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Article

The First η^5-Indenylnickel Chelate Complexes with a Pendant Phosphane Tether

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The synthesis of the first indenylnickel chelate complexes with a pendant phosphane ligand is described. In contrast to earlier attempts by others directed to chelates with a tethered diphenylphosphino ligand in our hands, the synthesis was successful with a di-*tert*-butylphosphino ligand. The anionic ligand system was generated by a nucleophilic ring-opening of spiroindene **3** with lithium di-*tert*-butylphosphide, a reaction that was significantly accelerated by microwave irradiation. Alternatively, the borane-protected ligand was obtained by using the lithiated borane adduct of di-*tert*-butylphosphane. Reaction of the anionic ligand with nickel(II) chloride gave chloro chelate **8**, which was transformed to azido, cyano, and isothiocyanato complexes **9**−**11**, the cationic acetonitrile complex **12**, and representatives containing nickel−carbon bonds, including the methyl and the ethynyl derivatives **13** and **18**. A crystal structure analysis of methyl chelate **13** is also included. The ^{13}C NMR data of a quarternized 2-pyridylethynyl derivative **20** suggest a significant contribution of the respective allenylidene resonance formulas **21** and **22**. Finally, bimetallic ferrocenylethynyl complex **23** has been included as a bimetallic representative. Some of the complexes were characterized by cyclovoltammetry.

Introduction

Cyclopentadienyl complexes, which are among the most common compounds in organometallic chemistry,[1] are known for all transition metals, and many variations of the ligand system have been realized. This includes substituted ones such as the pentamethylcyclopentadienyl ligand,[2] heterocyclic analogues such as phosphacyclopentadienyl ligands,[3,4] or asymmetrically disubstituted ligands causing planar chirality of the respective complexes.[5] This latter feature is the main reason for the extended application of ferrocene complexes of this kind in asymmetric catalysis.[6,7] In addition, variations of the coordination mode in the course of associative ligand exchange reactions−η^5, η^3, or even η^1−have been investigated.[8]

A feature common to most cyclopentadienyl complexes is the rotation of the cyclopentadienyl ligand, which usually requires little energy of activation.[9] A class of related compounds, which does not allow for facile cyclopentadienyl rotation, are complexes bearing a cyclopentadienyl ligand with a chelating tether, usually with O, N, or P donor atoms.[10−14] We have investigated the chemistry of cobalt complexes of type **1** for some time and found several examples in which these complexes were stable with highly strained ligands L, such as cyclopropylalkynes, unsubstituted as well as spiro-anellated bicyclopropylidenes, or cyclopropene derivatives.[15−18] Most interestingly, the ethene complex **1** (L = H_2C═CH_2) facilitates the cleavage of the C,P

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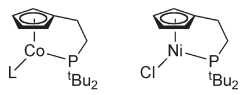
triple bond of a phosphaalkyne at low temperature.[19] In addition it was found that these complexes allow for oxidative silane additions, stereoselective catalytic alkyne hydrosilylations,[20−22] and alkyne trimerization, the latter in aqueous solvent.[23]

While cyclopentadienylalkylphosphane chelate complexes have been broadly investigated for transition metals of almost all groups of the periodic system, this remarkably is not the case for group 10 metals. This inspired us to investigate nickel complexes with a cyclopentadienylalkylphosphane ligand system, and we recently published the first of these complexes based on the stable and easily accessible nickel complex **2**.[24]



1 **2**

Indenyl complexes show properties different from those of usual cyclopentadienyl complexes. Beyond the fact that indenyl complexes with a substituent at C-1 or at C-3 are planar chiral, the striking feature is their ability to adopt the η^3 coordination mode as a result of a ring-slippage reaction much easier than cyclopentadienyl complexes lacking an anellated benzene ring.[8] This so-called indenyl effect[1] is a result of the formation of an intact benzenoid aromatic system upon ring slippage. The facilitated formation of η^3 coordination implies the formation of a vacant coordination site at the metal atom, which is attractive for such complexes to be applied in catalysis. In connection with our research on chelates derived from **2** we became interested in indenylnickel complexes bearing a phosphane tether.

Compared to the number of cyclopentadienyl chelate complexes with a phosphane tether known, the number of respective indenyl chelate complexes that have been reported is comparably small. Most of the known indenyl chelates with a phosphane tether are complexes of rhodium[25−36] and ruthenium.[25,26,37,38] In addition some complexes of iridium[28] and of chromium[39] have been reported. Particularly interesting in this context are some results of Zargarian et al., who attempted the synthesis of indenyl nickel chelates. While it was possible to obtain indenyl chelates with an amino tether,[40] efforts directed to the synthesis of a corresponding η^5-indenylnickel chelate with a 2-(diphenylphosphanyl)ethyl tether were unsuccessful. However, the authors succeeded in the synthesis of an interesting η^1-indenylnickel complex with two chelating (diphenylphosphanyl)ethyl substituents.[41] With only few exceptions[37,39] the complexes reported bear a diphenylphosphanyl group as the chelating ligand. Here we report on our syntheses of a variety of η^5-indenylnickel chelates with a [2-(di-*tert*-butyl)phosphanyl]ethyl tether.

Results and Discussion

According to our experience, those cobalt complexes bearing a sterically more bulky and more electron-donating 2-(di-*tert*-butylphosphanyl)ethyl tether at a cyclopentadienyl ligand are less sensitive, give higher yields, and have better crystallization properties than those with a 2-(diphenylphosphanyl)ethyl or 2-(diisopropylphosphanyl)-ethyl tethers as well as those with longer tethers.[42,43] This experience made us select the [2-(di-*tert*-butylphosphanyl)ethyl]cyclopentadienyl ligand for the nickel complexes, which we recently reported.[24] With respect to indenylnickel chelates we therefore focused on the respective indenyl ligand with a 2-(di-*tert*-butylphosphanyl)ethyl substituent at C-1. As the cyclopentadienyl system is easily available by nucleophilic addition of lithium di-*tert*-butylphosphide to spiro[2.4]hepta-4,6-diene,[44] the synthesis of the ligand desired here started from the respective spiroindene (**3**).[45] The addition of $LiPR_2$ (R = Ph, Cy, iBu, Et) to **3** has also been used for the syntheses of the ligands of known indenyl chelates.[27,39] While these addition reactions proceeded smoothly within a few hours, our attempts to add lithium di-*tert*-butylphosphide to **3** were, however, without success under the reaction conditions applied in the known cases. Only after extended heating for 120 h in THF at reflux was the addition finally achieved, and the electroneutral phosphane **5** was obtained in 90% yield by hydrolysis of the anionic ligand **4**. Remarkably, this extended period of time could be abbreviated to only 40 min by application

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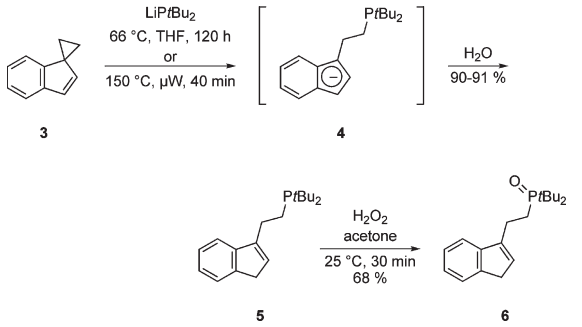
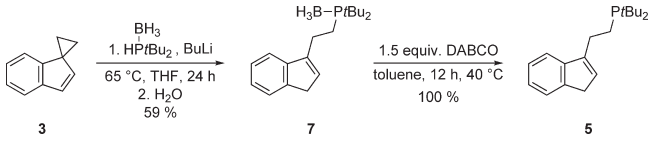
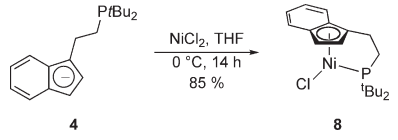
of microwave heating at 150 °C, the yield being slightly improved to 91%. **5** is stable under exclusion of air; in the presence of oxygen phosphane oxide **6** is formed, which is also obtained by oxidation with H_2O_2 as a stable compound (68% yield). **5** and **6** have fully been characterized spectroscopically.



Later it was found that the borane-protected ligand **7** is conveniently obtained as a colorless, air-stable solid by lithiation of the borane adduct of di-*tert*-butylphosphane with butyllithium in hexane followed by addition of **3**, heating at 65 °C for 24 h, hydrolysis, and purification by column chromatography. While diethylamine did not remove the borane from **7**, this was possible by using 1,4-diazabicyclo[2.2.2]octane (DABCO). Quantitative formation of **5** was finally achieved by treatment of **7** with 1.5 equiv of DABCO in toluene at 40 °C over 12 h.

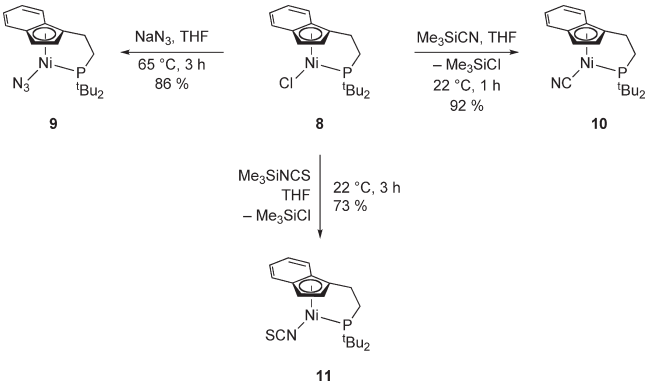


The first indenylnickel(II) chelate with a pendant phosphane ligand was obtained by treatment of **4** with anhydrous nickel(II) chloride in THF at 0 °C over 14 h. Chloro complex **8** was obtained in 85% yield as a purple crystalline material, which can be handled in air for 1 h without significant decomposition.



As a consequence of the asymmetry of **8**, the NMR spectra are more complicated than those of the related cyclopentadienyl complex **2**. In the ^{1}H NMR spectrum the diastereotopic *tert*-butyl substituents give rise to two doublets at $\delta = 1.31$ and 1.45 ppm, and the bridging CH_2 groups cause a complex ABCDX line system at $\delta = 1.87-1.94$ and 2.4−2.6 ppm. The asymmetry of **8** is also reflected by the ^{13}C NMR data, showing two signals for the *tert*-butyl methyl groups and the respective quarternary carbon atoms. A chemical shift of $\delta = 84.2$ ppm in the ^{31}P NMR spectrum indicates a coordinated phosphane.[14] A molecular ion peak in the mass spectrum at $m/z = 380$ (61%) is indicative of the monomeric nature of **8**.

