Heterobidentate ligand systems consisting of a cyclopentadienyl and a phosphane moiety separated by an alkyl spacer form chelate complexes as well as cyclopentadienyl complexes with an uncoordinated phosphane tether. These deserve interest as complexes with hemilabile ligands, which may reversibly provide a vacant coordination site.[1] Such complexes have been prepared for a number of transition metals, and those with an ethylene spacer with the general formula **1** came out to be particularly stable as chelates (Scheme 1).[2]

In most cases the phosphorus atom bears two identical substituents, usually phenyl or *tert*-butyl groups.[2] In some cases, however, the cyclopentadienyl as well as the phosphane moieties have been the subject of variations, for example by replacement of the cyclopentadienyl by an indenyl or fluorenyl system.[3–16] Variations at the phosphane part include unsymmetrical substitution patterns such as phenyl/alkyl,[5] alkyl/silyl,[17] or rare cases of secondary phosphane moieties.[17,18] We have investigated complexes such as **2–5** with cobalt, nickel and iron as the metal centers for a long time (Scheme 2).[4,5,17,19–34] Here we report some new reactions of cyclopentadienylnickel complexes with a secondary phosphane tether.

[a] Dr. S. L. Heinisch, Dr. I. Werner, Prof. Dr. H. Butenschön
Institut für Organische Chemie
Leibniz Universität Hannover
Schneiderberg 1B, 30167 Hannover, Germany
E-mail: holger.butenschoen@mbox.oci.uni-hannover.de
www.ak-butenschoen.uni-hannover.de

Scheme 1. (2-Phosphanylethyl)cyclopentadienyl chelate complex.;
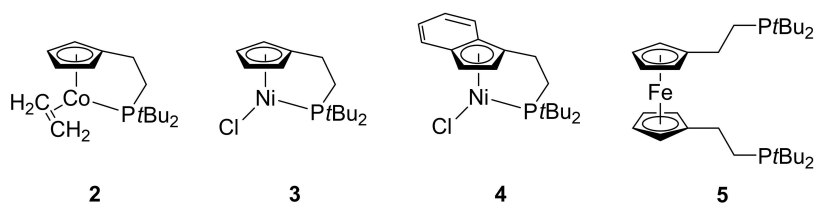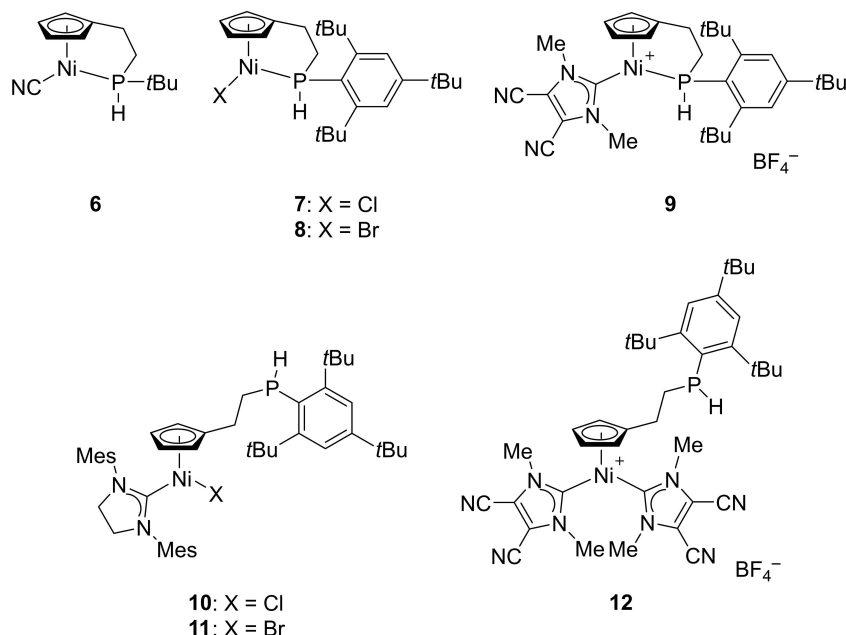
Results and Discussion

In the context of our research the first late transition metal cyclopentadienylalkylphosphane complexes **6–12** with a secondary phosphane tether have recently been prepared (Scheme 3).[17,35]

Chelate **6**, which was obtained in up to 50% yield, is the result of an unexpected protiodesilylation of the respective tertiary (*tert*-butyldimethylsilyl)-*tert*-butylphosphanyl chelate in the course of a column chromatography on silica gel.[17] Chelates **7** and **8** were obtained in a one pot reaction sequence starting from (2,4,6-tri-*tert*-butylphenyl)phosphane,[36] which was subsequently treated with butyllithium, spiro[2.4]hepta-4,6-diene,[37] and NiCl$_2$(dme)$_2$ or NiBr$_2$(thf)$_2$, in an overall yield of 48% or 69%, respectively.[17] The cationic chelate **9** was obtained upon treatment of precursor **7** with 0.5 equivalents of 1,3-dimethyl-4,5-dicyanoimidazolium tetrafluoroborate in the presence of sodium hexamethyldisilazide.[38] Beyond these chelates the unchelated derivatives **10–12** have been prepared. **10** and **11** were obtained upon treatment of **7** or **8** with 1,3-dimesityl-4,5-dihydroimidazol-2-ylidene in 63% and 85% yield, respectively, and **12** was obtained in 43% yield from **7** by treatment with 2.0 equivalents of 1,3-dimethyl-4,5-dicyanoimidazolium tetrafluoroborate in the presence of sodium hexamethyldisilazide.[38] In particular, cationic chelate **9** deserves interest with respect to a deprotonation at phosphorus.

Scheme 2. [2-(Di-*tert*-butylphosphanyl)ethyl]cyclopentadienyl complexes of Co, Ni and Fe.;
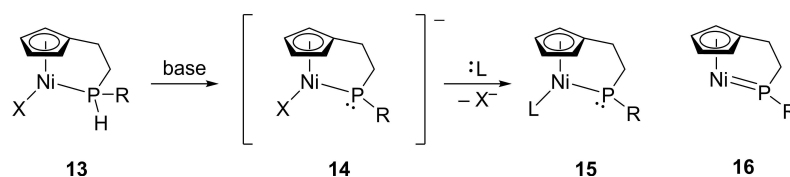

Scheme 3. (2-Phosphanylethyl)cyclopentadienyl complexes with secondary phosphane.;

However, preliminary investigations in this context gave only unclear results.

The idea behind this chemistry is the possibility of a deprotonation of the phosphorus atom in **13** to give intermediate **14** followed by a substitution of the halide ligand X by an electroneutral ligand L to give a phosphido complex **15**, which might generate a phosphinidene species like **16** by ligand dissociation (Scheme 4).

In order to enhance the acidity of the proton bound to phosphorus in chelate **8** we envisaged the exchange of the bromo ligand by the electron withdrawing, electroneutral tris(4-trifluoromethylphenyl)phosphane (**17**). As treatment of chelate **8** with 1.0 equiv. of **17** resulted in the isolation of starting material only, an abstraction of the bromo ligand by addition of
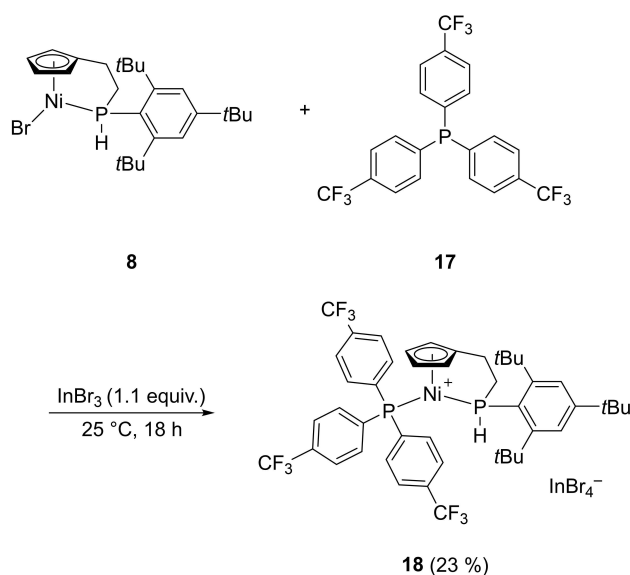
1.7 equiv. of silver tetrafluoroborate was tried. While a reaction took place, the dark brown solid obtained could not be characterized by NMR or IR spectroscopy nor by mass spectrometry; presumably decomposition had taken place. As the use of silver tetrafluoroborate may give rise to oxidation processes, the presence of fluoride ions and the formation of intermetallic bonds,[39–41] we wanted to use a less reactive, presumably more selective reagent for the bromide abstraction. Indium(III) bromide is a mild Lewis acid,[42] which may form the non-nucleophilic tetrabromoindate anion with bromide. Treatment of **8** with 1.0 equiv. of **17** and 1.1 equiv. of indium(III) bromide in THF at 25 °C caused a color change from purple to brown. Crystallization from the crude product solution in dichloromethane/hexane (3:2) gave the cationic chelate **18** as
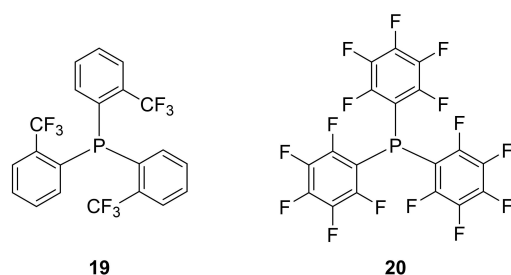

Scheme 4. Concept.;

EurJIC
European Journal of Inorganic Chemistry

Full Papers
doi.org/10.1002/ejic.202100147

**Chemistry
Europe**
European Chemical
Societies Publishing

the tetrabromoindate salt. **18** is a moderately air stable brown crystalline material, which was obtained in 23% yield (Scheme 5). While the yield is only moderate, this is the only case of a reaction giving a cationic complex such as **18** with a phosphane ligand. Although **18** was obtained as a crystalline material, several attempts to obtain an X-ray crystal structure analysis of sufficient quality failed because of crystallographic disorders in the ethylene bridge and the trifluoromethyl substituents. To make the data obtained available, the analysis is included in the Supporting Information.[43]
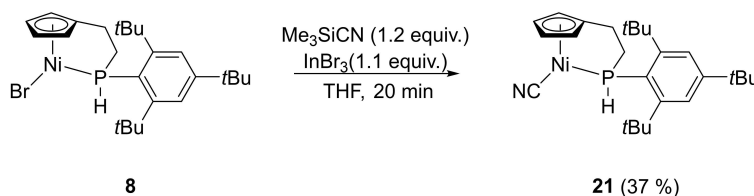
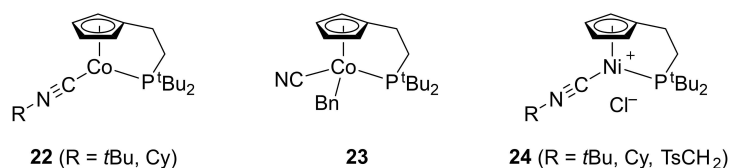Attempts to perform a corresponding ligand exchange at **8** with tris(2-trifluoromethylphenyl)phosphane (**19**) or with tris (pentafluorophenyl)phosphane (**20**) under similar reaction con-ditions failed, even at elevated temperature (Scheme 6). As the electronic properties of **17** and **19** should be similar, reasons may be the significantly larger cone angle θ of **19** ($\theta = 221°$) as compared to **17** ($\theta = 149°$).[44] The cone angle of **20** ($\theta = 184°$)[45] is smaller than that of **19**, however, the electron withdrawal is much larger than that of **17** or **19** thus decreasing the ligand σ donor ability.[45,46] The formation of **18** can thus be understood as a combination of moderate steric bulk and electron with-drawal of the incoming ligand **17**.
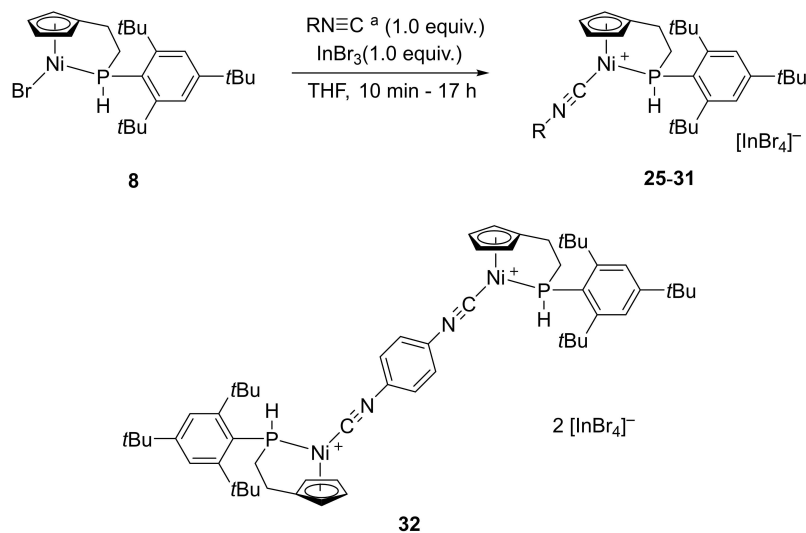
18 was fully characterized by spectroscopic methods. Significant features are the observation of the molecular cation of **18** in the mass spectrum ($m/z = 893.2598$) and the IR absorption for the trifluoromethyl groups at 1321 cm^{-1}. An absorption in the area of 2440–2350 cm^{-1} assignable to the P–H bond was not observed; however, there are other reports of secondary phosphane metal complexes, which also do not report the observation of such an absorption band.[47–49] In the ^{1}H NMR spectrum two signals for the diastereotopic *ortho-tert-*butyl groups are observed at $\delta = 1.33$ and 1.36 ppm. In accord with the asymmetry of the compound four signals are observed for the cyclopentadienyl protons. A signal assigned to the proton bound to phosphorus is observed at $\delta = 6.85$ ppm and appears as a doublet of doublets with $^1J_{P,H} = 380.9$ Hz (the exact value taken from the ^{31}P NMR spectrum, *vide infra*). As a consequence of the large $^1J_{P,H}$ coupling constant the signal shows two lines at 6.38 ppm ($^3J_{P,H} = 8$ Hz; $\nu = 400.1$ MHz). The other part of the signal is visible at $\delta = 7.33$ ppm ($\nu = 400.1$ MHz), but is partly covered by the signals of the aromatic systems. The ^{31}P{^{1}H} NMR spectrum shows two signals for the secondary ($\delta = -22.1$ ppm) and for the tertiary ($\delta = 36.7$ ppm) phosphorus atoms with a $^2J_{P,P}$ coupling constant of 29.8 Hz. The ^{31}P NMR spectrum clearly shows a coupling of $^1J_{P,H} = 380.9$ Hz within a dd signal for the secondary phosphorus atom. Compared to the electroneutral bromo complex **8** the secondary phosphorus atom in **18** is shielded by $\Delta\delta = 16.4$ ppm.

Another ligand exchange was achieved upon treatment of **8** with trimethylsilyl cyanide. The reaction afforded cyano com-plex **21** in 37% yield (Scheme 7). Remarkably, corresponding treatment of **8** with trimethylsilyl isocyanate, trimethylsilyl azide or sodium azide resulted in the re-isolation of starting material even after longer periods of time and at elevated temperature (6–7 h, 45 °C).

A possible reaction mechanism involves an oxidative addition of trimethylsilyl cyanide supported by a temporary decomplexation of the phosphane tether and followed by a reductive elimination of trimethylsilyl bromide. This reactivity

Scheme 5. Synthesis of cationic chelate **18**.;

Scheme 6. Phosphanes **19** and **20**.;

Scheme 7. Synthesis of cyano complex **21**.;

EurJIC
European Journal of Inorganic Chemistry

Full Papers
doi.org/10.1002/ejic.202100147

Chemistry Europe
European Chemical
Societies Publishing

Scheme 8. Isonitrile chelates with tertiary phosphane ligands.;

Scheme 9. Synthesis of isonitrile chelates with secondary phosphane ligands. [a] 0.5 equiv. of benzene-1,4-diisonitrile (Table 1, entry 8).

resembles that observed with chelates **3** and **4**,[4,50] while closely related chelate **6** had been formed by a protiodesilylation.[17] **21** was characterized spectroscopically. Key features are the CN absorption band in the IR spectrum at $\tilde{\nu} = 2160\ cm^{-1}$, the observation of the molecular ion in the mass spectrum ($m/z = 454$) and the expected signals in the ^1H and ^{13}C NMR spectra, which reflect the asymmetry of the compound. The signal assigned to the proton bound at phosphorus is observed at $\delta = 6.12$ ppm as a ddd signal with a P,H coupling constant of $^1J_{P,H} = 353.9$ Hz.

Another important electron withdrawing ligand type with potential for catalysis are isonitrile ligands.[51] In the context of our earlier research cobalt chelates **22** were obtained upon treatment of the respective ethene chelate complex with isonitriles; in the case of benzyl isonitrile an oxidative addition with formation of **23** was observed.[52,53] Cationic nickel chelates **24** were obtained as stable compounds from **3** by treatment with the respective isonitriles (Scheme 8).[50] Cyclopentadienyl-nickel(II) complexes with a phosphane and an isonitrile ligand are comparatively rare.[54–56]

As isonitrile ligands are isoelectronic with carbon monoxide and tunable by variation of the organic substituent, we reasoned that they may facilitate a deprotonation of secondary phosphorus ligands. Therefore, chelate **8** was treated with some isonitriles. However, in the cases of *tert*-butyl and cyclohexyl isonitrile, the reaction products decomposed during workup. With 4-cyanophenyl isonitrile no reaction was observed.

When an equimolar amount of indium tribromide was added, however, the reactions proceeded smoothly and afforded the respective products. Reactions with *tert*-butylisonitrile, cyclohexylisonitrile and 1,4-diisocyanobenzene (0.5 equiv.) were performed by addition of all components at −78 °C followed by heating to 0 °C. The isonitrile chelates were obtained in 79 %, 97 %, and 32 % yield, respectively. The somewhat lower yield of **32** may in part be explained by the reaction taking place twice. Reactions with other isonitriles required higher reaction temperatures and/or longer reaction times (Scheme 9, Table 1).

Table 1. Isonitrile chelates.

Entry	R	Product	Reaction temp. [°C]	Reaction time [min]	Yield [%]
1	*tert*-Butyl	**25**	0	60	79
2	Cyclohexyl	**26**	0	10	97
3	(4-Methylphenyl-sulfonyl)methyl	**27**	25	10	99
4	4-Methoxyphenyl	**28**	25	120	61
5	2,4-Dimethoxyphenyl	**29**	25	1020	91
6	3,5-Dimethoxyphenyl	**30**	25	120	80
7	4-Cyanophenyl	**31**	25	1020	75
8	1,4-Phenylene	**32**	0	—[a]	32

[a] Workup immediately after warming to 25 °C.

EurJIC
European Journal of Inorganic Chemistry

Full Papers
doi.org/10.1002/ejic.202100147

Chemistry Europe
European Chemical
Societies Publishing

The mass spectra of the complexes show the expected $[M^+]$ molecular ion peaks; for **32** the $[M^{2+}]$ peak is observed. The isonitrile chelates were characterized spectroscopically; selected spectroscopic data are compiled in Table 2.

The IR data of the complexes indicate strong σ donation with only little π backbonding. The increase in bond strength of the N≡C bonds in the complexes as compared with the uncoordinated ligands is indicated by an increase of the wavenumbers of the respective IR absorptions in accord with literature reports. This goes back to a partial antibonding C–N character of the ligand lone electron pair[64–67] and Coulombic interactions of the cationic nickel(II) complex.[65] The IR spectrum of **31** clearly indicates complexation of the isonitrile moiety, not the nitrile group. The IR absorption of the latter at $\tilde{\nu} = 2234$ cm^{-1} is very similar to that of the uncoordinated ligand ($\tilde{\nu} = 2220$ cm$^{-1[68]}$).

The ^{1}H NMR spectra show the signals of the cyclopentadienyl protons at lower field than in the case of the bromo complex **8**, presumably as a result of the cationic nature of the complexes. This is also reflected by the ^{13}C NMR signals of the substituted cyclopentadienyl carbon atoms, which are shielded by 17.3–20.1 ppm and appear as doublets with P,C coupling constants of $^2J_{P,C} = 10.8$–11.4 Hz. Due to the stereogenic phosphorus atoms four different signals are observed for the cyclopentadienyl CH carbon atoms. Signals for the isonitrile carbon atoms are observed at $\delta = 133.8$–150.8 ppm. For complexes **27** and **29**–**32** these signals are doublets with coupling to the phosphorus atom of $^2J_{P,C} = 17.7$–18.6 Hz. **32**, which contains two stereogenic phosphorus atoms and might therefore exist as a *meso* and as a *rac* diastereomer, shows only one signal set in the ^{13}C and ^{31}P NMR spectra. Rather than a diastereoselective formation of only one of them, we think that the large distance between the stereogenic phosphorus atoms precludes a differentiation of the diastereomers by NMR. The isonitrile carbon signal of **28** with a (4-methoxyphenyl)isonitrile ligand is a broad singlet. The respective signals of alkylisonitrile complexes **25** and **26** show four lines, thus indicating couplings

in addition to the expected $^2J_{P,C}$ coupling. Presumably the additional coupling results from the quadrupole moment of the ^{14}N nucleus. As the relaxation usually is rather fast, such couplings are rarely observed. However, they can be found for the ligands of complexes **25** (*tert*-butylisonitrile, $^1J_{14N,C} = 3.7$ Hz[69]), **26** (cyclohexylisonitrile, $^1J_{14N,C} = 5.3$ Hz[70]), and **28** [(4-methoxyphenyl)isonitrile, $^1J_{14N,C} = 4.9$ Hz[69]]. Isonitrile metal complexes often show $^1J_{14N,C}$ couplings in the range of 12–30 Hz.[71] Therefore we think that the four lines patterns in the ^{13}C NMR spectra of **25** and **26** as well as the broad singlet for **28** may be attributed to ^{14}N,^{13}C couplings in addition to the usual P,C couplings. As ^{14}N has a nuclear spin of 1 the triplet generated by the ^{14}N,^{13}C coupling may be duplicated with a similar coupling constant of the P,C coupling resulting in a four lines pattern. In addition, the intensity ratios of 1:2:2:1 clearly shows that the signal is not an ordinary quartet, which would show a 1:3:3:1 ratio.

In order to have a closer look at this phenomenon, variable temperature ^{13}C{^{1}H} and ^{13}C{^{31}P,^{1}H} NMR measurements were performed with **26** at 253–330 K (Figure 1 and Figure 2). Remarkably, the four lines signal increases in resolution with increasing temperature and becomes broader and less resolved with lower temperature. At 253 K only a broad, poorly resolved signal with weak couplings is visible. The ^{13}C{^{31}P,^{1}H} NMR spectrum shows a triplet with $^1J_{14N,C} = $ ca. 21 Hz, which is in accord with comparable literature data.[71]

While the isonitrile carbon atoms in the tosylmethyl and 4-methoxyphenylisonitrile complexes **27** and **28** give rise to broad singlets in the ^{13}C NMR spectrum, the related complexes **29**–**32** show doublets with P,C coupling constants in the range of 17.7–19.4 Hz.

The relaxation of the ^{14}N nucleus as a result of quadrupole interactions depends on the electric field gradient, which corresponds to the asymmetric charge distribution around the nucleus. An increasingly asymmetric charge distribution causes a larger electric field gradient and an increasing quadrupole moment with a shorter relaxation time. The latter causes the

Table 2. Selected spectroscopic data of isonitrile chelates.

Entry	Compd.	^{13}C NMR δ [ppm]		^{31}P NMR δ [ppm]	IR complex $\tilde{\nu}$[cm^{-1}] N≡C	IR uncoord. ligand $\tilde{\nu}$[cm^{-1}] N≡C
		$C_{Cp\ quart}$ ($^2J_{P,C}$ [Hz])	Ni−C≡N ($^2J_{P,C}$ [Hz])			
1	**25**	117.1 (d, 10.8)	133.8 (q, 19.4)	1.8	2187	2136[57]
2	**26**	116.9 (d, 11.6)	134.6 (q, 19.4)	3.2	2193	2144[58]
3	**27**	118.6 (d, 10.9)	147.8 (d, 17.7)	3.7	2180	2140[59]
4	**28**	118.0 (s)	143.0 (br s)	3.8	2166	2125[60]
5	**29**	117.6 (d, 11.0)	145.5 (d, 19.0)	4.5	2168	2127[61]
6	**30**	118.7 (d, 11.3)	144.9 (d, 18.8)	3.3	2164	2136[62]
7	**31**	119.7 (d, 11.4)	150.8 (d, 18.4)	3.7	2160	2135[63]
8	**32**	118.8 (d, 11.2)	149.1 (br d, 18.6)	3.3	2145	2131[60]

EurJIC
European Journal of Inorganic Chemistry

Full Papers
doi.org/10.1002/ejic.202100147
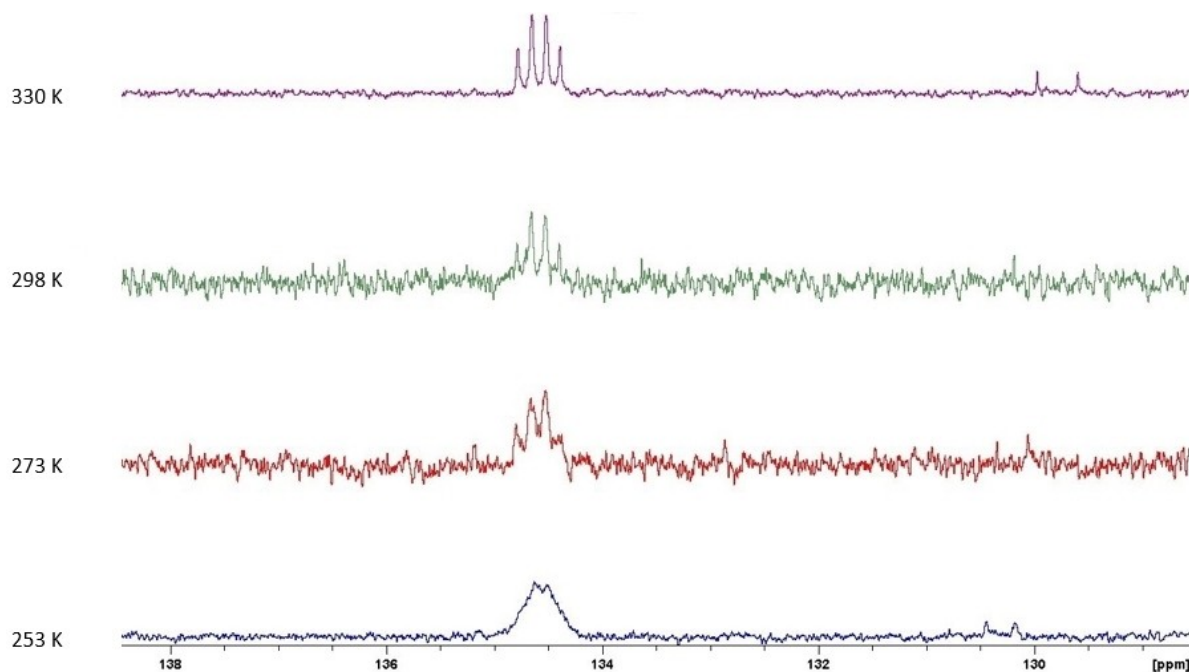
Chemistry Europe
European Chemical
Societies Publishing

Figure 1. Variable temperature ^{13}C{^{1}H} NMR expansion (151 MHz, CDCl$_3$) of the isonitrile carbon signal of **26**.