Starting from the well accessible complex **8**, it was possible to substitute the chloro ligand by other pseudohalo ligands: treatment of **8** with sodium azide in boiling THF over 3 h afforded azido chelate **9** in 86% yield. Milder reaction conditions were possible when **8** was treated with trimethylsilyl cyanide in THF: stirring at 22 °C for 1 h gave a 92% yield of cyano chelate **10**, and in a similar way the reaction of **8** with trimethylsilylisothiocyanate in THF at 22 °C over 3 h resulted in the formation of isothiocyanato chelate **11** in 73% yield. **9**, **10**, and **11** are purple, yellow-orange, or orange solids, respectively, which are stable in air for ca. 2 h. Their spectroscopic properties resemble those of **8**. The presence of the pseudohalo ligands is indicated by their characteristic IR absorptions[46] as well as by the molecular ion peaks and fragmentation patterns in the mass spectra. The isothiocyanate in contrast to a thiocyanate ligand in **11** is verified by the presence of the $[M^+ - S]$ fragmentation peak in the mass spectrum (84%).



While the chloro as well as the pseudohalo ligands in chelates **8**−**11** are coordinating, we wanted to test how far the formation of a cationic complex with a noncoordinating counteranion would be possible. For this purpose **8** was treated with sodium tetraphenylborate in acetonitrile at 25 °C. After 2 h the cationic complex **12** was obtained in 92% yield. The compound deserves interest, because after decomplexation of the weak acetonitrile ligand a planar chiral cationic, presumably Lewis acidic species would form. **12** was characterized spectroscopically. The presence of the tetraphenylborate anion as well as that of the acetonitrile ligand are confirmed by ^{1}H and ^{13}C NMR. Positive and negative ion mass spectra are also in accord with **12**. The number of known cationic indenylnickel complexes with a noncoordinating counteranion is rather limited; some have been investigated as styrene polymerization precatalysts.[47−51]

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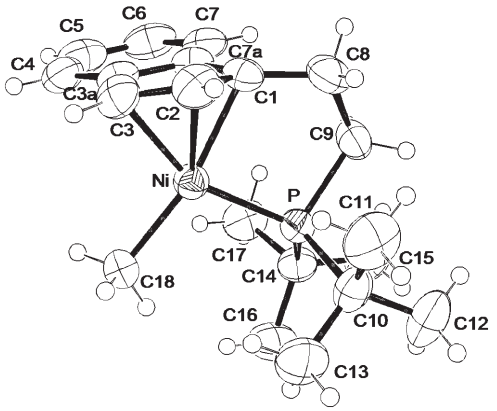
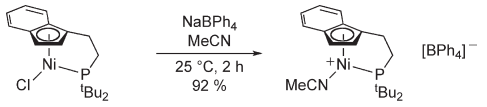


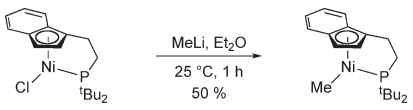
Figure 1. Structure of **13** in the crystal.[52] Selected bond lengths [pm] and angles [deg]: Ni−C1 207.1(2), Ni−C2 205.1(3), Ni−C3 208.5(3), Ni−C3a 231.6(3), Ni−C7a 233.4(3), Ni−C18 197.8(2), Ni−P 215.35(9), C1−C2 141.4(4), C1−C7a 144.9(4), C1−C8 150.3(4), C2−C3 139.8(4), C3−C3a 143.8(4), C3a−C4 139.6(4), C3a−C7a 142.6(4), C4−C5 136.8(4), C5−C6 138.9(5), C6−C7 137.3(4), C7−C7a 139.2(4), C8−C9 153.8(4), C9−P 186.2(3); C1−C8−C9 111.4(2), C10−P−C14 111.54(13), C18−Ni−P 104.04(8), Ni−P−C9 102.11(9).



8 **12**

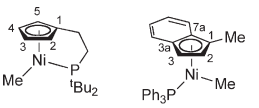
Having established indenylnickel chelates with halo and pseudohalo ligands as well as a cationic complex with an acetonitile ligand, we became interested in complexes with a nickel carbon bond other than that in **10**.

Treatment of chloro complex **8** with methyllithium in diethyl ether at 25 °C caused a color change from dark purple to dark brown. Subsequent filtration of the mixture through a Celite layer and crystallization of the product from the filtrate afforded the methylated nickel chelate **13** in 50% yield as a green crystalline solid. While the crystalline material can be handled in air for up to 2 h without significant decomposition, the compound tends to gradually decompose in solution, causing not fully resolved signals in the ^{1}H and ^{13}C NMR spectra. However, the ^{31}P NMR signal at $\delta = 85.1$ ppm clearly indicates the coordinated phosphorus ligand. The successful methylation is confirmed by the molecular ion peak in the mass spectrum at $m/z = 360$ (100%). Recrystallization from hexane at −20 °C afforded crystals that were suitable for an X-ray crystal structure analysis (Figure 1).



8 **13**

Indenyl nickel complexes and their structures have extensively been discussed in a review article by Zargarian.[53] The structure of **13**, which is the first stable indenyl chelate in this context to be structurally characterized, may be compared with those of the corresponding cyclopentadienyl chelate complex **14**[24] and of the unchelated triphenylphosphane complex **15**.[54] The conformations adopted by **13** and by **15** in the solid state are different in that the triphenylphosphane ligand in **15** adopts a position *anti* to C1, whereas the chelate nature of **13** causes the phosphane part of the ligand to stand *syn* to C1.



14 **15**

The Ni−Me bond lengths are comparable in all three cases in the range 197.2 to 199.1 pm, and this is also the case for the Ni−P bond lengths (212.1−215.35 pm). Remarkably, the bond length between the nickel atom and the alkylated cyclopentadienyl carbon atom C1 is also similar for all three compounds (207.1−209.9 pm), although **13** and **14**, but not **15**, are chelates. The bond lengths Ni−C2 show more variation: while this is 205.1 pm for **13**, the corresponding lengths are 213.2 pm for **14** and 207.2 pm for **15**. The Ni−C3 distances are almost equal for the indenyl complexes (**13**: 208.5, **15**: 208.2 pm) and not significantly longer for the cyclopentadienyl chelate **14** (211.0 pm). In addition to the shorter bond lengths Ni−C2 for the indenyl complexes as compared to **14** the indenyl effect is quite obvious from the bond lengths between the nickel atom and coordinated carbon atoms C3a and C7a, which are part of the anellated benzene rings: while Ni−C4 and Ni−C5 are 210.4 and 215.2 pm long, respectively, for the cyclopentadienyl chelate **14** the corresponding bond lengths Ni−C3a and Ni−C7a for **13** and **15** are significantly longer, with values of 227.5 and 227.3 pm for **15** and 231.6 and 233.4 pm for **13**. The C−C bond distances in the cyclopentadienyl rings vary considerably for the indenyl complexes **13** and **15**: while C1−C2 (**13**: 141.4, **15**: 140.7 pm) and C2−C3 (**13**: 139.8, **15**: 140.4 pm) are comparatively short, the bonds C1−C7a (**13**: 144.9, 15: 143.8 pm) and C3−C3a (**13**: 143.8, **15**: 142.4 pm) are relatively long. The bond length C3a−C7a is 142.6 pm for **13** and 142.4 pm for **15**. The data of **13** are rather similar to those of **15** and clearly indicate a ring slippage of the nickel atom toward η^3 corresponding to a separation between the allyl and the ene moiety of the cyclopentadienyl part of the ligand system (indenyl effect). The larger distances Ni−C3a and Ni−C7a in **13** as compared to those of **15** indicate that this effect is more pronounced in **13**, presumably as a consequence of the stronger donor character of the di-*tert*-butylphosphanylethyl ligand as compared to triphenylphosphane. The increased effect is quantitatively reflected by the slip-fold parameters[55,56] used to describe the extent of the distortion, HA = 10.5°, FA = 9.3°, and ΔM−C = 25 pm, which all exceed those of **15**[54] but are in the

(52) CCDC 723313 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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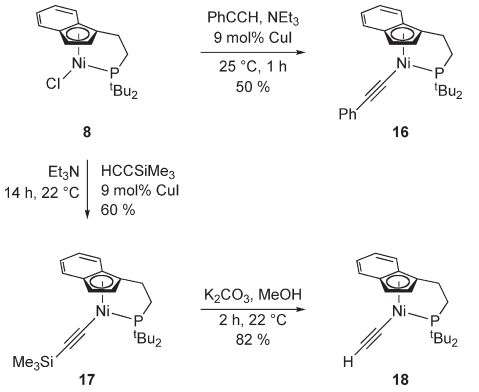
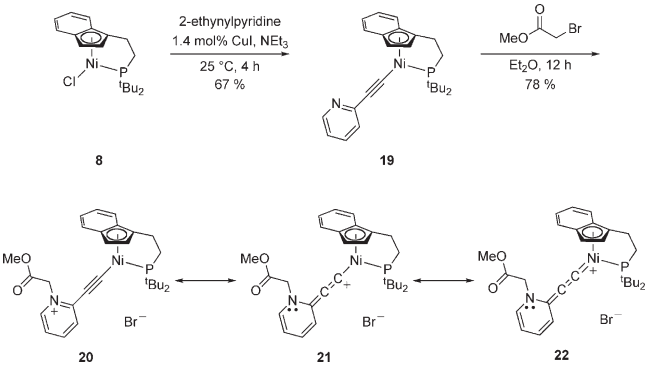
(56) HA: hinge angle between normals to the least-squares planes defined by C1, C2, C3 and C1, C7a, C3. FA: fold angle between normals to least-squares planes defined by C1, C2, C3 and C3a, C4, C5, C6, C7, C7a. ΔM−C = 0.5[(M−C3a) + (M−7a)] − 0.5[(M−C1) + (M−C3)].

usual range of a number of other unchelated indenylnickel complexes.[53]



Treatment of chloro chelate **8** with phenylethyne at 25 °C for 14 h in the presence of a catalytic amount of CuI in triethylamine gave alkynylnickel chelate **16** in 67% yield. **16** is a deep brown solid, which can be handled in the air for 2−3 h without significant decomposition. Likewise the corresponding reaction with ethynyltrimethylsilane gave the silylethynyl complex **17** in 60% yield. Protiodesilylation proceeded smoothly, affording the unsubstituted ethynyl chelate **18** in 82% yield.

As a heterocyclic representative, (2-pyridyl)ethynyl complex **19** was prepared accordingly in 67% yield. Subsequent treatment with methyl bromoacetate afforded pyridinium salt **20** in 78% yield. While the spectroscopic data of **19** are in the usual range, those of **20** deserve some comment: The ^{13}C NMR chemical shift of the acetylide carbon atom bound at nickel is $\delta = 105.0$ ($^2J_{C,P} = 26.2$ Hz) ppm in **19**. In contrast, the corresponding signal in the pyridinium salt **20** is observed at $\delta = 154.4$ ($^2J_{C,P} = 22.8$ Hz) ppm. Such a large difference in chemical shift ($\Delta\delta = 49.4$ ppm) clearly indicates a strong interaction between the positively charged pyridinium nitrogen atom and the acetylide carbon atom. Similar observations were recently published by Lin for some ruthenium complexes ($\Delta\delta = 64.9-66.4$ ppm). The authors conclude from the large $\Delta\delta$ values that a significant contribution of the respective allenylidene resonance formula is given.[57] The IR absorptions of the C,C triple bonds in **19** ($\tilde{\nu} = 2083$ cm^{-1}) and in **20** ($\tilde{\nu} = 2059$ cm^{-1}) are in accord with a weakened bond strength in **20**, which is in accord with a contribution of resonance formulas **21** and **22**. To our knowledge nickel allenylidene complexes have so far not been reported.