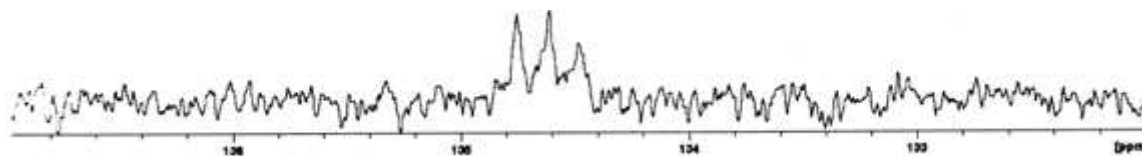**Figure 2.** ^{13}C{^{31}P,^{1}H} NMR expansion of the isonitrile carbon signal of **26** (151 MHz, CDCl$_3$, 298 K).

spin-spin coupling not to be observable. In contrast, an only slight deviation from an asymmetric charge distribution causes a small nuclear quadrupole moment with a longer relaxation time allowing for an observation of the spin-spin coupling.[72,73] In conclusion, the data suggest a more symmetric charge distribution in the isonitrile nitrogen atom in **25** and **26** than in those of arylisonitrile complexes **29–32**.

The ^{31}P NMR signals of the isonitrile complexes **25–32** ($\delta =$ 7.5–10.2 ppm) show some deshielding as compared to the starting bromo complex **8** ($\delta = -5.7$ ppm). The P,H coupling constants ($^1J_{\text{P,H}} = 365.8$–374.7 Hz) are in accord with a coordinated phosphane tether.[35]
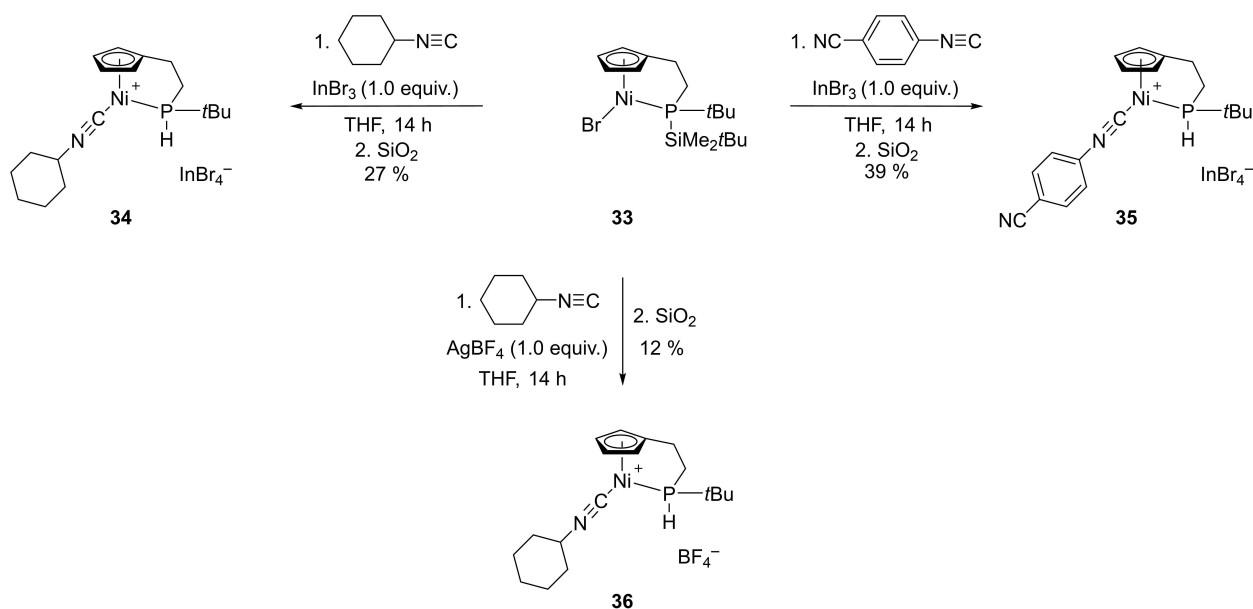
Isonitrile complexes **26**, **28**, and **31** were also crystallographically characterized. However, the analyses obtained suffered from poor crystal quality and were therefore not suited for deposition or a detailed discussion. Therefore, the data obtained are reported in the Supporting Information only.

While the syntheses of isonitrile chelates **25–32** started from **8**, which already contains a secondary phosphane tether, an alternative approach was the use of silylphosphane chelate **33** as the starting material. After introduction of the isonitrile ligand, a protiodesilylation would also lead to secondary phosphane tethered isonitrile chelates. Such an approach has

successfully been used by us in the synthesis of cyano chelate **6**.[17]

To test this approach **33** was treated with cyclohexylisonitrile and with (4-cyanophenyl)isonitrile, in both cases no ligand exchange was observed. However, in the presence of 1 equiv. of indium tribromide the reaction was achieved at 25 °C within 14 h. After chromatographic purification on silica gel the secondary phosphane chelates **34** and **35** were obtained as a result of a protiodesilylation in 27% and 39% yield, respectively. When in the reaction of cyclohexylisonitrile indium tribromide was replaced by silver tetrafluoroborate, the respective ligand exchange product **36** was obtained in a reduced yield of only 12% (Scheme 10) possibly indicating some side reactions of the silver salt. The only moderate yields are in accord with that of the reaction of **33** with trimethylsilylcyanide giving the cyano complex with protiodesilylation in 40% yield.[17]

Having prepared a number of cationic chelates with a secondary phosphane tether, some deprotonation experiments were undertaken. In a number of cases reactions were observed, however, attempts to isolate the sensitive products failed due to decomposition. Nevertheless, three experiments shall be presented here:

EurJIC
European Journal of Inorganic Chemistry

Full Papers
doi.org/10.1002/ejic.202100147

Chemistry Europe
European Chemical
Societies Publishing

Scheme 10. Cationic (2-phosphanylethyl)cyclopentadienylnickel chelates with secondary phosphane ligands.;

A sample of (4-cyanophenyl)isonitrile chelate **31** was dissolved in d_6-DMSO, and the ^{31}P NMR spectrum showed the phosphorus resonance at $\delta = 5.7$ ppm (dd, $^{1}J_{P,H} = 384.6$ Hz, $^{2}J_{P,H} = 60.3$ Hz). Remarkably, a ^{2}J coupling between phosphorus and only one of the diastereotopic H atoms of the adjacent methylene group is observed. Upon addition of potassium *tert*-butoxide no immediate reaction was observed. However, after 1 d the development of a new triplet signal at $\delta = -0.04$ (t, $J_{P,H} = 22.5$ Hz) ppm was observed, which increased in intensity over a longer period of time up to 25 d (Figure 3). The coupling

is a P,H coupling as indicated by the signal being a singlet in the $^{31}P\{^{1}H\}$ NMR spectrum. The coupling constant of 22.5 Hz is not in accord with a $^{1}J_{P,H}$ coupling but more likely corresponds to a $^{2}J_{P,H}$ coupling, which points to a PCH_2 substructure with two non-diastereotopic protons. However, the desired phosphinidene species is unreasonable, as this should show a much higher ^{31}P chemical shift.[74] A compound deuterated at phosphorus can also be excluded as this should show a 1:1:1 three lines NMR signal as the result of a P,D coupling in either one of the spectra, be it ^{31}P or $^{31}P\{H\}$, which is not observed.
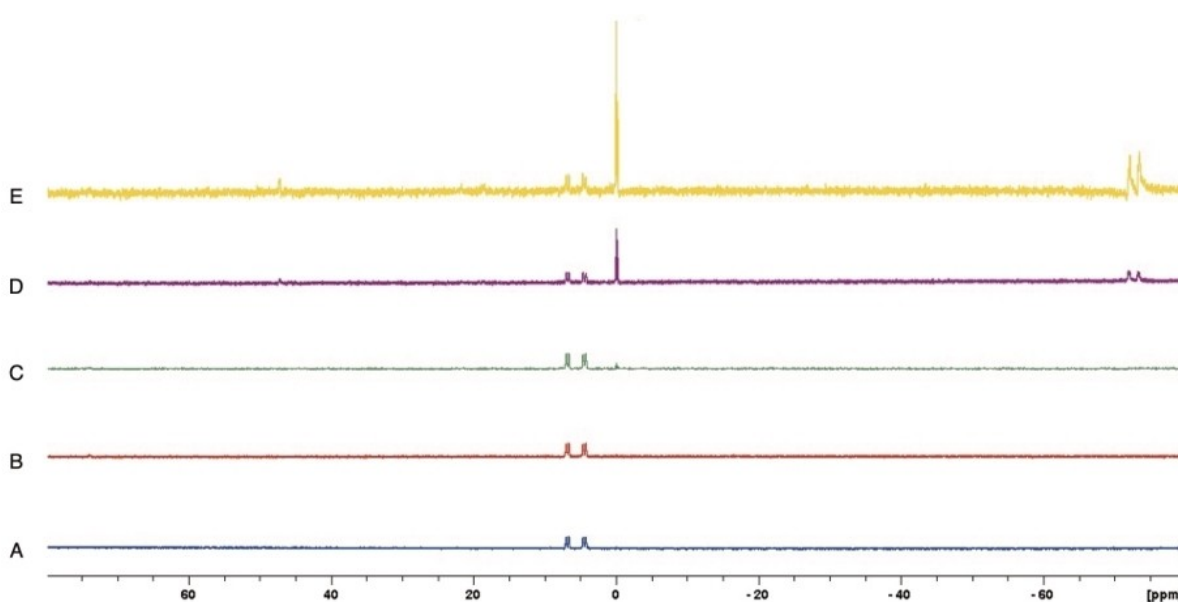
Figure 3. ^{31}P NMR spectra (d_6-DMSO) of the reaction of **31** with potassium *tert*-butoxide. A: Starting material before addition of KO*t*Bu; B: immediately after addition of KO*t*Bu; C: 1 d after addition of KO*t*Bu; D: 18 d after addition of KO*t*Bu; E: 25 d after addition of KO*t*Bu.

EurJIC
European Journal of Inorganic Chemistry

Full Papers
doi.org/10.1002/ejic.202100147

Chemistry Europe
European Chemical Societies Publishing

After 18 d another species is observed with a ^{31}P NMR signal at $\delta = -73.8$ (d, $^1J_{P,H} = 23.2$ Hz) ppm hinting towards a decomplexation of the phosphane tether. Based on these observations, we can only speculate that a *tert*-butoxy ligand has been coordinated to the nickel atom.

In the second experiment 1.1 equiv. of butyllithium in hexane were put into an NMR tube, and the hexane was removed at reduced pressure. Then **31** in d_6-DMSO was added, and an immediate color change from green to red-brown was observed. The ^{31}P NMR spectrum (Figure 4) indicated a reaction, and two new signals appeared at $\delta = -71.6$ ppm and at $\delta = -73.1$ ppm. In the ^{1}H-coupled ^{31}P NMR spectrum the signal at $\delta = -71.6$ ppm is a doublet with $^1J_{P,H} = 219.0$ Hz. These data support a decomplexation of the secondary phosphane tether; the resulting coordination site may be occupied by a dimsyl (methylsulfinyl) ligand as in **37**. The ^{31}P NMR signal at $\delta = -73.1$ ppm in the ^{1}H-coupled spectrum is a triplet and hints to a hydrogen/deuterium exchange at the phosphorus atom with formation of **38** as indicated by the coupling constant $^1J_{P,D} = 33.7$ Hz.[75] Deuterium NMR measurements showed a number of signals not allowing for a clear-cut interpretation; a broad resonance at $\delta = 2.0$ ppm possibly corresponds to a deuterium atom at the decoordinated phosphorus ligand. The results of this experiment are in accord with the reaction shown in Scheme 11.

In the third experiment a solution of **31** in d_6-DMSO was subjected to a ca. 100fold excess of diisopropylethyl amine (DIPEA). Upon addition of DIPEA an immediate color change from green to red-brown was observed. ^{31}P NMR measurements indicated complete conversion as evidenced by the disappearance of the signal of **31** at $\delta = 5.7$ pm. A new signal is observed in the ^{1}H-coupled ^{31}P NMR spectrum showing a doublet at δ

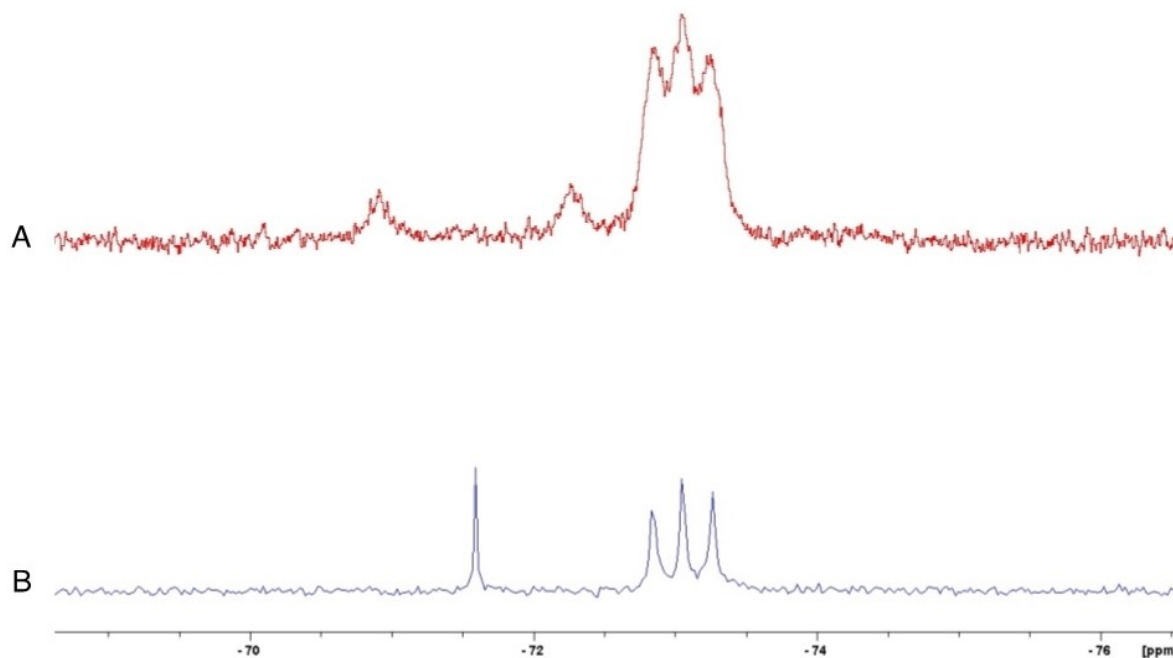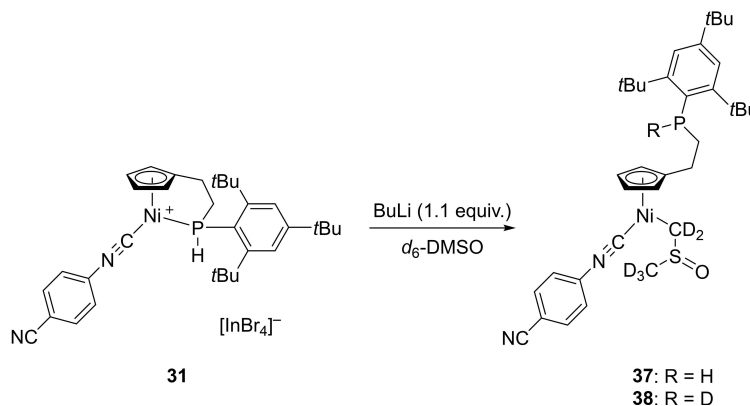**Figure 4.** ^{31}P NMR signals in d_6-DMSO after reaction of **31** with butyllithium. A: ^{1}H-coupled; B: ^{1}H-decoupled.

Scheme 11. Reaction of **31** with butyllithium (Experiment 2).;

EurJIC
European Journal of Inorganic Chemistry

Full Papers
doi.org/10.1002/ejic.202100147
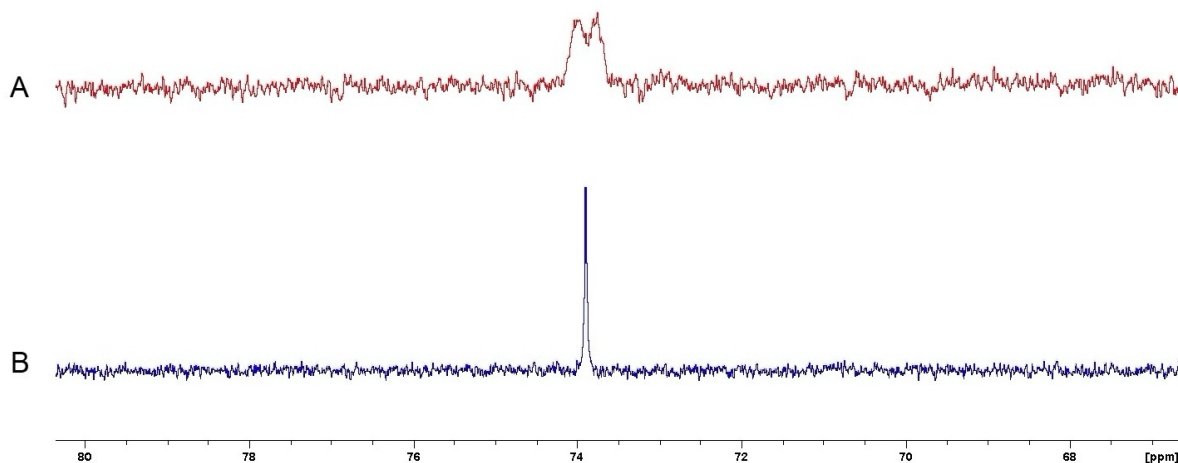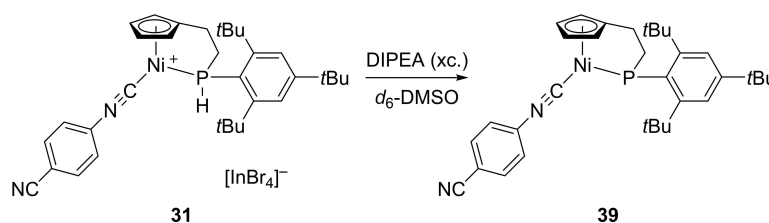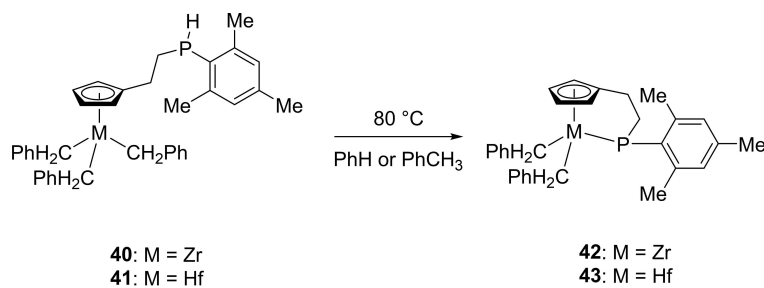
Chemistry Europe
European Chemical Societies Publishing

Figure 5. ^{31}P NMR spectrum (d_6 DMSO) of the reaction product formed from **31** by addition of an excess of DIPEA. A: H-coupled; B: H-decoupled.

Scheme 12. Reaction of **31** with diisopropylethylamine (DIPEA) (Experiment 3).;

Scheme 13. Formation of zirconium and hafnium phosphido chelates by Miyoshi and Nakazawa.[18,76]

$=73.9$ ppm with a coupling constant of $J=36.7$ Hz (Figure 5). This coupling is not in accord with a proton directly bound to the phosphorus atom (**31**: $^1J_{P,H}=384.6$ Hz), but more likely is a ^2J coupling to one of the diastereotopic methylene protons. In consequence this is some evidence for the formation of the phosphido chelate **39** (Scheme 12)

In this context it is of interest, that Miyoshi, Nakazawa et al. reported the formation of phosphide chelates **42** and **43** from zirconium and hafnium benzyl complexes **40** and **41** by heating at 80 °C in benzene or toluene (Scheme 13).[18,76]

Conclusions

We succeeded in the preparation of the first cationic cyclopentadienylalkylphosphanenickel chelate complexes with a secondary phosphane tether. This was achieved by reaction of the respective bromo chelate **8** with tris(4-trifluoromethylphenyl)phosphane (**17**) or with a number of isonitriles in the presence of indium tribromide leading to the respective tetrabromoindates. In the absence of indium tribromide no reaction was observed, and other Lewis acids or silver tetrafluoroborate were unsuccessful, clearly emphasizing the importance of indium tribromide in these reactions. The complexes obtained were characterized spectroscopically. Finally, three experiments directed towards a deprotonation of the cationic complexes at the secondary phosphane moiety are

EurJIC
European Journal of Inorganic Chemistry

Full Papers
doi.org/10.1002/ejic.202100147

**Chemistry
Europe**
European Chemical
Societies Publishing

reported. Even though the deprotonation products could not be isolated due to rapid decomposition, these experiments provide some evidence for the desired deprotonation and are the basis for further investigations directed towards the catalytic properties of the complexes currently being pursued in our laboratories.

Experimental Section

General: All manipulations involving air-sensitive material were performed in flame-dried reaction vessels in an argon or nitrogen atmosphere by using vacuum-line and standard Schlenk techniques. Toluene and THF were distilled from sodium benzophenone ketyl. Hexane, pentane, and dichloromethane were dried with calcium hydride and freshly distilled before use. Petroleum ether was dried with calcium chloride. Column chromatography was carried out by flash chromatography.[77] Silica gel (J. T. Baker, 40 μm) was degassed three times by heating it with a flame at reduced pressure followed by setting it under normal pressure with nitrogen. IR: Perkin-Elmer FTIR spectrometer 580 and FT 1170 (ATR). Mass spectra: VG autospec (Micromass), Finnegan MAT 112 and MAT 312. HRMS (ESI): Micromass GCT and LCT with lock spray ion source combined with Water Alliances 2695 HPLC unit; VG autospec (peak-matching method, PFK). ^{1}H NMR: Bruker AVS 200 (200.1 MHz), AVS 400 (400.1 MHz), and AVS 500 (500.1 MHz). ^{13}C NMR: Bruker AVS 200 (50.3 MHz) and AVS 400 (100.6 MHz). Signal multiplicities are based on DEPT, COSY, HSQC and HMBC measurements. ^{31}P NMR: Bruker AVS 400 (161.9 MHz) with 85% aqueous phosphoric acid as external standard. Melting points: Electrothermal IA 9200 Series Digital Melting Point Apparatus.

{[2-(2,4,6-Tri-*tert*-butylphenylphosphanyl)ethyl] cyclopentadienyl][tris-4-trifluormethylphenyl)phosphan]nickel(II) tetrabromoindate (18):[43] At 25 °C tris-(4-trifluoromethylphenyl) phosphane (**17**, 62 mg, 0.14 mmol) in THF (10 mL) was added to **8** (70 mg, 0.14 mmol) and InBr$_3$ (49 mg, 0.14 mmol) in THF (15 mL). After stirring for 17 h the solvent was removed at reduced pressure, the residue was taken up with dichloromethane (5 mL) and filtered through a P3 frit covered with a 3 cm thick layer of kieselguhr. The residue was washed with toluene (4×5 mL), then with hexane (3× 5 mL). Subsequent crystallization from dichloromethane/pentane (3:2) at 25 °C afforded **18** (42 mg, 0.03 mmol, 23%) as a brown, crystalline solid (m. p. 216 °C).

^{1}H NMR (400.1 MHz, CDCl$_3$): δ = 1.33 [s, 9H, PHCCC(CH_3)$_3$], 1.36 [s, 9H, PHCCC(CH_3)$_3$], 1.48 [s, 9H, PCCCHC(CH_3)$_3$], 2.09–2.19 (m, 1H, PCH$_2$CH_2), 2.21–2.34 (m, 1H, PHCH$_2$CH_2), 3.05–3.19 (m, 1H, PCH_2CH$_2$), 3.22–3.35 (m, 1H, PHCH_2CH$_2$), 4.45 (m, 1H, Cp–H), 4.99 (m, 1H, Cp–H), 6.18 (m, 1H, Cp–H H), 6.38 (dm, 0.5H, PH), 6.49 (m, 1H, Cp–H), 7.28–7.36 (m, 0.5H, PH), 7.35 [m, 6H, PCCH], 7.50 (m, 2H, PHCCCH), 7.56 [m, 6H, PCCHCH] ppm. ^{13}C{^{1}H} NMR (151 MHz, CDCl$_3$): δ = 24.1 (br. s, PHCH$_2$CH$_2$), 30.9 [s, PHCCCHCC(CH$_3$)$_3$], 34.5 [s, PHCCC(CH$_3$)$_3$], 35.4 [d, $^5J_{P,C}$ = 1.9 Hz, PHCCC(CH$_3$)$_3$], 35.5 [s, PHCCHCC(CH$_3$)$_3$], 38.9 [s, PHCCC(CH$_3$)$_3$], 40.6 [s, PHCCC(CH$_3$)$_3$], 46.5 (dd, $^1J_{P,C}$ = 31.9 Hz, $^3J_{C,P}$ = 6.2 Hz, PHCH$_2$), 90.1 (d, $J_{P,C}$ = 6.5 Hz, C$_{Cp}$H), 100.5 (s, C$_{Cp}$H), 101.8 (s, C$_{Cp}$H), 103.4 (s, C$_{Cp}$H), 117.8 [d, $^1J_{P,C}$ = 26.4 Hz, PHCCC(CH$_3$)$_3$], 121.2 (m, C$_{Cp}$C), 124.7 (d, $^3J_{P,C}$ = 7.7 Hz, PHCCCH), 123.2 (q, $^1J_{C,F}$ = 273.1 Hz, CF$_3$), 126.3–126.7 [m, PCCHCHCCF$_3$], 126.9 (d, $^3J_{P,C}$ = 10.9 Hz, PHCCCH), 133.8 [d, $^2J_{P,C}$ = 12.2 Hz, PCCHCHCCF$_3$], 134.5 (d, $^1J_{P,C}$ = 45.1 Hz, PCCHCHCCF$_3$], 154.8 (s, PHCCCH), 157.9 (d, $^4J_{P,C}$ = 10.0 Hz, PHCCCHCC(CH$_3$)$_3$] ppm. A signal for F$_3$CC could, presumably due to signal overlap, not be observed. ^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$): δ = −22.1 d, 1P, $^2J_{P,P}$ = 29.8 Hz, PH), 36.7 [d, 1P $^2J_{P,P}$ = 29.8 Hz, P(C$_6$H$_4$CF$_3$)$_3$] ppm. ^{31}P NMR (162 MHz, CDCl$_3$): δ = −22.1 (dm, 1P, $^1J_{P,H}$ = 380.9 Hz, PH), 36.7 [m,

P(C$_6$H$_4$CF$_3$)$_3$] ppm. ^{19}F NMR (376.6 MHz, CDCl$_3$): δ = −63.5 ppm. IR: $\tilde{\nu}$ = 2968 (w), 1606 (w), 1466 (w), 1437 (w, P–C) 1396 (w), 1321 (s, C–F), 1163 (m), 1128 (s), 1061 (s), 1015 (m), 868 (w), 827 (m), 704 (m), 696 (m), 600 (m), 534 (m), 411 (m) cm^{-1}. HRMS (ESI, MeOH): Calcd. for C$_{46}$H$_{50}$F$_9$NiP$_2$ [M$^+$] 893.2598; found 893.2608; calcd. for InBr$_4^-$ [M$^-$] 430.5772, found 430.5772.