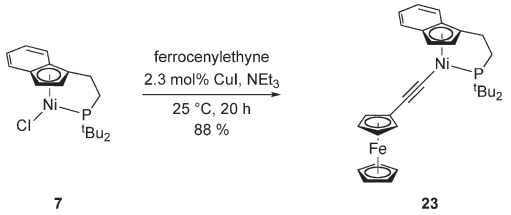


Finally, as a bimetallic derivative, ferrocenylethynyl-substituted chelate **21** has been prepared in the usual way by treatment of chloride **8** with ferrocenylethyne.[58] Complex **23** has been obtained in 88% yield.

Table 1. Cyclovoltammetry Data[a]

compound	E_{pa} [V]	E_{pc} [V]	ΔE_p [V]	$E_{1/2}$ [V]
8	0.221	0.096	0.125	0.162
10	0.544			
	0.787			
16	0.212	0.034	0.178	0.123
18	0.326	0.040	0.286	0.183
19	0.284	0.073	0.211	0.179
23	0.389	0.175	0.214	0.282
	0.158	0.091	0.067	0.125
	−0.137	−0.270	0.133	−0.204

[a] $v = 1.000$ V s^{-1}, $T = 20$ °C, $c = 2.0$ mmol L^{-1}, $c_{TBAHFP} = 0.1$ mol L^{-1}, one scan, solvent dichloromethane, potential vs FcH/FcH$^+$.



Indenylnickel chelates **8**, **10**, **16**, **18**, **19**, and **23** were also characterized by cyclovoltammetry. Results are summarized in Table 1; all plotted cyclovoltammograms are given in the Supporting Information.

Chloride **8** shows a cyclovoltammogram similar to that of the corresponding cyclopentadienyl derivative **2**[24] with a reversible redox wave at positive potential relative to FcH/FcH$^+$. However, the process in **8** takes place at about 0.100 V lower potential than in **2**, indicating **2** to be less electron rich as compared to **8**. In contrast to **8**, cyano complex **10** shows two irreversible oxidation steps. As a second oxidation wave has not been observed for **8**, this is presumably due to an oxidation of the CN ligand of **10**. Alternatively one might envisage a Ni(III)−Ni(IV) oxidation process. The cyclovoltammogram of phenylethynyl complex **16** resembles that of the corresponding 4-tolylethynyl cyclopentadienylnickel chelate and shows one reversible redox process at $E_{1/2} = 0.123$ V, which is ca. 0.12 V higher than in the related cyclopentadienyl chelate.[24] While the reduction wave at 0.034 V is clearly visible in the cyclovoltammogram of **16**, this is not the case for the unsubstituted ethynyl derivative **18** nor for the 2-pyridylethynyl complex **19**, both of which show cyclovoltammograms with hardly visible reduction waves corresponding to essentially irreversible oxidation waves .

The cyclovoltammogram of ferrocenylethynyl chelate **23** (Figure 2) is somewhat more complicated and shows two clearly visible reversible redox processes and a less clearly visible one, the waves being covered by the other two. For an interpretation a comparison with the CV data of the related unchelated complex **24** is instructive.[59] According to this, the reversible redox wave at $E_{1/2} = -0.204$ V ($E_{pc} = -0.137$ V, $E_{pa} = -0.270$ V) is assigned to the ferrocenyl redox process [Fe(II)−Fe(III)]. The redox process at $E_{1/2} = 0.282$ V

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(58) Doisneau, G.; Balavoine, G.; Fillebeen-Khan, T. *J. Organomet. Chem.* **1992**, *425*, 113–117.
(59) Butler, P.; Gallagher, J. F.; Manning, A. R.; Mueller-Bunz, H.; McAdam, C. J.; Simpson, J.; Robinson, B. H. *J. Organomet. Chem.* **2005**, *690*, 4545–4556.

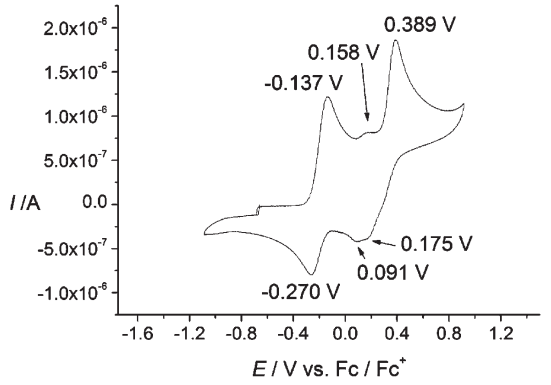
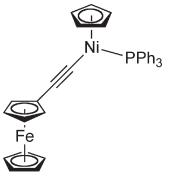


Figure 2. Cyclovoltammogram of **23** (1.000 V s^{-1}, T = 20 °C, c = 2.0 mmol L^{-1}, c_{TBAHFP} = 0.1 mol L^{-1}, one scan, dichloromethane).

therefore refers to the ferrocenium-substituted ethynylnickel chelate thus generated. The nature of the barely visible redox process at $E_{1/2}$ = 0.125 V remains unclear, although among the processes observed this is the one with almost perfect reversibility (ΔE_p = 0.067 V).

A comparison of the E_{pa} and the E_{pc} values of the alkynylnickel chelates shows an overall increase in the order **16** < **19** ≈ **18** < **23**, which corresponds to the substituent order Ph < Py ≈ H < Fc. On one hand this order reflects the increased propensity for electron-rich systems for oxidation. On the other hand it becomes clear that the E_{pa} and E_{pc} values taken from the cyclovoltammogram of ferrocenyl derivative **23** refer to the cationic, electron-withdrawing ferrocenium species generated by the preceding oxidation step ($E_{1/2}$ = −0.204 V).



24

In conclusion, we found the nucleophilic ring-opening of spiroindene with lithium di-*tert*-butylphosphide, affording a new chelate ligand. With this we prepared the first indenylnickel chelates with a tethered phosphane. The complexes include those with pseudohalide, labile acetonitrile, methyl, and alkynyl ligands at the nickel atom. Our future investigations will be directed toward the reactivity and the catalytic properties of these compounds as well as toward the synthesis of enantiopure representatives of this hardly investigated class of compounds.

Experimental Section

General Procedures. All manipulations involving air-sensitive material were performed in flame-dried reaction vessels in an argon or nitrogen atmosphere using vacuum line and standard Schlenk techniques. [4,5]Benzospiro[2.4]hepta-4,6-diene (**3**) was prepared according to a published procedure.[45] Diethyl ether (EE) and THF were distilled from sodium benzophenone ketyl. Hexane, pentane, *tert*-butyl methyl ether (TBME), dichloromethane, and chloroform were dried with calcium hydride and freshly distilled before use. Petroleum ether (PE) was dried with calcium chloride. All the solvents were purged with nitrogen before use. Column chromatography was carried out by flash chromatography.[60] Silica gel (J. T. Baker, 40 μm) was degassed three times by heating it with a flame at reduced pressure followed by setting it at normal pressure with nitrogen. Microwave heating was carried out using a CEM Discover Labmate microwave apparatus (300 W with ChemDriver software). IR spectra: Bruker FT-IR spectrometer 580 and 1170 (ATR). Mass spectra: VG autospec (Micromass), Finnegan MAT 112 and MAT 312. HRMS (ESI): Micromass LCT with lock spray ion source combined with Waters Alliance 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 were determined with ATP and DEPT techniques. Signals with negative phase (CH, CH_3) are labeled with "−", those with positive phase (C, CH_2) with "+". ^{31}P NMR: Bruker AVS 400 (161.9 MHz). Cyclovoltammetry (CV): Heka PG 285 potentiostat, reference electrode Ag/AgCl (Alfa), counter electrode Pt wire. Melting points: Electrothermal IA9000 series digital melting point apparatus. Elemental analyses: Elementar Vario EL.

Di-*tert*-butyl-2-(1′-indenylethyl)phosphane (5). At 0 °C butyllithium (9.5 mL, 15.0 mmol, 1.6 M in hexane) was added dropwise to a solution of di-*tert*-butylphosphane (2.92 g. 20.0 mmol) in THF (400 mL). After stirring for 2 h at 0 °C, the reaction mixture was heated at reflux, and [4,5]benzospiro[2.4]hepta-4,6-diene (**3**) (2.84 g, 20.0 mmol) was added. The solution was heated at reflux for 120 h, the color of the reaction mixture changing to red. Then the solution was cooled to 25 °C. After solvent removal at reduced pressure, the residue was washed with degassed pentane (3 × 30 mL). The reaction mixture was hydrolyzed by addition of water (50 mL), and the product was extracted with pentane (3 × 100 mL). The combined organic layers were dried over sodium carbonate and filtered. Solvent removal at reduced pressure yielded 3.90 g (14.0 mmol, 93%) of **5** as a light yellow oil. IR (ATR): $\tilde{\nu}$ = 2953 (w), 2903 (w), 2858 (w), 1462 (w), 1393 (w), 1366 (w), 1260 (w), 1155 (m), 1018 (w), 798 (s), 769 (s), 720 (m) cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.21 (d, $^3J_{PH}$ = 11.0 Hz, 18H, 6 × CH_3), 1.73−1.78 (m, 2H, 8-H), 2.75−2.81 (m, 2H, 9-H), 3.35 (d, $^3J_{HH}$ = 1.6, 2H, 3-H), 6.29 (br. s, 1H, 2-H), 7.21 (dd, ABCD line system, 1H, 4-H), 7.26 (dd, ABCD line system, 1H, 6-H), 7.39 (d, ABCD line system, 1H, 5-H), 7.48 (d, ABCD line system, 1H, 7-H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz, BB): δ 20.0 (d, $^1J_{CP}$ = 20.2 Hz, C-8), 29.4 (d, $^2J_{CP}$ = 29.1 Hz, C-9), 29.8 (d, $^2J_{CP}$ = 13.1 Hz, CH_3), 31.5 [d, $^1J_{CP}$ = 19.8 Hz, $C(CH_3)_3$], 37.7 (s, C-3), 119.0 (s, C-2), 123.9 (s, C-4), 124.6 (s, C-6), 126.1 (s, C-5), 127.6 (s, C-7), 144.6 (s, C-7a), 145.2 (s, C-3a), 145.8 (d, $^3J_{CP}$=15.4 Hz, C-1) ppm. ^{31}P NMR ($CDCl_3$, 161 MHz): δ 32.2 (s) ppm. MS (ESI acetonitrile): m/z (%) = 368 (9) [M^+ + CH_3CN + K], 306 (22) [M^+ + H_2O], 305 (100) [M^+−H+H_2O], 289 (54) [M^++H]. HRMS (ESI acetonitrile): calcd for $C_{19}H_{29}P$ [M + H]$^+$ 289.2085, found 289.2090.