Cyano{[2-(2,4,6-tri-*tert*-butylphenylphosphanyl)ethyl] cyclopentadienyl}nickel(II) (21): At 25 °C trimethylsilylcyanide (14 mg, 0.02 mL, 0.14 mmol) was added to **8** (63 mg, 0.12 mmol) and InBr$_3$ (48 mg, 0.14 mmol) in THF (15 mL). After stirring for 1 h the solvent was removed at reduced pressure, the residue was taken up with dichloromethane (5 mL) and filtered through a P3 frit covered with a 3 cm thick layer of kieselguhr. The residue was purified by column chromatography (SiO$_2$, 6×3 cm, petroleum ether/ethyl acetate 9:1→8:2→7:3→1:1) affording **21** (20 mg, 0.04 mmol, 37%) as a green, amorphous solid (m. p. 176–177 °C).

^{1}H NMR (400.1 MHz, CDCl$_3$): δ = 1.28 [s, 9H, PCCCHCC(CH_3)$_3$], 1.65 [s, 9H, PCCC(CH$_3$)$_3$], 1.70 [s, 9H, PCCC(CH$_3$)$_3$], 1.80–1.99 (dm, 2H, PCH$_2$CH_2), 2.31–2.44 (m, 1H, PCH$_2$), 2.69–2.82 (m, 1H, PCH$_2$), 5.34 (m, 1H, C$_{Cp}$H), 5.60 (m, 2H, C$_{Cp}$H), 6.12 (ddd, 1H, $^1J_{P,H}$ = 353.9 Hz, $^3J_{H,H}$ = 11.6 Hz, $^3J_{H,H}$ = 3.8 Hz, PH) 5.71 (m, 1H, C$_{Cp}$H), 7.35 (m, 1H, PCCCH), 7.37 (m, 1H, PCCCH) ppm. ^{13}C{^{1}H} NMR (100.6 MHz, CDCl$_3$): δ = 23.5 (d, $^2J_{P,C}$ = 6.8 Hz, PCH$_2$CH$_2$), 31.1 [s, PCCCHCC(CH$_3$)$_3$], 34.6 [m, PCC(CH$_3$)$_3$], 34.97 (m, PCC(CH$_3$)$_3$), 34.98, [s, PCCCHCC(CH$_3$)$_3$],39.0 [m, PCC(CH$_3$)$_3$], 39.9 [m, PCC(CH$_3$)$_3$], 45.9 (d, $^2J_{P,C}$ = 30.3 Hz, PCH$_2$), 88.7 (d, $J_{P,C}$ = 6.5 Hz, C$_{Cp}$H), 95.5 (d, $J_{P,C}$ = 3.6 Hz, C$_{Cp}$H), 96.9 (s, C$_{Cp}$H), 98.6 (d, $J_{P,C}$ = 1.9 Hz, C$_{Cp}$H), 108.8 (d, $^3J_{P,C}$ = 9.1 Hz, C$_{Cp}$C), 119.7 (d, $^1J_{P,C}$ = 32.2 Hz, PC), 123.3 (d, $^3J_{P,C}$ = 8.5 Hz, PCCCH), 125.1 (d, $^3J_{P,C}$ = 10.4 Hz, PCCCH), 152.2 (d, $^4J_{P,C}$ = 3.1 Hz, PCCCHC), 157.1 (br. s, PCC), 157.2 (d, $^2J_{P,C}$ = 8.3 Hz, PCC) ppm. The signal for NiCN was not detected. ^{31}P NMR (162 MHz, CDCl$_3$): δ = 0.98 (ddm, $^1J_{P,H}$ = 356.4 Hz, $^2J_{P,H}$ = 54.5 Hz). IR: $\tilde{\nu}$ = 3107 (w), 3094 (m), 2160 (s, CN), 1600 (m), 1495 (w), 1443 (w), 1362 (w, *t*Bu), 1098 (w), 912 (w), 860 (m), 843 (m), 820 (m), 650(w), 612 (w), 550 (m), 436 (m) cm^{-1}. HRMS (ESI, MeOH): Calcd. for C$_{26}$H$_{39}$NNiP [M$^+$ + H] 454.2174, found 454.2180; calcd. for C$_{26}$H$_{38}$NNiPNa [M$^+$ + Na] 476.1993, found 476.1992.

(*tert*-Butylisonitrile){[2-(2,4,6-tri-*tert*-butylphenylphosphanyl) ethyl]cyclopentadienyl}nickel(II) tetrabromoindate (25): At −78 °C *tert*-butylisonitrile (0.02 mL, 0.16 mmol) was added to **8** (40 mg, 0.08 mmol) and InBr$_3$ (28 mg, 0.08 mmol) in THF (15 mL). After stirring for 1 h the mixture was warmed to 25 °C, and the solvent was removed at reduced pressure and the residue was taken up with dichloromethane (5 mL) and filtered through a P3 frit covered with a 3 cm thick layer of kieselguhr. The residue was washed with pentane (3×5 mL) and then purified by column chromatography (SiO$_2$, 3×2 cm, dichloromethane/ethanol 7:1→6:1) affording **25** (60 mg, 0.06 mmol, 79%) as a green-brown viscous oil.

^{1}H NMR (400.1 MHz, CDCl$_3$): δ = 1.30 [s, 9H, PCCCHCC(CH_3)$_3$], 1.35 [s, 9H, NiCNC(CH$_3$)$_3$], 1.64 [s, 9H, PCCC(CH$_3$)$_3$], 1.66, (s, 9H, PCCC(CH$_3$)$_3$], 1.95–2.27 (m, 2H, PCH$_2$CH_2), 2.71–2.82 (m, 1H, PCH$_2$), 2.98–3.12 (m, 1H, PCH$_2$), 5.48 (m, 1H, C$_{Cp}$H), 5.78 (m, 1H, C$_{Cp}$H), 5.83 (m, 1H, C$_{Cp}$H), 5.87 (m, 1H, C$_{Cp}$H), 6.46 (ddd, $^1J_{P,H}$ = 371.3 Hz, $^3J_{H,H}$ = 11.8 Hz, $^3J_{H,H}$ = 3.8 Hz, 1H, PH), 7.44 (m, 1H, PCCCH), 7.46 (m, 1H, PCCCH) ppm. ^{13}C {^{1}H} NMR (151 MHz, CDCl$_3$): δ = 23.8 (d, $^2J_{P,C}$ = 4.8 Hz, PCH$_2$CH$_2$), 30.4 [s, NiCNC(CH$_3$)$_3$], 31.1 [s, PCCCHCC(CH$_3$)$_3$], 34.6 [d, $^4J_{P,C}$ = 1.7 Hz, PCCC(CH$_3$)$_3$], 34.9 (d, $^4J_{P,C}$ = 2.0 Hz, PCCC(CH$_3$)$_3$], 35.3 (s, PCCCHCC(CH$_3$)$_3$], 39.1 (d, $^3J_{P,C}$ = 1.7 Hz, PCCC(CH$_3$)$_3$], 39.9 (d, $^3J_{P,C}$ = 1.4 Hz, PCCC(CH$_3$)$_3$], 47.0 (d, $^1J_{P,C}$ = 30.5 Hz, PCH$_2$), 59.4 (t, $^1J_{14N,C}$ = 4.2 Hz, NiCNC(CH$_3$)$_3$], 91.1 (d, $J_{P,C}$ = 5.7 Hz, C$_{Cp}$H), 97.3 (d, $J_{P,C}$ = 2.8 Hz, C$_{Cp}$H), 98.5 (s, C$_{Cp}$H), 100.4 (d, $J_{P,C}$ = 2.0 Hz, C$_{Cp}$H), 117.1 (d, $^3J_{P,C}$ = 11.0 Hz, C$_{Cp}$C), 118.2 (d, $^3J_{P,C}$ = 34.8 Hz, PC), 124.0 (d, $^3J_{P,C}$ = 8.9 Hz, PCCCH), 125.5 (d, $^3J_{P,C}$ = 11.0 Hz, PCCCH), 133.8 (q, J = 19.4 Hz, NiC), 154.1 (d, $^4J_{P,C}$ = 3.3 Hz, PCCCHC), 157.4 (d, $^2J_{P,C}$ = 1.1 Hz, PCC), 157.8 (d, $^2J_{P,C}$ = 8.5 Hz, PCC), ppm. ^{31}P NMR (162 MHz, CDCl$_3$): δ = 1.8 (ddm, $^1J_{P,H}$ = 371.1 Hz, $^2J_{P,H}$ =

EurJIC
European Journal of Inorganic Chemistry

Full Papers
doi.org/10.1002/ejic.202100147

Chemistry Europe
European Chemical Societies Publishing

59.1 Hz) ppm. IR: $\tilde{\nu} = 2961$ (m), 2926 (m), 2187 (s, NC), 1591 (w), 1460 (m), 1696 (w), 1362 (m, tBu), 1232 (w), 1194 (s), 1097 (w), 1045 (w), 862 (m), 804 (m), 620 (w), 525 (w), 426 (w) cm^{-1}. HRMS (ESI, AcCN): Calcd. for $C_{30}H_{47}NNiP$ [M$^+$] 510.2800, found 510.29797; calcd. for InBr$_4^-$ [M$^-$] 430.5772, found 430.5780.

(Cyclohexylisonitrile){[2-(2,4,6-tri-$tert$-butylphenylphosphanyl)ethyl]cyclopentadienyl}nickel(II) tetrabromoindate (26): At $-78\,°C$ cyclohexylisonitrile (0.02 mL, 0.15 mmol) was added to **8** (75 mg, 0.15 mmol) and InBr$_3$ (52 mg, 0.15 mmol) in THF (15 mL). The mixture was warmed to 25 °C, and after stirring for 10 min the solvent was removed at reduced pressure, the residue was taken up with dichloromethane (5 mL) and filtered through a P3 frit covered with a 3 cm thick layer of kieselguhr. The crude product was washed with pentane (3×5 mL). Crystallization from ethyl acetate afforded **26** (140 mg, 0.14 mmol, 97%) as dark green crystals (m. p. 125–127 °C).

^{1}H NMR (400.1 MHz, CDCl$_3$): $\delta = 1.16$–1.34 (m, 3H, NiCNCHCH_2CH_2CH_2), 1.27 [s, 9H, PCCCHCC(CH_3)$_3$], 1.43–1.56 (m, 7H, NiCNCHCH_2CH_2CH_2), 1.63 [s, 9H, PCCC(CH$_3$)$_3$], 1.65 [s, 9H, PCCC(CH$_3$)$_3$], 1.78–1.88 (m, 2H, NiCNCHCH_2), 1.92–2.24 (dm, 2H, PCH$_2$CH_2), 2.65–2.76 (m, 1H, PCH$_2$), 2.95–3.09 (m, 1H, PCH$_2$), 3.83 (m, 1H, NiCNCH), 5.50 (m, 1H, C$_{Cp}$H), 5.78 (m, 1H, C$_{Cp}$H), 5.85 (m, 2H, C$_{Cp}$H), 6.39 (ddd, 1H, $^1J_{P,H} = 369.7$ Hz, $^3J_{H,H} = 11.7$ Hz, $^3J_{H,H} = 3.6$ Hz, PH), 7.43 (m, 1H, PCCCH), 7.45 (m, 1H, PCCCH) ppm. ^{13}C NMR (100.6 MHz, CDCl$_3$): $\delta = 22.9$ (s, NiCNCHCH_2), 23.7 (d, $^2J_{P,C} = 4.7$ Hz, PCH$_2$CH_2), 24.6 (s, NiCNCHCH_2CH_2), 31.1, [s, PCCCHCC(CH$_3$)$_3$], 32.4 (d, $^5J_{P,H} = 3.8$ Hz, NiCNCHCH_2), 34.5 [d, $^4J_{P,C} = 2.3$ Hz, PCCC(CH$_3$)$_3$], 35.0 [d, $^4J_{P,C} = 2.3$ Hz, PCCC(CH$_3$)$_3$], 35.2 [d, $^5J_{P,C} = 1.5$ Hz, PCCCHCC(CH$_3$)$_3$], 39.1 [d, $^3J_{P,C} = 2.3$ Hz, PCCC(CH$_3$)$_3$], 39.9 [d, $^3J_{P,C} = 1.5$ Hz, PCCC(CH$_3$)$_3$], 46.9 (d, $^1J_{P,C} = 30.6$ Hz, PCH$_2$), 56.0 (t, $^1J^{14}_{N,C} = 4.9$ Hz, NiCNCH), 91.0 (d, $J_{P,C} = 5.4$ Hz, C$_{Cp}$H), 97.4 (d, $J_{P,C} = 2.4$ Hz, C$_{Cp}$H), 98.5 (s, C$_{Cp}$H), 100.3 (d, $J_{P,C} = 2.5$ Hz, C$_{Cp}$H), 116.9 (d, $^3J_{P,C} = 11.6$ Hz, C_{Cp}C), 118.2 (d, $^1J_{P,C} = 34.7$ Hz, PC), 123.9 (d, $^3J_{P,C} = 9.1$ Hz, PCCCH), 125.6 (d, $^3J_{P,C} = 10.8$ Hz, PCCCH), 134.6 (q, $J = 19.4$ Hz, NiCN), 154.0 (d, $^4J_{P,C} = 3.1$ Hz, PCCCHC), 157.3 (d, $^2J_{P,C} = 1.5$ Hz, PCC), 157.8 (d, $^2J_{P,C} = 8.3$ Hz, PCC) ppm. ^{31}P NMR (162 MHz, CDCl$_3$): $\delta = 3.2$ (ddm, $^1J_{P,H} = 365.8$ Hz, $^2J_{P,H} = 58.6$ Hz) ppm. IR: $\tilde{\nu} = 2936$ (m), 2860 (m), 2193 (s, NC), 1592 (m), 1449 (m), 1398 (m), 860 (s), 804 (m), 619 (m), 434 (m) cm^{-1}. HRMS (ESI, MeOH): Calcd. for $C_{32}H_{49}NNiP$ [M$^+$] 536.2956, found 536.2952; calcd. for InBr$_4^-$ [M$^-$] 430.5772, found 430.5773.

{[(4-Tolylsulfonyl)methyl]isonitrile}{[2-(2,4,6-tri-$tert$-butylphenylphosphanyl)ethyl]cyclopentadienyl}nickel(II) tetrabromoindate (27): At 25 °C [(4-tolylsulfonyl)methyl]isonitrile (15 mg, 0.08 mmol) was added to **8** (40 mg, 0.08 mmol) and InBr$_3$ (28 mg, 0.08 mmol) in THF (4 mL). After stirring for 10 min the solvent was removed at reduced pressure, the residue was taken up with dichloromethane (5 mL) and filtered through a P3 frit covered with a 3 cm thick layer of kieselguhr. The filtrate was washed with hexane (3×5 mL). Crystallization from ethyl acetate afforded **27** (83 mg, 0.08 mmol, 99%) as dark green, amorphous solid (m. p. 138–140 °C).

^{1}H NMR (400.1 MHz, CDCl$_3$): $\delta = 1.32$ [s, 9H, PCCCHCC(CH_3)$_3$], 1.60 [s, 9H, PCCC(CH$_3$)$_3$], 1.64, [s, 9H, PCCC(CH$_3$)$_3$], 1.90–2.23 (m, 2H, PCH$_2$CH_2), 2.48 (s, 3H, SCCHCHCCH_3) 2.60–2.74 (m, 1H, PCH$_2$), 2.98–3.12 (m, 1H, PCH$_2$), 4.89 [dd (AB line system), $^2J_{H,H} = -15.5$ Hz, 2H, NCH$_2$], 5.51 (m, 1H, C$_{Cp}$H), 5.79 (m, 1H, C$_{Cp}$H), 5.82 (m, 1H, C$_{Cp}$H), 5.83–5.87 (m, 0.5H, PH), 5.86 (m, 1H, C$_{Cp}$H), 6.77 (dm, 0.5H, P–H), 7.36 (d, 2H, $^3J_{H,H} = 8.1$ Hz, SCCHCH), 7.43 (m, 1H, PCCCH), 7.47 (m, 1H, PCCCH), 7.73 [dm, 2H, $^3J_{H,H} = 8.4$ Hz, SCCH] ppm. ^{13}C NMR (100.6 MHz, CDCl$_3$): $\delta = 22.1$ (s, SCCHCHCCH_3), 23.6 (d, $^2J_{P,C} = 4.9$ Hz, PCH$_2$CH_2), 31.1 [s, PCCCHCC(CH$_3$)$_3$], 34.4 [d, $^4J_{P,C} = 2.5$ Hz, PCCC(CH$_3$)$_3$], 35.0 [d, $^4J_{P,C} = 2.5$ Hz, PCCC(CH$_3$)$_3$], 35.2 s, PCCCHCC(CH$_3$)$_3$], 39.2 [d, $^3J_{P,C} = 1.8$ Hz, PCCC(CH$_3$)$_3$], 40.0 [d, $^3J_{P,C} = 1.6$ Hz, PCCC(CH$_3$)$_3$], 47.1 (d, $^1J_{P,C} = 31.5$ Hz, PCH$_2$), 64.2 (s, NCH$_2$), 91.9 (d, $^4J_{P,C} = 4.9$ Hz, C$_{Cp}$H), 98.37 (d, $^4J_{P,C} = 3.1$ Hz, C$_{Cp}$H), 98.4 (s, C$_{Cp}$H), 100.4 (d, $^5J_{P,C} = $

2.4 Hz, C$_{Cp}$H), 118.0 (d, $^1J_{P,C} = 36.6$ Hz, PC), 118.6 (d, $^3J_{P,C} = 10.9$ Hz, C_{Cp}C), 124.1 (d, $^3J_{P,C} = 8.8$ Hz, PCCCH), 126.0 (d, $^3J_{P,C} = 11.1$ Hz, PCCCH), 129.2 (s, SCCH), 130.9 (s, SCCHCH), 132.4 (s, SCCHCHCC), 147.6 (s, SC), 147.8 (br. d, $^2J_{P,C} = 17.7$ Hz, NiC), 154.2 (d, $^4J_{P,C} = 3.8$ Hz, PCCCHC), 157.6 (d, $^2J_{P,C} = 2.6$ Hz, PCC), 158.0 (d, $^2J_{P,C} = 7.9$ Hz, PCC), ppm. ^{31}P NMR (162 MHz, CDCl$_3$): $\delta = 3.7$ (ddm, $^1J_{P,H} = 365.8$ Hz, $^2J_{P,H} = 58.6$ Hz) ppm. IR: $\tilde{\nu} = 2963$ (m), 2924 (m), 2868 (m), 2180 (s, NC), 1593 (m), 1341 (m, SO$_2$), 1152 (s, SO$_2$), 862 (s), 812 (s), 586 (s), 513 (s) cm^{-1}. HRMS (ESI, MeOH): Calcd. for $C_{34}H_{47}NNiO_2PS$ [M$^+$] 622.2419, found 622.2418; calcd. for InBr$_4^-$ [M$^-$] 430.5772, found 430.5773.

(4-Methoxyphenylisonitrile){[2-(2,4,6-tri-$tert$-butylphenylphosphanyl)ethyl]cyclopentadienyl}nickel(II) tetrabromoindate (28): At 25 °C (4-methoxyphenyl)isonitrile (7 mg, 0.05 mmol) was added to **8** (27 mg, 0.05 mmol) and InBr$_3$ (19 mg, 0.05 mmol) in THF (5 mL). After stirring for 2 h the solvent was removed at reduced pressure, the residue was taken up with dichloromethane (5 mL) and filtered through a P3 frit covered with a 3 cm thick layer of kieselguhr. The crude product was purified by column chromatography (SiO$_2$, 3× 2 cm, dichloromethane). Crystallization from ethyl acetate afforded **28** (32 mg, 0.03 mmol, 61%) as dark green (m. p. 146–149 °C).

^{1}H NMR (400.1 MHz, CDCl$_3$): $\delta = 1.28$ [s, 9H, PCCCHCC(CH_3)$_3$], 1.64 [s, 9H, PCCC(CH$_3$)$_3$], 1.67 [s, 9H, PCCC(CH$_3$)$_3$], 2.01–2.33 (m, 2H, CH$_2$CH_2), 2.74–2.84 (m, 1H, PCH$_2$), 3.05–3.19 (m, 1H, PCH$_2$), 3.80 (s, 3H, OCH$_3$), 5.59 (m, 1H, C$_{Cp}$H), 5.85 (m, 1H, C$_{Cp}$H), 5.93 (m, 2H, C$_{Cp}$H), 6.50 (ddm, $^1J_{P,H} = 372.5$ Hz, $^3J_{H,H} = 11.9$ $^3J_{H,H} = 3.7$, 1H, PH), 6.86 [dm, $^3J_{H,H} = 9.1$ Hz, 2H, NCCH], 7.17 [dm, $^3J_{H,H} = 9.1$ Hz, 2H, NCCHCH], 7.41 (m, 1H, PCCCH), 7.45 (m, 1H, PCCCH) ppm. ^{13}C NMR (100.6 MHz, CDCl$_3$): $\delta = 23.8$ (d, $^2J_{P,C} = 4.6$ Hz, PCH$_2$CH_2), 31.0 [s, PCCCHCC(CH$_3$)$_3$], 34.4 [d, $^4J_{P,C} = 1.6$ Hz, PCCC(CH$_3$)$_3$], 35.0 [d, $^4J_{P,C} = 2.3$ Hz, PCCC(CH$_3$)$_3$], 35.2 [s, PCCCHCC(CH$_3$)$_3$], 39.2 [d, $^3J_{P,C} = 2.3$ Hz, PCCC(CH$_3$)$_3$], 40.0 (d, $^3J_{P,C} = 1.5$ Hz, PCCC(CH$_3$)$_3$], 47.2 (d, $^1J_{P,C} = 30.8$ Hz, PCH$_2$), 56.0 (s, OCH$_3$), 91.5 (d, $^4J_{P,C} = 5.4$ Hz, C$_{Cp}$H), 97.8 (d, $J_{P,C} = 3.1$ Hz, C$_{Cp}$H), 98.6 (s, $-$C$_{Cp}$H), 100.4 (d, $J_{P,C} = 2.3$ Hz, C$_{Cp}$H), 115.2 (s, NCCH), 118.0 (s, C_{Cp}C), 118.3 (d, $^1J_{P,C} = 25.4$ Hz, PC), 119.4 (m, NCCH), 124.0 (d, $^3J_{P,C} = 9.2$ Hz, PCCCH), 125.7 (d, $^3J_{P,C} = 10.8$ Hz, PCCCH), 128.1 (s, NCCHCH), 143.0 (br. s, NiC), 154.2 (d, $^4J_{P,C} = 3.9$ Hz, PCCCHC), 157.4 (d, $^2J_{P,C} = 2.0$ Hz, PCC), 158.0 (d, $^2J_{P,C} = '8.5$ Hz, PCC), 161.0 (s, NCCHCHC) ppm. ^{31}P NMR (162 MHz, CDCl$_3$): $\delta = 3.3$ (ddm, $^1J_{P,H} = 373.3$ Hz, $^2J_{P,H} = 61.3$ Hz) ppm. IR: $\tilde{\nu} = 2963$ (m), 2166 (s, NC), 1601 (m), 1502 (s), 1460 (m), 1439 (m), 1362 (m, tBu), 1302 (m), 1254 (s, Ar–O), 1163 (m), 1024 (m, O–CH$_3$), 860 (s), 831 (s), 619 (m), 542 (m) cm^{-1}. HRMS (ESI, MeOH): Calcd. for $C_{33}H_{45}NNiOP$ [M$^+$] 560.2592, found 560.2592; calcd. for InBr$_4^-$ [M$^-$] 430.5772, found 430.5773.

(2,4-Dimethoxyphenylisonitrile){[2-(2,4,6-tri-$tert$-butylphenylphosphanyl)ethyl]cyclopentadienyl}nickel(II) tetrabromoindate (29): At 25 °C (2,4-dimethoxyphenyl)isonitrile (12 mg, 0.08 mmol) was added to **8** (38 mg, 0.08 mmol) and InBr$_3$ (27 mg, 0.08 mmol) in THF (10 mL). After stirring for 17 h the solvent was removed at reduced pressure, the residue was taken up with dichloromethane (5 mL) and filtered through a P3 frit covered with a 3 cm thick layer of kieselguhr. The crude product was purified by column chromatography (SiO$_2$, 4×2 cm, dichloromethane) affording **29** (70 mg, 0.07 mmol, 91%) as a dark green, viscous oil.

^{1}H NMR (500.1 MHz, CDCl$_3$): $\delta = 1.29$ [s, 9H, PCCCHCC(CH_3)$_3$], 1.63 [s, 9H, PCCC(CH$_3$)$_3$], 1.67 [s, 9H, PCCC(CH$_3$)$_3$], 1.99–2.08 (m, 1H, PCH$_2$CH_2), 2.13–2.30 (dm, 1H, PCH$_2$CH_2), 2.70–2.79 (m, 1H, PCH$_2$), 3.04–3.16 (m, 1H, PCH$_2$), 3.51 (s, 3H, NCCOCH$_3$), 3.80 (s, 3H, NCCCHCOCH_3), 5.58 (m, 1H, C$_{Cp}$H), 5.86 (m, 1H, C$_{Cp}$H), 5.88–5.92 (m, 0.5H, PH), 5.89 (m, 1H, C$_{Cp}$H), 5.91 (m, 1H, C$_{Cp}$H), (6.83, dd, $^3J_{H,H} = 12.0$ $^3J_{H,H} = 3.5$, 0.5H, PH), 6.38 (d, $^4J_{H,H} = 2.4$ Hz, 1H, NCCCH), 6.43 (dd, $^3J_{H,H} = 8.8$ Hz, $^4J_{H,H} = 2.5$ Hz, 1H, NCCHCH), 7.18 (d, $^3J_{H,H} = 8.8$ Hz, 1H, NCCH), 7.42 (m, 1H, PCCCH), 7.46 (m, 1H, PCCCH) ppm. ^{13}C NMR (125.8 MHz, CDCl$_3$): $\delta = 23.7$ (d, $^2J_{P,C} = 5.1$ Hz, PCH$_2$CH_2), 31.1 [s, PCCCHCC(CH$_3$)$_3$], 34.4 [d, $^4J_{P,C} = 2.2$ Hz, PCCC(CH$_3$)$_3$], 35.0 (d, $^4J_{P,C} = $