Microwave-Assisted Synthesis of Di-*tert*-butyl-2-(1′-indenylethyl)phosphane (5). At 25 °C butyllithium (0.6 mmol, 0.4 mL, 1.6 M in hexane) was added dropwise to a solution of di-*tert*-butylphosphane (0.10 g, 0.7 mmol) in THF (4 mL). After stirring the deep yellow solution for 2 h at 25 °C [4,5]benzospiro[2.4]hepta-4,6-diene (**3**) (0.1 g, 0.7 mmol) was added. The solution was heated under microwave irradiation (200 W, 150 °C, ramp time = 3 min, hold time = 40 min). The color of the reaction mixture changed from deep yellow to red. After cooling to 25 °C and solvent removal the residue was washed with degassed pentane (3 × 5 mL). The reaction mixture was hydrolyzed with water (10 mL), and the product was extracted with pentane (3 × 10 mL). The combined organic layers were dried

(60) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923–2925.

over sodium carbonate and filtered. After solvent removal at reduced pressure 0.15 g (0.5 mmol, 91%) of **5** was isolated as a light yellow oil.

Di-*tert*-butyl-2-(1′-indenyl)ethylphosphanoxide (6). Crude **5** (5.67 g, 18.6 mmol) was dissolved in 30 mL of acetone and treated with aqueous hydrogen peroxide (5 mL, 30%). After stirring the reaction mixture for 30 min ferrous sulfate was added to decompose the excess of hydrogen peroxide. The solvent was removed, and water (50 mL) was added to the reaction mixture. The product was extracted with chloroform (2×30 mL). After solvent removal and recrystallization of the crude product from a mixture of methanol and hexane 3.1 g of phosphanoxide **6** (0.10 mol, 68%) was obtained as an off-white solid (mp 108 °C). IR (ATR): $\tilde{\nu}$ 2967 (w), 2926 (w), 2903 (w), 2868 (w), 1477 (w), 1388 (w), 1361 (w), 1304 (w), 1260 (m), 1099 (s), 1092 (w), 1014 (s), 946 (w), 815 (m), 797 (m), 761 (s), 727 (s), 720 (m), 650 (w), 620 (m) cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 1.31 (d, $^3J_{PH}$ = 13.1 Hz, 18H, CH_3), 2.07 (m, 2H, PCH_2CH_2), 2.93 (br, 2H, PCH_2), 3.34 (s, 2H, 3-H), 6.25 (d, $^3J_{HH}$ = 7.4 Hz, 1H, 2-H), 7.28−7.47 (m, 4H, H_{arom}) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz, BB): δ 24.8 (s, PCH_2CH_2), 27.2 (d, $^1J_{CP}$ = 70.9 Hz, PCH_2), 31.5 (d, $^2J_{CP}$ = 19.5 Hz, CH_3), 36.3 [d, $^1J_{CP}$ = 58.7 Hz, $C(CH_3)_3$], 37.8 (s, C-3), 119.2 (s, C-2), 124.0 (s, C-4), 124.9 (s, C-6), 126.3 (s, C-5), 127.9 (s, C-7), 144.7 (s, C-7a), 144.9 (s, C-3a), 145.2 (s, C-1) ppm. ^{31}P NMR ($CDCl_3$, 161 MHz): δ 60.2 (s) ppm. MS (ESI acetonitrile): *m*/*z* (%) 402 (16) [$M^+ + H_2O + K + CH_3CN$], 368 (15) [$M^+ + CH_3CN + Na$], 361 (58) [$M^+ + H_2O + K$], 321 (100) [$M^+ + OH$], 305 (55) [$M^+ + H$]. HRMS (ESI acetonitrile): calcd for $C_{19}H_{29}OP$ $[M + H]^+$ 305.2034, found 305.2028.

Di-*tert*-butyl-2-(1′-indenylethyl)phosphane Borane Adduct (7). At 0 °C butyllithium in hexane (1.88 mL, 3.1 mmol, 1.6 M) was added to di-*tert*-butylphosphane borane adduct (0.500 g, 3.1 mmol) in THF (10 mL). After stirring for 1 h at 20 °C the mixture was cooled to 0 °C, [4,5]benzospiro[2.4]hepta-4,6-diene (**3**, 0.440 g, 3.1 mmol) was added, and the mixture was heated at 65 °C for 24 h. After cooling to 25 °C 1 mL of water was added and the solvent was removed at reduced pressure. The residue was dissolved in dichloromethane (20 mL), and the organic layer was washed with water (10 mL) and with saturated aqueous NaCl solution (5 mL). After drying the organic layer over $MgSO_4$ the solvent was removed at reduced pressure, and the residue was purified by column chromatography (4×40 cm, PE/TBME, 70:1). **7** (0.550 g, 1.81 mmol, 59%) was obtained as a colorless solid (mp 99.3 °C). IR (ATR): $\tilde{\nu}$ 2960 (m), 2903 (s), 2870 (m), 2366 (m), 2343 (w), 2281 (m), 1462 (m), 1393 (m), 1368 (m), 1124 (w), 1061 (s), 1021 (w), 779 (s), 720 (m) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 1.23 (d, $^3J_{H,P}$ = 12.4 Hz, 18H, CH_3), 1.88 (m, 2H, PCH_2), 2.84 (m, 2H, PCH_2CH_2), 3.27 (d, $^3J_{H,H}$ = 1.5 Hz, 2H, 3-H), 6.19 (br. s, 1H, 2-H), 7.14 (t, $^3J_{H,H}$ = 7.3 Hz, 1H, 5-H), 7.24 (t, $^3J_{H,H}$ = 7.4 Hz, 1H, 4-H), 7.33 (d, $^3J_{H,H}$ = 7.5 Hz, 1H, 6-H), 7.39 (d, $^3J_{H,H}$ = 7.2 Hz, 1H, 7-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 17.2 (d, $^1J_{C,P}$ = 27.8 Hz, PCH_2), 23.7 (PCH_2CH_2), 28.0 (d, $^2J_{C,P}$ = 1.3 Hz, CH_3), 32.3 (d, $^1J_{C,P}$ = 27.0 Hz, $PCCH_3$), 37.8 (C-3), 119.1 (C-6), 124.0 (C-7), 124.9 (C-5), 126.3 (C-4), 128.0 (C-2), 144.6 (C-3a), 144.8 (C-7a), 144.9 (d, $^3J_{C,P}$ = 13.4 Hz, C-1) ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ 45.3 (q, $^1J_{B,P}$ = 50.0 Hz) ppm. HRMS (ESI) ($C_{19}H_{32}BP$ − H): calcd 301.2259, found 301.2256. Anal. Calcd for $C_{19}H_{32}BP$ (302.0): C 75.50 H 10.67. Found: C 75.11 H 10.27.

Di-*tert*-butyl-2-(1′-indenylethyl)phosphane (5) from 7. At 20 °C 1,4-diazabicyclo[2.2.2]octane (0.340 g, 3.0 mmol, 1.5 equiv) was added to di-*tert*-butyl-2-(1′-indenylethyl)phosphane borane adduct (**7**) (0.600 g, 2.0 mmol) in toluene (5 mL). After stirring for 12 h at 40 °C the mixture was cooled to 20 °C. After solvent removal at reduced pressure water (5 mL) was added. The residue was dissolved in diethyl ether (10 mL), and the organic layer was washed with water (10 mL) and with saturated aqueous NaCl solution (5 mL). After drying the organic layer over $MgSO_4$ the solvent was removed at reduced pressure, and the residue was purified by column chromatography (4 × 40 cm, PE/TBME, 100:1) to give **5** (0.570 g, 2.0 mmol, 100%).

[(Di-*tert*-butylphosphanylethyl)indenyl]chloronickel(II) (8). At 0 °C butyllithium (22.0 mmol, 15 mL, 1.6 M in hexane) was added dropwise to a solution of di-*tert*-butylphosphane (4.3 g, 30.0 mmol) in THF (400 mL). The solution was stirred for 2 h at 0 °C. After heating to 65 °C **3** (4.12 g, 30.0 mmol) was added, and the solution was heated at reflux for 120 h. The red solution was cooled to 25 °C, unconsumed di-*tert*-butylphosphane and solvent were removed at reduced pressure at 100 °C, and the residue was dissolved in THF (400 mL). After the addition of anhydrous $NiCl_2$ (12.9 g, 100.0 mmol) at 0 °C, the reaction mixture was stirred for 14 h at this temperature, the color of the solution changing to deep red. The reaction mixture was warmed slowly to 25 °C and was filtered through a 5 cm thick pad of Celite. After solvent removal at reduced pressure the residue was dissolved in diethyl ether (400 mL). The solution was again filtered through a 5 cm thick pad of Celite. The product was crystallized from diethyl ether at −20 °C to yield 7.1 g (18.0 mmol, 85%) of **8** as a deep purple-red solid (mp 91 °C, dec). IR (ATR): $\tilde{\nu}$ 2964 (w), 2903 (w), 2858 (w), 1459 (w), 1388 (w), 1259 (s), 1127 (s), 1016 (w), 796 (s), 749 (m), 684 (w) cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 1.31 (d, $^3J_{PH}$ = 13.6 Hz, 9H, 3 CH_3), 1.45 (d, $^3J_{PH}$ = 13.1 Hz, 9H, CH_3), 1.87−1.94 (m, 2H, PCH_2CH_2), 2.4−2.6 (m, 2H, PCH_2), 5.42 (dd, $^3J_{H,H}$ = 3.3, $J_{P,H}$ = 2.2 Hz, 1H, 3-H), 6.76 (d, $^3J_{HH}$ = 3.4 Hz, 1H, 2-H), 7.00 (dd, $^3J_{HH}$ = 7.5, 7.2, Hz, 1H, 5-H), 7.09 (d, $^3J_{HH}$ = 7.5 Hz, 1H, 4-H), 7.16−7.13 (m, 2H, 7.0 Hz, 6-H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz, BB): δ 25.8 (d, $^2J_{CP}$ = 5.5 Hz, C-8), 28.8 (d, $^2J_{CP}$ = 3.6 Hz, CH_3), 29.4 (d, $^2J_{CP}$ = 4.0 Hz, CH_3), 34.5 (d, $^1J_{CP}$ = 20.5 Hz, C-9), 34.7 [d, $^1J_{CP}$ = 13.3 Hz, $C(CH_3)_3$], 35.9 [d, $^1J_{CP}$ = 13.1 Hz, $C(CH_3)_3$], 81.2 (d, J_{CP} = 13.9 Hz, C-3), 89.8 (d, J_{CP} = 7.2 Hz, C-1), 105.7 (d, J_{CP} = 2.4 Hz, C-2), 117.3 (s, C-7), 119.3 (s, C-6), 124.5 (s, C-5), 127.3 (s, C-4), 129.3 (s, C-3a), 131.2 (d, J_{CP} = 2.8 Hz, C-7a) ppm. ^{31}P NMR ($CDCl_3$, 161 MHz): δ 84.2 (s) ppm. MS (70 eV): *m*/*z* (%) 380 (61) [M^+], 318 (20) [$M^+ - C_2H_3Cl$], 304 (23) [$M^+ - C_6H_4$], 288 (66) [M^+ − NiCl +1], 232 (59) [$M^+ - C_8H_{17}Cl$], 186 (23) [$M^+ - C_9H_{20}ClP$], 173 (26) [$M^+ - C_8H_{18}ClNi$], 162 (55) 141 (76). HRMS: calcd for $C_{19}H_{28}PClNi$ 380.0971; found 380.0971. Anal. Calcd for $C_{19}H_{28}ClNiP$ (380.1): C 59.81, H 7.40. Found: C 60.28, H 7.97.