EurJIC
European Journal of Inorganic Chemistry

Full Papers
doi.org/10.1002/ejic.202100147

Chemistry Europe
European Chemical
Societies Publishing

2.4 Hz, PCCC(CH$_3$)$_3$], 35.2 [s, PCCCHCC(CH$_3$)$_3$], 39.2 [d, $^3J_{P,C}$=1.9 Hz, PCCC(CH$_3$)$_3$], 40.0 (d, $^3J_{P,C}$=1.4 Hz, PCCC(CH$_3$)$_3$], 47.2 (d, $^1J_{P,C}$= 31.4 Hz, PCH$_2$), 55.9 (s, NCCOCH$_3$), 56.1 (s, NCCCHCOCH$_3$) 91.2 (d, $J_{P,C}$=5.2 Hz, C$_{Cp}$H), 97.6, (d, $J_{P,C}$=3.1 Hz, C$_{Cp}$H), 98.6 (d, $J_{P,C}$=1.2 Hz, C$_{Cp}$H), 99.2 (s, NCCCH), 100.2 (d, $J_{P,C}$=2.4 Hz, C$_{Cp}$H), 105.4 (s, NCCHCH), 109.4 (br. s, NCCH), 117.6 (d, $^3J_{P,C}$=11.0 Hz, C_{Cp}C), 118.5 (d, $^1J_{P,C}$=35.8 Hz, PC), 124.0 (d, $^3J_{P,C}$=9.1 Hz, PCCCH), 125.9 (d, $^3J_{P,C}$= 10.7 Hz, PCCCH), 128.5 (s, NCCH), 145.5 (br. d, $^2J_{P,C}$=19.0 Hz, NiC) 154.0 (d, $^4J_{P,C}$ 3.3 Hz, PCCCHC), 157.4 (d, $^2J_{P,C}$ 2.0 Hz, PCC), 157.0 (s, NCCO), 157.9 (d, $^2J_{P,C}$ 7.8 Hz, PCC), 162.3 (s, NCCHCHC) ppm. ^{31}P NMR (162 MHz, CDCl$_3$): δ=4.5 (ddm, $^1J_{P,H}$=373.2 Hz, $^2J_{P,H}$=60.1 Hz) ppm. IR: $\tilde{\nu}$=2963 (m), 2168 (s, NC), 1601 (m), 1504 (m), 1465 (m), 1437 (m), 1419 (m) 1362 (w, tBu), 1313 (m), 1288 (m), 1211 (s, Ar–O), 1163 (m), 1125 (m), 1024 (m, O–CH$_3$), 860 (s). 802 (m), 606 (m), 519 (m), 447 (m) cm^{-1}. HRMS (ESI, MeOH): Calcd. for C$_{34}$H$_{47}$NNiO$_2$P [M$^+$] 590.2698, found 590.2699; calcd. for InBr$_4^-$ [M$^-$] 430.5772, found 430.5772.

(3,5-Dimethoxyphenylisonitrile){[2-(2,4,6-tri-*tert*-butylphenyl-phosphanyl)ethyl]cyclopentadienyl}nickel(II) tetrabromoindate (30): At 25 °C (3,5-dimethoxyphenyl)isonitrile (23 mg, 0.15 mmol) was added to **8** (73 mg, 0.15 mmol) and InBr$_3$ (50 mg, 0.15 mmol) in THF (10 mL). After stirring for 2 h the solvent was removed at reduced pressure, the residue was taken up with dichloromethane (5 mL) and filtered through a P3 frit covered with a 3 cm thick layer of kieselguhr. The crude product was washed with pentane (3× 10 mL). Precipitation from ethyl acetate gave **30** (117 mg, 0.11 mmol, 80%) as a dark green, amorphous solid (m. p. 129– 130 °C).

^{1}H NMR (400.1 MHz, CDCl$_3$): δ=1.28 [s, 9H, PCCCHCC(CH$_3$)$_3$], 1.65 [s, 9H, PCCC(CH$_3$)$_3$], 1.67 [s, 9H, PCCC(CH$_3$)$_3$], 2.00–2.34 (m, 2H, PCH$_2$CH$_2$), 2.76–2.86 (m, 1H, PCH$_2$), 3.06–3.20 (m, 1H, PCH$_2$), 3.74 [s, 6H, OCH$_3$], 5.65 (m, 1H, C$_{Cp}$H), 5.85 (m, 1H, C$_{Cp}$H), 5.98 (m, 2H, C$_{Cp}$H), 6.47 (ddd, $^1J_{P,H}$=373.9 Hz, $^3J_{H,H}$=11.8 Hz, $^3J_{H,H}$=3.7 Hz, 1H, PH), 6.34 [d, $^4J_{H,H}$=2.2 Hz, 2H, NCH], 6.47 (t, $^4J_{H,H}$=2.2 Hz, 1H, NCHCCH) 7.43 (m, 1H, PCCCH), 7.46 (m, 1H, PCCCH) ppm. ^{13}C NMR (151 MHz, CDCl$_3$): δ=23.8 (d, $^2J_{P,C}$=4.8 Hz, PCH$_2$CH$_2$), 31.0 [s, PCCCHCC(CH$_3$)$_3$], 34.4 [d, $^4J_{P,C}$=1.4 Hz, PCCC(CH$_3$)$_3$], 35.0 (d, $^4J_{P,C}$=2.3 Hz, PCCC(CH$_3$)$_3$], 35.2 (s, PCCCHCC(CH$_3$)$_3$], 39.2 (d, $^3J_{P,C}$=1.8 Hz, PCCC(CH$_3$)$_3$], 40.0 (d, $^3J_{P,C}$=1.4 Hz, PCCC(CH$_3$)$_3$], 47.3 (d, $^1J_{P,C}$=30.5 Hz, PCH$_2$), 56.1 (s, CH$_3$), 91.8 (d, $J_{P,C}$=5.3 Hz, C$_{Cp}$H), 98.0 (d, $J_{P,C}$=2.8 Hz, C$_{Cp}$H), 98.6 (s, C$_{Cp}$H), 100.6 (d, $J_{P,C}$=2.4 Hz, C$_{Cp}$H), 103.2 (s, NCCHCCH), 104.9 (s NCCH), 118.2 (d, $^1J_{P,C}$=35.9 Hz, PC) 118.7 (d, $^3J_{P,C}$=11.3 Hz, C_{Cp}C), 124.1 (d, $^3J_{P,C}$=9.2 Hz, PCCCH), 125.8 (d, $^3J_{P,C}$=10.9 Hz, PCCCH), 127.7 (s, NCCH), 144.9 (br. d, $^2J_{P,C}$=18.8 Hz, NiC) 154.3 (d, $^4J_{P,C}$ 3.4 Hz, PCCCHC), 157.5 (d, $^2J_{P,C}$ 1.7 Hz, PCCCH), 158.0 (d, $^2J_{P,C}$ 8.2 Hz, PCCCH), 161.3 (s, NCCHCC) ppm. ^{31}P NMR (162 MHz, CDCl$_3$): δ=3.8 (ddm, $^1J_{P,H}$=374.2 Hz, $^2J_{P,H}$=58.6 Hz) ppm. IR: $\tilde{\nu}$=2963 (m), 2164 (s, NC), 1591 (s), 1458 (m), 1427 (m), 1360 (m, tBu), 1329 (m), 1206 (s, Ar–O), 1157 (s), 1061 (s, O–CH$_3$), 860 (m), 814 (m), 619 (m) cm^{-1}. HRMS (ESI, MeOH): Calcd. for C$_{34}$H$_{47}$NNiO$_2$P [M$^+$] 590.2698, found 590.2699; calcd. for InBr$_4^-$ [M$^-$] 430.5772, found 430.5768.

(4-Cyanophenylisonitrile){[2-(2,4,6-tri-*tert*-butylphenylphosphan-yl)ethyl]cyclopentadienyl}nickel(II) tetrabromoindate (31): At 25 °C (4-cyanophenyl)isonitrile (28 mg, 0.22 mmol) in THF (10 mL) was added to **8** (110 mg, 0.22 mmol) and InBr$_3$ (77 mg, 0.22 mmol) in THF (20 mL). After stirring for 17 h the solvent was removed at reduced pressure, the residue was taken up with dichloromethane (5 mL) and filtered through a P3 frit covered with a 3 cm thick layer of kieselguhr. The crude product was purified by column chromatography (SiO$_2$, 7×2 cm, hexane/ethyl acetate 1:1). Crystal-lization from hexane/dichloromethane/ethyl acetate (1:1:2) gave **31** (160 mg, 0.16 mmol, 75%) as a dark green crystals (m. p. 181– 182 °C).

^{1}H NMR (400.1 MHz, CDCl$_3$): δ=1.28 [s, 9H, PCCCHCC(CH$_3$)$_3$], 1.64 [s, 9H, PCCC(CH$_3$)$_3$], 1.67 [s, 9H, PCCC(CH$_3$)$_3$], 2.06–2.35 (m, 2H, PCH$_2$CH$_2$), 2.79–2.89 (m, 1H, PCH$_2$), 3.09–3.22 (m, 1H, PCH$_2$), 5.73 (m, 1H, C$_{Cp}$H), 5.83 (m, 1H, C$_{Cp}$H), 5.95 (m, 1H, C$_{Cp}$H), 6.06 (m, 1H, C$_{Cp}$H), 6.56 (ddd, 1H, $^1J_{P,H}$=374.7 Hz, $^3J_{H,H}$=11.9 Hz, $^3J_{H,H}$=3.6 Hz, PH), 7.40 (dm, 2H, $^3J_{H,H}$=8.7 Hz, CCN), 7.43 (m, 1H, PCCCH), 7.46 (m, 1H, PCCCH), 7.70 [dm, 2H, $^3J_{H,H}$=8.7 Hz, NCCH] ppm. ^{13}C NMR (100.6 MHz, CDCl$_3$): δ=23.8 (d, $^2J_{P,C}$=4.6 Hz, PCH$_2$CH$_2$), 31.0 [s, PCCCHCC(CH$_3$)$_3$], 34.4 [d, $^4J_{P,C}$=1.6 Hz, PCCC(CH$_3$)$_3$], 35.0 [d, $^4J_{P,C}$= 2.1 Hz, PCCC(CH$_3$)$_3$], 35.2 [s, PCCCHCC(CH$_3$)$_3$], 39.2 [d, $^3J_{P,C}$=2.1 Hz, PCCC(CH$_3$)$_3$], 40.0 [d, $^3J_{P,C}$=1.3 Hz, PCCC(CH$_3$)$_3$], 47.4 (d, $^1J_{P,C}$= 30.9 Hz, PCH$_2$), 92.4 (d, $J_{P,C}$=5.4 Hz, C$_{Cp}$H), 98.6, (m, C$_{Cp}$H), 98.7 (d, $J_{P,C}$=2.3 Hz, C$_{Cp}$H), 100.7 (d, $^4J_{P,C}$=2.3 Hz, C$_{Cp}$H), 114.4 (s, NiCNC or NiCNCCHCHCCN), 117.0 (s, NiCNC or NiCNCCHCHCCN), 118.1 (d, $^1J_{P,C}$=36.3 Hz, PC), 119.7 (d, $^3J_{P,C}$=11.4 Hz, C_{Cp}C), 124.1 (d, $^3J_{P,C}$= 9.2 Hz, PCCCH), 125.7 (d, $^3J_{P,C}$=10.9 Hz, PCCCH), 127.6 (s, NiCNCCH or NiCNCCHCH), 129.9 (br. s, CCN), 134.0 (s, NiCNCCH or NiCNCCHCH), 150.8 (br. d, $^2J_{P,C}$=18.4 Hz, NiC), 154.5 (d, $^4J_{P,C}$ 3.9 Hz, PCCCHC), 157.6 (d, $^2J_{P,C}$ 2.3 Hz, PCC), 158.1 (d, $^2J_{P,C}$ 8.5 Hz, PCC) ppm. ^{31}P NMR (162 MHz, CDCl$_3$): δ=3.7 (ddm, $^1J_{P,H}$=374.5 Hz, $^2J_{P,H}$= 60.3 Hz) ppm. IR: $\tilde{\nu}$=2961 (w), 2234 (w, CN), 2160 (s, NC), 1601 (w), 1495 (w) 1464 (w), 1362 (w, tBu), 1211 (w), 1190 (w), 1098 (w), 912 (w), 860 (s), 843 (s), 820 (s), 691 (w), 621 (w), 550 (s), 434 (s) cm^{-1}. HRMS (ESI, MeOH): Calcd. for C$_{33}$H$_{42}$N$_2$NiP [M$^+$] 555.2439, found 555.2438; calcd. for InBr$_4^-$ [M$^-$] 430.5772, found 430.5771.

Compound 32: At −78 °C benzene-1,4-diisonitrile (6 mg, 0.22 mmol) in THF (15 mL) was added to **8** (47 mg, 0.09 mmol) and InBr$_3$ (32 mg, 0.09 mmol) in THF (15 mL). After addition the mixture was warmed to 25 °C. and the solvent was removed at reduced pressure. The crude product was purified by column chromatography (SiO$_2$, 5.5×2 cm, dichloromethane/methanol 9:1) affording compound **32** (30 mg, 0.02 mmol, 32%) as a dark green viscous oil.