(Azido)[1-(di-*tert*-butylphosphanylethyl)indenyl]nickel(II) (9). Sodium azide (100 mg, 1.0 mmol) was added to a solution of **8** (90 mg, 0.2 mmol) in THF (10 mL), and the solution was heated at reflux for 3 h. After solvent removal at reduced pressure the crude product was extracted with diethyl ether (30 mL) and concentrated. The residue was washed with hexane (10 mL) to yield 70 mg (0.2 mmol, 86%) of **9** as a deep purple-red solid (mp 154 °C, dec). IR (ATR): $\tilde{\nu}$ 2958 (m), 2865 (m), 2025 (s), 1469 (m), 1398 (w), 1368 (m), 1324 (w), 1282 (m), 1261 (m), 1172 (m), 1045 (w), 1015 (s), 935 (m), 863 (m), 812 (s), 756 (s), 736 (m), 685 (w) cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 1.21 (d, $^3J_{PH}$ = 13.7 Hz, 9H, CH_3), 1.38 (d, $^3J_{PH}$ = 13.2 Hz, 9H, CH_3), 1.85−1.96 (m, 2H, PCH_2CH_2), 2.42−2.54 (m, 2H, PCH_2), 5.50 (dd, $^3J_{HH}$ = 5.1, 3.3 Hz, 1H, 3-H), 6.66 (d, $^3J_{HH}$ = 3.3 Hz, 1H, 2-H), 6.99−7.02 (m, 1H, 5-H), 7.11−7.12 (m, 1H, 7-H), 7.17−7.24 (m, 2H, 4-H, 6-H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz, BB): δ 25.7 (d, $^2J_{CP}$ = 5.2 Hz, PCH_2CH_2), 28.8 (d, $^2J_{CP}$ = 3.8 Hz, CH_3), 29.4 (d, $^2J_{CP}$ = 4.2 Hz, CH_3), 34.5 [d, $^1J_{CP}$ = 21.1 Hz, PCH_2], 34.9 [d, $^1J_{CP}$ = 13.4 Hz, $C(CH_3)_3$], 35.6 [d, $^1J_{CP}$ = 13.3 Hz, $C(CH_3)_3$], 79.0 (d, J_{CP} = 13.0 Hz, C-3), 90.3 (d, $^3J_{CP}$ = 7.6 Hz, C-1), 106.0 (d, J_{CP} = 2.3 Hz, C-2), 117.5 (s, C-7), 118.0 (s, C-6), 124.9 (s, C-5), 127.6 (s, C-4), 128.2 (s, C-3a), 129.1 (d, J_{CP} = 2.5 Hz, C-7a). ^{31}P NMR ($CDCl_3$, 161 MHz): δ 86.0 (s) ppm. MS (70 eV): *m*/*vz* (%) 387 (69) [M^+], 345 (10) [$M^+ - N_3$], 288 (47) [$M^+ - N_3 - C_4H_9$], 246 (100) [$M^+ - N_3 - C_4H_9 - C_3H_6$], 232 (33), 186 (24) [$M^+ - C_9H_{20}N_3P$], 141 (59), 129 (22), 115 (55), 104 (30), 57 (60). HRMS: calcd for $C_{19}H_{28}N_3PNi$ 387.1374; found 387.1375. Anal. Calcd for $C_{19}H_{28}N_3NiP$ (387.1): C 58.80, H 7.27, N 10.83. Found: C 58.59, H 6.98, N 10.49.

[1-(Di-*tert*-butylphosphanylethyl)indenyl]cyanonickel(II) (10). Trimethylsilyl cyanide (90 mg, 0.9 mmol) was added to a solution of **8** (0.1 g, 0.3 mmol) in THF (10 mL), and the solution was stirred for 1 h. After solvent removal at reduced pressure the crude product was extracted with diethyl ether (30 mL) and concentrated. The residue was washed with hexane (10 mL) to yield 90 mg (0.2 mmol, 92%) of **10** as a yellow-orange solid (mp 169 °C, dec). IR (ATR): $\tilde{\nu}$ 2995 (m), 2949 (m), 2900 (m), 2867 (m), 2107 (s, CN), 1473 (m), 1391 (w), 1369 (m), 1221 (w), 1182 (m), 1155 (w), 1131 (m), 1017 (w), 936 (w), 924 (w), 830 (m), 812 (s), 802 (s), 747 (s) cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 1.15 (d, $^3J_{PH}$ = 13.9 Hz, 9H, CH_3), 1.38 (d, $^3J_{PH}$ = 13.6 Hz, 9H, CH_3), 2.22−2.53 (m, 2H, PCH_2CH_2), 2.68−2.76 (m, 2H, PCH_2), 5.70 (t, $^3J_{HH}$ = 3.6 Hz, 1H, 3-H), 6.28 (d, $^3J_{HH}$ = 3.1 Hz, 1H, 2-H), 7.07−7.09 (m, 1H, 5-H), 7.14−7.19 [m, 2H, 4-H, 6-H], 7.21−7.26 (m, 1H, 7-H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz, BB): δ 25.7 (d, $^2J_{CP}$ = 4.2 Hz, PCH_2CH_2), 29.1 (d, $^2J_{CP}$ = 3.5 Hz, CH_3), 29.6 (d, $^2J_{CP}$ = 3.6 Hz, CH_3), 35.4 [d, $^1J_{CP}$ = 15.3 Hz, $C(CH_3)_3$], 36.0 [d, $^1J_{CP}$ = 15.3 Hz, $C(CH_3)_3$], 38.0 [d, $^1J_{CP}$ = 19.9 Hz, PCH_2], 75.5 (d, J_{CP} = 10.4 Hz, C-3), 101.6 (d, $^3J_{CP}$ = 8.8 Hz, C-1), 104.2 (d, J_{CP} = 2.3 Hz, C-2), 117.8 (s, C-7), 120.2 (s, C-6), 123.3 (s, C-3a), 124.1 (d, J_{CP} = 1.5 Hz, C-7a), 124.2 (s, C-5), 127.1 (s, C-4), 132.9 (d, $^2J_{CP}$ = 18.4 Hz, Ni*C*N). ^{31}P NMR ($CDCl_3$, 161 MHz): δ 100.2 (s) ppm. MS (70 eV): *m*/*z* (%) 371 (72) [M^+], 315 (35) [$M^+ - C_4H_9$], 329 (71) [$M^+ - CN - C_4H_9$], 259 (18), 232 (33), 186 (70) [$M^+ - C_{10}H_{20}NP$], 128 (42), 115 (38), 106 (11), 85 (10). HRMS: calcd for $C_{20}H_{28}NPNi$ 371.1313; found 371.1314. Anal. Calcd for $C_{20}H_{28}NNiP$ (371.1): C 64.55, H 7.58, N 3.76. Found: C 64.19, H 7.71, N 3.53.

[1-(Di-*tert*-butylphosphanylethyl)indenyl]isothiocyanatonickel-(II) (11). Trimethylsilylisothiocyanate (130 mg, 1.0 mmol) was added to a solution of **8** (140 mg, 0.4 mmol) in THF (20 mL), and the solution was stirred for 3 h. After solvent removal at reduced pressure the crude product was extracted with diethyl ether (30 mL) and concentrated. The residue was chromatographed (10 × 1 cm, petroleum ether/ethyl acetate, 3:2) to yield 100 mg (0.3 mmol, 73%) of **11** as an orange solid (mp 193 °C, dec). IR (ATR): $\tilde{\nu}$ 3065 (w), 2963 (m), 2947 (m), 2900 (m), 2093 (s, SCN), 1711 (w), 1466 (m), 1392 (w), 1369 (m), 1325 (w), 1260 (m), 1075 (s), 1015 (s), 796 (s), 746 (m), 686 (w) cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 1.21 (d, $^3J_{PH}$ = 13.9 Hz, 9H, CH_3), 1.40 (d, $^3J_{PH}$ = 13.4 Hz, 9H, CH_3), 1.89−2.05 (m, 2H, PCH_2CH_2), 2.44−2.64 (m, 2H, PCH_2), 5.71 (dd, $^3J_{HH}$ = 5.1, 3.4 Hz, 1H, 3-H), 6.54 (d, $^3J_{HH}$ = 3.4 Hz, 1H, 2-H), 7.02−7.06 (m, 1H, 5-H), 7.09−7.13 (m, 2H, 4-H, 6-H), 7.17−7.21 (m, 1H, 7-H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz, BB): δ 25.9 (d, $^2J_{CP}$ = 4.2 Hz, PCH_2CH_2), 28.9 (d, $^2J_{CP}$ = 3.6 Hz, CH_3), 29.4 (d, $^2J_{CP}$ = 3.6 Hz, CH_3), 34.5 [d, $^1J_{CP}$ = 15.3 Hz, PCH_2], 35.1 [d, $^1J_{CP}$ = 14.0 Hz, $C(CH_3)_3$], 35.9 [d, $^1J_{CP}$ = 13.6 Hz, $C(CH_3)_3$], 80.4 (d, J_{CP} = 12.3 Hz, C-3), 91.4 (d, $^3J_{CP}$ = 8.1 Hz, C-1), 105.7 (d, J_{CP} = 2.5 Hz, C-2), 117.9 (s, C-7), 119.8 (s, C-6), 125.3 (s, C-5), 127.7 (s, C-3a), 127.9 (s, C-4), 129.2 (d, J_{CP} = 2.3 Hz, C-7a), 141.3 (s, N*C*S). ^{31}P NMR ($CDCl_3$, 161 MHz): δ 90.5 (s) ppm. MS (70 eV): *m*/*z* (%) 403 (20) [M^+], 371 (84) [$M^+ - S$], 288 (21) [$M^+ - NCS - C_4H_9$], 186 (18) [$M^+ - C_{10}H_{20}NSP$], 141 (42), 128 (30), 106 (32), 57 (100). HRMS: calcd for $C_{20}H_{28}NNiPS$ 403.1034; found 403.1036. Anal. Calcd for $C_{20}H_{28}NNiPS$ (403.1): C 59.43, H 6.98, N 3.47. Found: C 59.21, H 7.16, N 3.31.

{[1-(Di-*tert*-butylphosphanylethyl)indenyl](acetonitrile)}nickel(II) Tetraphenylborate (12). A solution of **8** (100 mg, 0.3 mmol) and sodium tetraphenylborate (0.20 g, 0.6 mmol) in acetonitrile (5 mL) was stirred for 2 h at 25 °C. After removal of the acetonitrile at reduced pressure, the residue was dissolved in dichloromethane (20 mL) and filtered through a 3 cm thick pad of Celite. The solvent was removed at reduced pressure, and residue was washed with diethyl ether (2×30 mL) to yield 0.18 g (0.28 mmol, 92%) of **12** as a light green solid (mp 151 °C). IR (ATR): $\tilde{\nu}$ 2963 (w), 2917 (w), 2361 (w), 2262 (w), 2183 (w), 2157 (w), 2039 (w), 2023 (w), 2010 (w), 1957 (w), 1259 (s), 1092 (s), 1013 (s), 862 (w), 794 (s), 743 (w), 731 (m), 704 (m) cm^{-1}. ^1H NMR (acetone-d_6, 200 MHz): δ 1.23 (d, $^3J_{PH}$ = 13.9 Hz, 9H, $PCCH_3$), 1.46 (d, $^3J_{PH}$ = 13.9 Hz, 9H, $PCCH_3$), 2.24 (s, 3H, $NiNCCH_3$), 2.79−2.95 (m, 2H, PCH_2CH_2), 3.35−3.45 (m, 2H, PCH_2), 5.85 (dd, $^3J_{HH}$ = 4.3, 3.7 Hz, 1H, 3-H), 6.75 (s, 1H, 2-H), 6.78−6.82 (m, 4H, *p*-CH), 6.89−6.97 (m, 9H, 5-H, *m*-CH), 7.21−7.34 (m, 2H, 6-H, 7-H), 7.35 (br, 8H, *o*-CH), 7.6 (d, $^3J_{HH}$ = 7.6 Hz, 1H, 4-H) ppm. ^{13}C NMR (acetone-d_6, 100 MHz, BB): δ 4.0 (s, $NiNCCH_3$), 26.9 (d, $^2J_{CP}$ = 3.6 Hz, PCH_2CH_2), 28.5 (d, $^2J_{CP}$ = 3.6 Hz, $PCCH_3$), 28.9 (d, $^2J_{CP}$ = 3.9 Hz, $PCCH_3$), 34.5 (d, $^1J_{CP}$ = 23.2 Hz, PCH_2), 36.5 [d, $^1J_{CP}$ = 15.4 Hz, $C(CH_3)_3$], 37.4 [d, $^1J_{CP}$ = 14.9 Hz, $C(CH_3)_3$], 83.2 (d, J_{CP} = 9.2 Hz, C-3), 108.5 (s, C-2), 120.9 (s, C-5), 121.3 (s, C-6), 122.9 (d, $^4J_{B-C}$ = 0.5 Hz, *p*-CH), 126.6 (d, $^3J_{B-C}$ = 2.7 Hz, *m*-CH), 126.7 (s, C-7), 127.9 (s, C-1), 128.4 (s, C-3a), 129.8 (s, C-4), 130.4 (s, C-7a), 130.9 (s, NiNC), 137.7(dd, $^2J_{B-C}$ = 1.5, 1.2 Hz, *o*-CH), 165.8 (q, $^1J_{B-C}$ = 49.1 Hz, BC) ppm. ^{31}P NMR (acetone-d_6, 161 MHz): δ 47.5 (s) ppm. MS (ESI acetonitrile): *m*/*z* (%) 716 (12) [M^+ + B], 435 (8) [$M^+ - C_{20}H_{19}B$], 386 (100) [$M^+ - C_{24}H_{20}B$], 372 (28) [$M^+ - C_{25}H_{22}B$], 305 (16) [$C_{19}H_{28}P + H_2O$], 289 (8) [$C_{19}H_{30}P$]. HRMS (ESI acetonitrile): calcd for $C_{21}H_{31}NNiP$ [M^+] 386.1548, found 386.1548; calcd for $C_{24}H_{20}B$ [M^-] 319.1658, found 319.1656.

[1-(Di-*tert*-butylphosphanylethyl)indenyl]methylnickel(II) (13). At 25 °C methyllithium (0.2 mL, 0.3 mmol, 1.6 M in diethyl ether) was added dropwise to a solution of **8** (0.12 g, 0.3 mmol) in diethyl ether (30 mL). The color of the reaction mixture changed from deep purple to dark brown. The solution was stirred for 1 h and filtered through a 5 cm thick pad of Celite. After solvent removal at reduced pressure, the product was recrystallized from hexane at −20 °C to yield 0.05 g (0.15 mmol, 50%) of **13** as a green crystalline solid (mp 268 °C). In solution gradual decomposition was observed, causing the NMR spectra to be less resolved. IR (ATR): $\tilde{\nu}$ 2948 (w), 2913 (w), 2858 (w), 1599 (w), 1548 (w), 1530 (w), 1513 (w), 1468 (w), 1451 (w), 1367 (w), 1261 (w), 1118 (w), 1017 (w), 816 (w), 734 (s), 630 (m) cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ −1.19 (d, J = 2.3 Hz, 3H, $NiCH_3$), 1.31 (d, $^3J_{PH}$ = 12.8 Hz, 9H, 3 CCH_3), 1.28 (d, $^3J_{PH}$ = 12.5 Hz, 9H, CCH_3), 2.09−2.44 (m, 2H, PCH_2CH_2), 2.46−2.59 (m, 2H, PCH_2), 4.99 (s, 1H, 3-H), 6.43 (s, 1H, 2-H), 6.89 (s, 1H, 5-H), 7.01−7.10 [m, 2H, 4(7)-H], 7.26 (s, 1H, 6-H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz, BB): δ −35.8 (d, $^2J_{CP}$ = 18.4 Hz, Ni*C*), 24.8 (d, $^2J_{CP}$ = 5.3 Hz, C-8), 29.6 (d, $^2J_{CP}$ = 3.9 Hz, CH_3), 29.9 (d, $^2J_{CP}$ = 4.4 Hz, CH_3), 35.4 [d, $^1J_{CP}$ = 8.3 Hz, $C(CH_3)_3$], 35.6 [d, $^1J_{CP}$ = 7.4 Hz, $C(CH_3)_3$], 41.0 (d, $^1J_{CP}$ = 17.7 Hz, C-9), 71.6 (s, C-3), 98.2 (d, $^3J_{CP}$ = 8.5 Hz, C-1), 103.2 (s, C-2), 116.5 (s, C-7), 117.1 (s, C-6), 120.6 (s, C-5), 122.8 (s, C-3a), 123.2 (s, C-7a), 123.4 (s, C-4) ppm. ^{31}P NMR ($CDCl_3$, 161 MHz): δ 85.1 (s) ppm. MS (70 eV): *m*/*z* (%) 360 (100) [M^+], 345 (31) [$M^+ - CH_3$], 318 (10) [$M^+ - C_3H_6$], 304 (40) [$M^+ - C_4H_8$], 289 (21) [$M^+ - NiCH_3 + 2$], 247 (39) [$M^+ - C_8H_{17}$], 233 (49) [$M^+ - C_9H_{19}$], 186 (51) [$M^+ - C_{10}H_{23}P$], 173 (10) [$M^+ - C_9H_{21}Ni$], 162 (35) 141 (62), 120 (47), 57 (64). HRMS: calcd for $C_{20}H_{31}NiP$ 360.1517; found 360.1514.

Crystal structure analysis:[52] Empirical formula $C_{20}H_{31}NiP$, molecular weight 361.13, crystal system orthorhombic, space group *Pcab*, a = 11.668(3) Å, b = 12.848(5) Å, c = 25.332(3) Å, α = 90°, β = 90°, γ = 90°, V = 3798(2) Å^3, Z = 8, d_{calc} = 1.263 Mg/m^3, $F(000)$ = 1552, μ = 1.102 mm^{-1}, crystal size 0.41 × 0.37 × 0.37 mm, Stoe IPDS area detector diffractometer, T = 300(2) K, Mo Kα = 0.71073 Å, θ_{min} = 2.26°, θ_{max} = 24.10°, $-13 \le h \le 13$, $-14 \le k \le 14$, $-29 \le l \le 29$, no absorption correction, no extinction correction, reflections collected 37 611, unique 3004 [R(int) = 0.0680], completeness to theta = 24.1, 99.9%, refinement method full-matrix least-squares on F^2, data 3004, restraints 0, parameters 199, goodness-of-fit on F^2 1.162, final R indices [$I > 2\sigma(I)$] R_1 = 0.0301, wR_2 = 0.0663, R indices (all data) R_1 = 0.0498, wR_2 = 0.0693, largest diff peak and hole 0.263 and −0.203 e A^{-3}.

{[1-(Di-*tert*-butylphosphanylethyl)indenyl](2-phenylethynyl)}-nickel(II) (16). Phenylethyne (0.10 g, 1.0 mmol) was added dropwise to a suspension of **8** (0.12 g, 0.3 mmol) and CuI (5 mg, 0.03 mmol) in freshly distilled triethylamine (5 mL).

The color of the reaction mixture became violet brown. After stirring the mixture for 14 h the solvent was removed at reduced pressure. The crude product was extracted with diethyl ether (3 × 25 mL) and was chromatographed (30 × 4 cm, petroleum ether/ethyl acetate, 10:1) to yield 0.09 g (0.2 mmol, 67%) of **16** as a deep brown solid (mp 109 °C, dec). IR (ATR): $\tilde{\nu}$ 3051 (w), 2958 (w), 2899 (w), 2869 (w), 2168 (w), 2085 (m, CC), 1471 (m), 1429 (m), 1259 (s), 1124 (s), 1079 (s), 1014 (s), 845 (w), 790 (s), 750 (m), 730 (s), 697 (s) cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 1.20 (d, $^3J_{PH}$ = 13.6 Hz, 9H, CH_3), 1.40 (d, $^3J_{PH}$ = 13.1 Hz, 9H, CH_3), 2.19−2.47 (m, 4H, PCH_2CH_2), 5.63 (dd, $^3J_{HH}$ = 3.1, 1.2 Hz, 1H, 3-H), 6.44 (d, $^3J_{HH}$ = 3.1 Hz, 1H, 2-H), 6.95−7.02 (m, 2H, 5-H, *p*-H), 7.06−7.12 (m, 3H, 4-H, *m*-H), 7.14−7.16 [m, 2H, 6-H, 7-H), 7.23 (d, $^3J_{HH}$ = 7.6 Hz, 2H, *o*-H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz, BB): δ 25.6 (d, $^2J_{CP}$ = 4.6 Hz, PCH_2CH_2), 29.2 (d, $^2J_{CP}$ = 3.4 Hz, CH_3), 29.7 (d, $^2J_{CP}$ = 3.6 Hz, CH_3), 35.4 [d, $^1J_{CP}$ = 14.4 Hz, $C(CH_3)_3$], 36.0 [d, $^1J_{CP}$ = 14.6 Hz, $C(CH_3)_3$], 38.9 (d, $^1J_{CP}$ = 18.1 Hz, PCH_2), 74.5 (d, J_{CP} = 12.2 Hz, C-3), 97.6 (d, $^2J_{CP}$ = 26.9 Hz, Ni*C*C), 98.7 (d, $^3J_{CP}$ = 7.2 Hz, C-1), 104.4 (d, J_{CP} = 2.2 Hz, C-2), 117.2 (s, C-7), 117.4 (s, NiC*C*), 119.4 (s, C-6), 123.2 (s, C-5), 124.4 (s, *p*-CH), 124.7 (s, C-3a), 125.8 (s, C-4), 125.9 (d, J_{CP} = 1.5 Hz, C-7a) 127.6 [s, ImI-CH], 128.8 (d, $^4J_{CP}$ = 1.0 Hz, 13a-C), 131.2 [d, $^5J_{CP}$ = 0.7 Hz, *o*-CH] ppm. ^{31}P NMR ($CDCl_3$, 161 MHz): δ 95.6 (s) ppm. MS (ESI acetonitrile): *m*/*z* (%) 716 (14) [$M^+ - C_4H_8 + C_{19}H_{28}P + K$], 460 (28) [$M^+ + H - C_2H_4 + CH_3CN$], 447 (13) [$M^+ + H$], 435 (4) [$M^+ - C_4H_4 + Na + H_2O$], 386 (100) [$M^+ - C_8H_5 + CH_3CN$], 372 (62) [$M^+ - C_8H_{17}$], 352 (12) [$M^+ - C_{12}H_{14} + CH_3CN + Na$], 336 (9) [$M^+ - C_{10}H_8 + H_2O$], 319 (6) [$M^+ - C_{14}H_{23} + CH_3CN + Na$], 303 (12) [$C_{19}H_{28}PO$]. HRMS (ESI acetonitrile): calcd for $C_{27}H_{33}NiP$ [$M^+ + H$] 447.1752; found 447.1751.