^{1}H NMR (400.1 MHz, CDCl$_3$): δ=1.28 br. s, 18H, PCCCHCC(CH$_3$)$_3$], 1.63 [s, 18H, PCCC(CH$_3$)$_3$], 1.65 [s, 18H, PCCC(CH$_3$)$_3$], 1.97–2.30 (m, 4H, PCH$_2$CH$_2$), 2.65–2.78 (m, 2H, PCH$_2$), 2.99–3.14 (m, 2H, PCH$_2$), 5.70 (m, 2H, C$_{Cp}$H), 5.78 (m, 2H, C$_{Cp}$H), 5.90 (m, 2H, C$_{Cp}$H), 6.05 (m, 2H, C$_{Cp}$H), 6.00–6.49 (ddm, $^1J_{P,H}$=372.7 Hz, $^3J_{H,H}$=12.0 Hz, 2H, PH), 7.43 [m, 4H, 10(12)-H], 7.53 [br. s, 4H, NCCH] ppm. ^{13}C NMR (125.8 MHz, CDCl$_3$): δ=23.7 (d, $^2J_{P,C}$=5.3 Hz, PCH$_2$CH$_2$), 31.1 [s, PCCCHCC(CH$_3$)$_3$], 34.4 [d, $^4J_{P,C}$=1.6 Hz, PCCC(CH$_3$)$_3$], 35.1 [d, $^4J_{P,C}$=2.1 Hz, PCCC(CH$_3$)$_3$], 35.3 [d, $^5J_{P,C}$=1.2 Hz, PCCCHCC(CH$_3$)$_3$], 39.2 [d, $^3J_{P,C}$=1.9 Hz, PCCC (CH$_3$)$_3$], 40.0 (d, $^3J_{P,C}$=1.2 Hz, PCCC(CH$_3$)$_3$], 47.1 (d, $^1J_{P,C}$=31.5 Hz, PCH$_2$), 92.4 (d, $J_{P,C}$=5.5 Hz, C$_{Cp}$H), 98.3 (br. s, C$_{Cp}$H), 99.0 (m, C$_{Cp}$H), 100.4 (d, $J_{P,C}$=2.4 Hz, C$_{Cp}$H), 117.8 (d, $^1J_{P,C}$=36.7 Hz, PC), 118.8 (d, $^3J_{P,C}$=11.2 Hz, C_{Cp}C), 124.1 (d, $^3J_{P,C}$=9.6 Hz, PCCCH), 125.9 (d, $^3J_{P,C}$= 11.4 Hz, PCCCH), 127.6 (br. s, NiCNC), 128.8 (s, NiCNCCH), 149.1 (br. d, $^2J_{P,H}$=18.6 Hz, NiC), 154.5 (d, $^4J_{P,C}$ 3.3 Hz, PCCCHC), 157.6 (d, $^2J_{P,C}$ 1.7 Hz, PCC), 158.0 (d, $^2J_{P,C}$ 8.6 ppm Hz, PCC) ppm. ^{31}P NMR (162 MHz, CDCl$_3$): δ=3.3 (ddm, $^1J_{P,H}$=373.5 Hz, $^2J_{P,H}$=63.7 Hz) ppm. IR: $\tilde{\nu}$=2961 (m), 2868 (m), 2145 (s, NC), 1655 (w), 1593 (w), 1495 (w) 1460 (w), 1362 (m, tBu), 1211 (w), 860 (m), 619 (m), 507 (m) cm^{-1}. HRMS (ESI, MeOH): Calcd. for C$_{58}$H$_{80}$N$_2$Ni$_2$P$_2$ [M^{2+}] 491.2246, found 491.2244; calcd. for InBr$_4^-$ [M$^-$] 430.5772, found 430.577.

Conflict of Interest

The authors declare no conflict of interest.

[1] P. Braunstein, F. Naud, *Angew. Chem.* **2001**, *113*, 702–722; *Angew. Chem. Int. Ed.* **2001**, *40*, 680–699.
[2] H. Butenschön, *Chem. Rev.* **2000**, *100*, 1527–1564.
[3] A. Doppiu, U. Englert, V. Peters, A. Salzer, *J. Organomet. Chem.* **2007**, *692*, 4495–4505.
[4] M. Hussain, S. Kohser, K. Janssen, R. Wartchow, H. Butenschön, *Organometallics* **2009**, *28*, 5212–5221.
[5] K. Janssen, H. Butenschön, *New J. Chem.* **2011**, *35*, 2287–2298.
[6] S. Y. Ng, G. K. Tan, L. L. Koh, W. K. Leong, L. Y. Goh, *Organometallics* **2007**, *26*, 3352–3361.
[7] L. F. Groux, F. Belanger-Gariepy, D. Zargarian, *Can. J. Chem.* **2005**, *83*, 634–639.
[8] Y. Kataoka, Y. Nakagawa, A. Shibahara, T. Yamagata, K. Mashima, K. Tani, *Organometallics* **2004**, *23*, 2095–2099.
[9] A. Doppiu, U. Englert, A. Salzer, *Chem. Commun.* **2004**, 2166–2167.
[10] A. Döhring, V. R. Jensen, P. W. Jolly, W. Thiel, J. C. Weber, *Organometallics* **2001**, *20*, 2234–2245.
[11] D. C. Brookings, S. A. Harrison, R. J. Whitby, B. Crombie, R. V. H. Jones, *Organometallics* **2001**, *20*, 4574–4583.
[12] Y. Kataoka, A. Shibahara, T. Yamagata, K. Tani, *Organometallics* **2001**, *20*, 2431–2433.
[13] Y. Kataoka, Y. Iwato, A. Shibahara, T. Yamagata, K. Tani, *Chem. Commun.* **2000**, 841–842.
[14] Y. Kataoka, A. Shibahara, Y. Saito, T. Yamagata, K. Tani, *Organometallics* **1998**, *17*, 4338–4340.
[15] Y. Kataoka, Y. Iwato, T. Yamagata, K. Tani, *Organometallics* **1999**, *18*, 5423–5425.
[16] Y. Kataoka, Y. Saito, A. Shibahara, K. Tani, *Chem. Lett.* **1997**, 621–622.
[17] I. Werner, H. Butenschön, *Eur. J. Inorg. Chem.* **2014**, 6051–6060.
[18] T. Ishiyama, H. Nakazawa, K. Miyoshi, *J. Organomet. Chem.* **2002**, *648*, 231–236.
[19] R. T. Kettenbach, H. Butenschön, *New J. Chem.* **1990**, *14*, 599–601.
[20] H. Butenschön, R. T. Kettenbach, C. Krüger, *Angew. Chem.* **1992**, *104*, 1052–1054; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1066–1068.
[21] J. Foerstner, R. Wartchow, H. Butenschön, *New J. Chem.* **1998**, *22*, 1155–1157.
[22] J. Foerstner, S. Kozhushkov, P. Binger, P. Wedemann, M. Noltemeyer, A. de Meijere, H. Butenschön, *Chem. Commun.* **1998**, 239–240.
[23] J. Foerstner, A. Kakoschke, D. Stellfeldt, H. Butenschön, R. Wartchow, *Organometallics* **1998**, *17*, 893–896.
[24] J. Foerstner, F. Olbrich, H. Butenschön, *Angew. Chem.* **1996**, *108*, 1323–1325; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1234–1237.
[25] J. Foerstner, R. Kettenbach, R. Goddard, H. Butenschön, *Chem. Ber.* **1996**, *129*, 319–325.
[26] M. Hussain, D. Albert, R. Wartchow, H. Butenschön, *Chem. Asian J.* **2007**, *2*, 782–793.
[27] L. Yong, K. Kirleis, H. Butenschön, *Adv. Synth. Catal.* **2006**, *348*, 833–836.
[28] S. I. Kozhushkov, J. Foerstner, A. Kakoschke, D. Stellfeldt, L. Yong, R. Warchow, A. de Meijere, H. Butenschön, *Chem. Eur. J.* **2006**, *12*, 5642–5647.
[29] L. Yong, E. Hofer, R. Wartchow, H. Butenschön, *Organometallics* **2003**, *22*, 5463–5467.
[30] A. Kakoschke, L. Yong, R. Wartchow, H. Butenschön, *J. Organomet. Chem.* **2003**, *674*, 86–95.
[31] L. Yong, H. Butenschön, *Chem. Commun.* **2002**, 2852–2853.
[32] J. Foerstner, A. Kakoschke, R. Goddard, J. Rust, R. Wartchow, H. Butenschön, *J. Organomet. Chem.* **2001**, *617/618*, 412–422.
[33] J. Foerstner, A. Kakoschke, R. Wartchow, H. Butenschön, *Organometallics* **2000**, *19*, 2108–2113.
[34] S. Kohser, H. Butenschön, *Eur. J. Inorg. Chem.* **2018**, 31–45.
[35] I. Werner, S. Kohser, H. Butenschön, *Eur. J. Inorg. Chem.* **2020**, 2545–2551.
[36] K. Issleib, H. Schmidt, C. Wirkner, *Z. Anorg. Allg. Chem.* **1982**, *488*, 75–79.
[37] C. F. Wilcox Jr, R. R. Craig, *J. Am. Chem. Soc.* **1961**, *83*, 3866–3871.
[38] D. M. Khramov, V. M. Lynch, C. W. Bielawski, *Organometallics* **2007**, *26*, 6042–6049.
[39] G. Smith, D. J. Cole-Hamilton, A. C. Gregory, N. G. Gooden, *Polyhedron* **1982**, *1*, 97–103.
[40] D. J. Liston, C. A. Reed, C. W. Eigenbrot, W. R. Scheidt, *Inorg. Chem.* **1987**, *26*, 2739–2740.
[41] R. Usón, J. Forniés, M. Tomás, J. M. Casas, F. A. Cotton, L. R. Falvello, *J. Am. Chem. Soc.* **1985**, *107*, 2556–2557.
[42] Z.-H. Zhang, *Synlett* **2005**, 711–712.
[43] Deposition Number 2063484 (for **18**) contains the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.
[44] P. Suomalainen, H. K. Reinius, H. Riihimaki, R. H. Laitinen, S. Jaaskelainen, M. Haukka, J. T. Pursiainen, T. A. Pakkanen, A. O. I. Krause, *J. Mol. Catal. A* **2001**, *169*, 67–78.
[45] G. A. Ardizzoia, S. Brenna, *Phys. Chem. Chem. Phys.* **2017**, *19*, 5971–5978.
[46] M. P. Mitoraj, A. Michalak, *Inorg. Chem.* **2010**, *49*, 578–582.
[47] A. Rabiee Kenaree, E. R. Sauve, P. J. Ragogna, J. B. Gilroy, *Dalton Trans.* **2016**, *45*, 2859–2867.
[48] M. Esteban, A. Pequerul, D. Carmona, F. J. Lahoz, A. Martin, L. A. Oro, *J. Organomet. Chem.* **1991**, *402*, 421–434.
[49] I. V. Kourkine, D. S. Glueck, *Inorg. Chem.* **1997**, *36*, 5160–5164.
[50] S. Kohser, Dissertation, Leibniz Universität Hannover, **2009**.
[51] M. Knorn, E. Lutsker, O. Reiser, *Chem. Soc. Rev.* **2020**, *49*, 7730–7752.
[52] A. Kakoschke, Dissertation, Universität Hannover, **2000**.
[53] H. Werner, G. Hörlin, W. D. Jones, *J. Organomet. Chem.* **1998**, *562*, 45–51.
[54] F. Glockling, A. McGregor, *J. Inorg. Nucl. Chem.* **1973**, *35*, 1481–1485.
[55] M. Herberhold, T. Schmalz, W. Milius, B. Wrackmeyer, *Inorg. Chim. Acta* **2002**, *334*, 10–16.
[56] A. F. G. Ribeiro, P. T. Gomes, A. R. Dias, J. L. Ferreira da Silva, M. T. Duarte, R. T. Henriques, C. Freire, *Polyhedron* **2004**, *23*, 2715–2724.
[57] E. Traversa, J. L. Templeton, H. Y. Cheng, M. Mohadjer Beromi, P. S. White, N. M. West, *Organometallics* **2013**, *32*, 1938–1950.
[58] M. Hanack, R. Thies, *Chem. Ber.* **1988**, *121*, 1225–1230.
[59] U. Schöllkopf, R. Schröder, E. Blume, *Justus Liebigs Ann. Chem.* **1973**, *766*, 130–141.
[60] S. Kamijo, T. Jin, Y. Yamamoto, *J. Am. Chem. Soc.* **2001**, *123*, 9453–9454.
[61] M. Liu, O. Reiser, *Org. Lett.* **2011**, *13*, 1102–1105.
[62] D. Riedel, T. Wurm, K. Graf, M. Rudolph, F. Rominger, A. S. K. Hashmi, *Adv. Synth. Catal.* **2015**, *357*, 1515–1523.
[63] R. Deschenaux, C. Masoni, H. Stoeckli-Evans, S. Vaucher, J. Ketterer, R. Steiger, A. L. Weisenhorn, *J. Chem. Soc. Dalton Trans.* **1994**, 1051–1059.
[64] A. C. Sarapu, R. F. Fenske, *Inorg. Chem.* **1975**, *14*, 247–253.
[65] M. L. Kuznetsov, *Russ. Chem. Rev.* **2002**, *71*, 265–282.
[66] R. M. Nielson, S. Wherland, *Inorg. Chem.* **1985**, *24*, 1803–1808.
[67] B. Shong, K. T. Wong, S. F. Bent, *J. Am. Chem. Soc.* **2014**, *136*, 5848–5851.
[68] D. Britton, *Acta Crystallogr. Sect. E* **2002**, *58*, o637-o639.
[69] R. W. Stephany, M. J. A. De Bie, W. Drenth, *Org. Magn. Reson.* **1974**, *6*, 45–47.
[70] A. Guirado, A. Zapata, J. L. Gomez, L. Trabalon, J. Galvez, *Tetrahedron* **1999**, *55*, 9631–9640.
[71] D. L. Cronin, J. R. Wilkinson, L. J. Todd, *J. Magn. Reson.* **1975**, *17*, 353–361.
[72] A. Schmidpeter, B. Wrackmeyer, *Z. Naturforsch. B* **1986**, *41B*, 553–559.
[73] J. Autschbach, S. Zheng, R. W. Schurko, *Concepts Magn. Reson. Part A* **2010**, *36 A*, 84–125.
[74] A. T. Termaten, H. Aktas, M. Schakel, A. W. Ehlers, M. Lutz, A. L. Spek, K. Lammertsma, *Organometallics* **2003**, *22*, 1827–1834.
[75] W. J. Stec, N. Goddard, J. R. Van Wazer, *J. Phys. Chem.* **1971**, *75*, 3547–3549.
[76] T. Ishiyama, T. Mizuta, K. Miyoshi, H. Nakazawa, *Organometallics* **2003**, *22*, 1096–1105.
[77] W. C. Still, M. Kahn, A. Mitra, *J. Org. Chem.* **1978**, *43*, 2923–2925.