{[1-(Di-*tert*-butylphosphanylethyl)indenyl](2-trimethylsilylethynyl)}nickel(II) (17). Ethynyltrimethylsilane (180 mg, 1.8 mmol) was added dropwise to a suspension of **8** (380 mg, 1.0 mmol) and CuI (5 mg, 0.03 mmol) in freshly distilled triethylamine (5 mL). The color of the reaction mixture became brown. After stirring the mixture for 14 h the solvent was removed at reduced pressure. The crude product was extracted with diethyl ether (2 × 30 mL) and was chromatographed (20 × 3 cm, petroleum ether/diethyl ether, 9:1) to yield 270 mg (0.6 mmol, 60%) of **17** as a green solid (mp 141 °C, dec). IR (ATR): $\tilde{\nu}$ 2948 (w), 2897 (w), 2864 (w), 2022 (s, CC), 1737 (w), 1737 (w), 1474 (m), 1390 (m), 1367 (w), 1324 (w), 1237 (m), 1182 (m), 1128 (w), 1016 (m), 857 (s), 832 (s), 811 (s), 752 (s), 733 (m), 684 (s) cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ −0.05 [s, 9H, $Si(CH_3)_3$], 1.17 (d, $^3J_{PH}$ = 13.6 Hz, 9H, CCH_3), 1.37 (d, $^3J_{PH}$ = 13.4 Hz, 9H, CCH_3), 2.15−2.19 (m, 1H, PCH_2CH_2), 2.38−2.43 (m, 1H, PCH_2CH_2), 2.64−2.71 (m, 1H, PCH_2), 2.79−2.84 (m, 1H, PCH_2), 5.57 (d, $^3J_{HH}$ = 3.9 Hz, 1H, 3-H), 6.37 (d, $^3J_{HH}$ = 3.1 Hz, 1H, 2-H), 6.98 (t, $^3J_{HH}$ = 7.5 Hz, 1H, 5-H), 7.06−7.12 (m, 2H, 4-H, 7-H), 7.21 (d, $^3J_{HH}$ = 7.8 Hz, 1H, 6-H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz, BB): δ 1.31 [s, $Si(CH_3)_3$], 25.3 (d, $^2J_{CP}$ = 4.8 Hz, PCH_2CH_2), 29.1 (d, $^2J_{CP}$ = 3.4 Hz, CH_3), 29.6 (d, $^2J_{CP}$ = 3.6 Hz, CH_3), 35.2 [d, $^1J_{CP}$ = 14.6 Hz, $C(CH_3)_3$], 35.9 [d, $^1J_{CP}$ = 14.6 Hz, $C(CH_3)_3$], 38.8 (d, $^1J_{CP}$ = 18.2 Hz, PCH_2), 74.1 (d, J_{CP} v 12.1 Hz, C-3), 98.7 (d, $^3J_{CP}$ = 8.1 Hz, C-1), 104.4 (d, J_{CP} = 2.3 Hz, C-2), 117.0 (s, C-7), 119.4 (s, C-6), 122.2 (d, $^2J_{CP}$ = 25.3 Hz, Ni*C*C), 123.0 (s, C-5), 124.6 (s, NiC*C*), 125.4 (s, C-4), 125.6 (d, J_{CP} = 1.3 Hz, C-3a), 125.6 (d, J_{CP} = 1.5 Hz, C-7a). ^{31}P NMR ($CDCl_3$, 161 MHz): δ 94.8 (s) ppm. MS (70 eV): *m*/*z* (%) 442 (100) [M^+], 385 (19) [$M^+ - C_4H_9$], 329 (13) [$M^+ - 2\,C_4H_9$], 231 (15) [$M^+ - 2\,C_4H_9 - Si(CH_3)_3 - C_2$], 186 (24) [$M^+ - C_{14}H_{29}PSi$], 128 (24), 106 (14), 83 (10), 57 (60). HRMS: calcd for $C_{24}H_{37}NiPSi$ 442.1756; found 442.1753.

[1-(Di-*tert*-butylphosphanylethyl)indenyl](ethynyl)nickel(II) (18). Potassium carbonate (0.17 g, 1.2 mmol) was added to a solution of **17** (0.18 g, 0.4 mmol) in methanol (20 mL). After stirring the solution for 2 h the solvent was removed at reduced pressure. The crude product was chromatographed (10 × 1 cm, petroleum ether/diethyl ether, 3:1) to yield 0.12 g (0.3 mmol, 82%) of **18** as a red-brown solid (mp 122 °C, dec). IR (ATR): $\tilde{\nu}$ 3278 (w), 2943 (m), 2895 (w), 2861 (w), 1946 (s, CC), 1467 (m), 1389 (m), 1366 (w), 1321 (w), 1260 (w), 1183 (m), 1128 (w), 1110 (w), 1012 (m), 933 (w), 923 (w), 822 (m), 802 (s), 742 (s) cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 1.18 (d, $^3J_{PH}$ = 13.4 Hz, 9H, CH_3), 1.39 (d, $^3J_{PH}$ = 13.2 Hz, 9H, CH_3), 1.61 (d, J = 1.6 Hz, 1H, CC*H*), 2.15−2.50 (m, 2H, PCH_2CH_2), 2.64−2.88 (m, 2H, PCH_2), 5.58 (dd, $^3J_{HH}$ = 4.1, 3.3 Hz, 1H, 3-H), 6.39 (d, $^3J_{HH}$ = 3.0 Hz, 1H, 2-H), 6.98−7.00 (m, 1H, 5-H), 7.02−7.11 (m, 2H, 4-H, 7-H), 7.19−7.21 (m, 1H, 6-H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz, BB): δ 25.5 (d, $^2J_{CP}$ = 5.0 Hz, PCH_2CH_2), 29.2 (d, $^2J_{CP}$ = 3.5 Hz, CH_3), 29.7 (d, $^2J_{CP}$ = 3.6 Hz, CH_3), 35.4 [d, $^1J_{CP}$ = 14.6 Hz, $C(CH_3)_3$], 36.0 [d, $^1J_{CP}$ = 14.8 Hz, $C(CH_3)_3$], 38.8 (d, $^1J_{CP}$ = 18.6 Hz, PCH_2), 74.8 (d, J_{CP} = 11.9 Hz, C-3), 93.2 (d, $^2J_{CP}$ = 25.3 Hz, Ni*C*C), 98.7 (d, $^3J_{CP}$ = 8.1 Hz, C-1), 102.8 (d, J_{CP} = 1.3 Hz, NiC*C*), 104.2 (d, J_{CP} = 2.1 Hz, C-2), 117.3 (s, C-7), 119.3 (s, C-6), 123.3 (s, C-5), 124.4 (s, 3a), 125.5 (d, J_{CP} = 1.3 Hz, C-7a), 126.0 (s, C-4). ^{31}P NMR ($CDCl_3$, 161 MHz): δ 95.7 (s) ppm. MS (70 eV): *m*/*z* (%) 370 (57) [M^+], 313 (14) [$M^+ - C_4H_9$], 288 (22) [$M^+ - C_4H_9 - C_2H$], 257 (39) [$M^+ - C_4H_9 - C_4H_8$], 232 (14), 186 (43) [$M^+ - C_{11}H_{21}P$], 173 (22), 141 (47), 128 (34), 115 (40), 104 (10). HRMS: calcd for $C_{21}H_{29}NiP$ 370.1360; found 370.1360. Anal. Calcd for $C_{21}H_{29}NiP$ (370.1): 67.96, H 7.88. Found: C 68.18, H 7.88.

{[1-(Di-*tert*-butylphosphanylethyl)indenyl][2-(2-pyridyl)ethynyl)}nickel(II) (19). 2-Ethynylpyridine (0.25 g, 2.2 mmol) was added dropwise to a suspension of **8** (0.76 g, 2.0 mmol) and CuI (5 mg, 0.03 mmol) in freshly distilled triethylamine (25 mL). The color of the reaction mixture became brown. After stirring the mixture for 4 h the solvent was removed at reduced pressure. The crude product was extracted with diethyl ether (3 × 50 mL) and chromatographed (15×3 cm, petroleum ether/diethyl ether, 6:1) to yield 0.60 g (1.3 mmol, 67%) of **19** as an orange-brown solid (mp 148 °C, dec). IR (ATR): $\tilde{\nu}$ 3156 (w), 2945 (m), 2896 (w), 2860 (w), 2083 (s, CC), 1580 (s), 1551 (m), 1456 (s), 1419 (m), 1390 (m), 1367 (w), 1322 (w), 1236 (m), 1175 (m), 1147 (w), 1129 (w), 1015 (m), 933 (w), 923 (w), 823 (w), 811 (m), 776 (s), 737 (s), 675 (m) cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 1.18 (d, $^3J_{PH}$ = 13.7 Hz, 9H, CH_3), 1.41 (d, $^3J_{PH}$ = 13.1 Hz, 9H, CH_3), 2.15−2.24 (m, 1H, PCH_2CH_2), 2.36−2.52 (m, 1H, PCH_2CH_2), 2.66−2.74 (m, 1H, PCH_2), 2.80−2.91 (m, 1H, PCH_2), 5.65 (dd, $^3J_{HH}$ = 4.2, 3.3 Hz, 1H, 3-H), 6.40 (d, $^3J_{HH}$ = 3.1 Hz, 1H, 2-H), 6.84 (ddd, $^3J_{HH}$ = 7.4, 4.9, 1.2 Hz, 1H, NCCH), 6.97−7.01 (m, 2H, 5-H, NCCHC*H*), 7.08−7.11 (m, 2H, 4-H, 6-H), 7.24 (dd, $^3J_{H,H}$ = 7.9, 0.6 Hz, 1H, 7-H), 7.35 (dt, $^3J_{H,H}$ = 7.6, 1.9 Hz, 1H, NCHC*H*), 8.34 (ddd, $^3J_{H,H}$ = 4.9, 1.8, 0.8 Hz, 1H, NCH) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz, BB): δ 25.5 (d, $^2J_{CP}$ = 4.8 Hz, PCH_2CH_2), 29.2 (d, $^2J_{CP}$ = 3.4 Hz, CH_3), 29.7 (d, $^2J_{CP}$ = 3.7 Hz, CH_3), 35.4 [d, $^1J_{CP}$ = 14.8 Hz, $C(CH_3)_3$], 36.0 [d, $^1J_{CP}$ = 15.0 Hz, $C(CH_3)_3$], 38.8 (d, $^1J_{CP}$ = 18.6 Hz, PCH_2), 74.9 (d, J_{CP} = 11.9 Hz, C-3), 99.3 (d, $^3J_{CP}$ = 8.2 Hz, C-1), 104.4 (d, J_{CP} = 2.2 Hz, C-2), 105.0 (d, $^2J_{CP}$ = 26.2 Hz, Ni*C*C), 117.2 (s, C-6), 118.5 (d, $^3J_{CP}$ = 1.6 Hz, NiC*C*), 119.3 (s, NC*C*H), 119.7 (s, C-7), 123.4 (s, C-5), 124.3 (s, C-3a), 125.5 (d, J_{CP} = 1.6 Hz, C-7a), 125.9 (s, C-4), 126.1 (s, NCCH*C*H), 135.2 (s, NCH*C*H), 146.6 (d, J_{CP} = 1.0 Hz, NiCC*C*), 149.2 (s, NCH) ppm. ^{31}P NMR ($CDCl_3$, 161 MHz): δ 96.3 (s) ppm. MS (70 eV): *m*/*z* (%) 447 (66) [M^+], 391 (13) [$M^+ - C_4H_9$], 334 (82) [$M^+ - C_4H_9 - C_4H_8$], 288 (31) [$M^+ - C_4H_8 - C_4H_4N - C_2H$], 232 (12), 207 (16), 192 (30), 173 (20), 141 (36), 128 (25), 115 (27), 103 (51), 76 (25), 57 (100). HRMS: calcd for $C_{26}H_{32}NNiP$ 447.1626; found 447.1627. Anal. Calcd for $C_{26}H_{32}NNiP$ (447.2): C 69.67, H 7.20, N 3.13. Found: C 69.18, H 7.34, N 3.29.

{[1-(Di-*tert*-butylphosphanylethyl)indenyl][2-(2-methoxy-2-oxoethyl)pyridiniumethynyl]}nickel(II) Bromide (20). Methylbromoacetate (1 mL, 0.1 mmol) was added dropwise to a suspension of **19** (0.05 g, 0.1 mmol) in diethyl ether (25 mL). The color of the reaction mixture became red. After stirring the mixture for 12 h the solvent was removed at reduced pressure. The crude product was washed with hexane (5 × 25 mL) to yield

0.047 g (0.1 mmol, 78%) of **20** as a red solid (mp 195 °C, dec). IR (ATR): $\tilde{\nu}$ 2945 (m), 2921 (w), 2890 (w), 2059 (s, CC), 1751 (s), 1619 (m), 1552 (m), 1495 (m), 1473 (w), 1417 (m), 1366 (m), 1282 (w), 1260 (m), 1221 (m), 1182 (m), 1096 (w), 1048 (w), 1017 (w), 922 (w), 810 (m), 680 (w) cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 1.08 (d, $^3J_{PH}$ = 13.9 Hz, 9H, CH_3), 1.38 (d, $^3J_{PH}$ = 13.4 Hz, 9H, CH_3), 2.28−2.37 (m, 1H, PCH_2CH_2), 2.46−2.62 (m, 1H, PCH_2CH_2), 2.75−2.83 (m, 1H, PCH_2), 2.88−2.99 (m, 1H, PCH_2), 3.79 (s, 3H, $COCH_3$), 5.57 (t, $^3J_{HH}$ = 5.6 Hz, 1H, 3-H), 6.08 (dd, J_{HH} = 31.4, 16.9 Hz, 2H, NCH_2), 6.30 (d, $^3J_{HH}$ = 3.1 Hz, 1H, 2-H), 7.09−7.11 (m, 1H, NCCH), 7.13−7.24 (m, 3H, 4-H, 6-H), 7.31 (d, $^3J_{HH}$ = 7.4 Hz, 1H, NCCHC*H*), 7.48 (m, 1H, 5-H), 7.99 (t, $^3J_{H,H}$ = 7.8 Hz, 1H, NCHC*H*), 9.73 (d, $J_{H,H}$ = 6.0 Hz, 1H, NCH) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz, BB): δ 25.6 (d, $^2J_{CP}$ = 3.8 Hz, PCH_2CH_2), 29.0 (d, $^2J_{CP}$ = 3.2 Hz, CCH_3), 29.5 (d, $^2J_{CP}$ = 3.6 Hz, CCH_3), 35.7 [d, $^1J_{CP}$ = 15.4 Hz, $C(CH_3)_3$], 36.3 [d, $^1J_{CP}$ = 15.6 Hz, $C(CH_3)_3$], 38.8 (d, $^1J_{CP}$ = 19.8 Hz, PCH_2), 53.3 (s, $COCH_3$), 58.8 (s, NCH_2), 76.1 (d, J_{CP} = 10.4 Hz, C-3), 103.6 (d, $^3J_{CP}$ = 9.0 Hz, C-1), 104.1 (d, J_{CP} = 2.6 Hz, C-2), 111.1 (d, $^3J_{CP}$ = 1.0 Hz, NiC*C*), 118.2 (s, C-6), 119.6 (s, C-7), 121.4 (s, C-5), 123.1 (d, J_{CP} = 0.6 Hz, C-7a), 124.3 (d, J_{CP} = 1.2 Hz, C-3a), 124.7 (s, NC*C*H), 127.4 (s, C-4), 129.2 (s, NCCH*C*H), 138.5.1 (s, NC), 143.0 (s, NCH*C*H), 146.4 (s, NCH), 154.4 (d, $^2J_{CP}$ = 22.8 Hz, Ni*C*C) ppm. ^{31}P NMR ($CDCl_3$, 161 MHz): δ 101.3 (s) ppm. HRMS (ESI acetonitrile): calcd for $C_{29}H_{37}NNiO_2P$ [M^+] 520.1915; found 520.1912.

{[**1-(Di-*tert*-butylphosphanylethyl)indenyl**](**ferrocenylethynyl**)}**nickel(II)** (**23**). Ethynylferrocene (0.27 g, 1.3 mmol) was added to a suspension of **8** (0.38 g, 1.0 mmol) and CuI (5 mg, 0.03 mmol) in freshly distilled triethylamine (50 mL). The color of the reaction mixture became brown. After stirring the mixture for 20 h the solvent was removed at reduced pressure. The crude product was extracted with diethyl ether (3 × 50 mL) and chromatographed (15×1 cm, petroleum ether/diethyl ether, 4:1) to yield 0.49 g (0.9 mmol, 88%) of **23** as a red-brown solid (mp 158 °C, dec). IR: $\tilde{\nu}$ 3092 (w), 2941 (m), 2862 (m), 2084 (w, CC), 1472 (m), 1446 (m), 1390 (w), 1368 (w), 1323 (w), 1224 (w), 1175 (m), 1129 (w), 1105 (m), 1018 (m), 1001 (m), 922 (m), 812 (s), 747 (s), 682 (m) cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 1.27 (d, $^3J_{PH}$ = 13.6 Hz, 9H, CH_3), 1.42 (d, $^3J_{PH}$ = 13.1 Hz, 9H, CH_3), 2.15−2.21 (m, 1H, PCH_2CH_2), 2.23−2.41 (m, 1H, PCH_2CH_2), 2.46−2.73 (m, 1H, PCH_2), 2.81−2.92 (m, 1H, PCH_2), 3.92 (m, 2H, NiCCCCH), 4.03 (s, 5H, H_{Cp}), 4.09 (dd, $^3J_{H,H}$ = 2.8, 1.4 Hz, 1H, NiCCCCHC*H*), 4.12 (dd, $^3J_{H,H}$ = 2.8, 1.5 Hz, 1H, NiCCCCHC*H*), 5.60 (dd, $^3J_{HH}$ = 4.3, J = 3.2 Hz, 1H, 3-H), 6.42 (d, $^3J_{HH}$ = 3.0 Hz, 1H, 2-H), 6.97−7.00 (m, 1H, 5-H), 7.09−7.13 (m, 2H, 4-H, 7-H), 7.17−7.20 (m, 1H, 6-H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz, BB): δ 25.6 (d, $^2J_{CP}$ = 4.8 Hz, PCH_2CH_2), 29.3 (d, $^2J_{CP}$ = 3.5 Hz, CH_3), 29.8 (d, $^2J_{CP}$ = 3.8 Hz, CH_3), 35.3 [d, $^1J_{CP}$ = 14.8 Hz, $C(CH_3)_3$], 36.0 [d, $^1J_{CP}$ = 14.8 Hz, $C(CH_3)_3$], 38.9 (d, $^1J_{CP}$ = 18.4 Hz, PCH_2), 66.6 (s, 2C, NiCCC*C*H), 69.5 (s, CH_{Cp}), 70.2 (s, NiCC*C*), 70.4 (s, NiCCCCH*C*H), 70.7 (s, NiCCCCH*C*H), 74.4 (d, J_{CP} = 12.5 Hz, C-3), 90.4 (d, $^2J_{CP}$ = 28.6 Hz, Ni*C*C), 98.3 (d, $^3J_{CP}$ = 8.1 Hz, C −1), 104.3 (d, J_{CP} = 2.3 Hz, C-2), 113.0 (s, C-NiC*C*), 117.2 (s, C-7), 119.4 (s, C-6), 123.1 (s, C-5), 125.2 (s, C-3a), 125.6 (s, C-4), 126.3 (d, J_{CP} = 1.5 Hz, C-7a) ppm. ^{31}P NMR ($CDCl_3$, 161 MHz): δ 95.7 (s) ppm. MS (70 eV): m/z (%) 554 (100) [M^+], 472 (29), 355 (18) [$M^+ - C_{10}H_9Fe - CH_2$], 299 (37) [$M^+ - C_{10}H_9Fe - CH_2 - C_4H_8$], 288 (21), 268 (15), 233 (20), 210 (32), 186 (23) [$M^+ - C_{21}H_{29}FeP$], 173 (10), 141 (20), 115 (11), 57 (41). HRMS: calcd for $C_{31}H_{37}FeNiP$ 554.1336; found 554.1339. Anal. Calcd for $C_{31}H_{37}FeNiP$ (554.1): C 67.07, H 6.72. Found: C 67.19, H 6.65.

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