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The First Cyclopentadienylalkylphosphane Nickel Chelates: Synthesis, Structures, and Reactions

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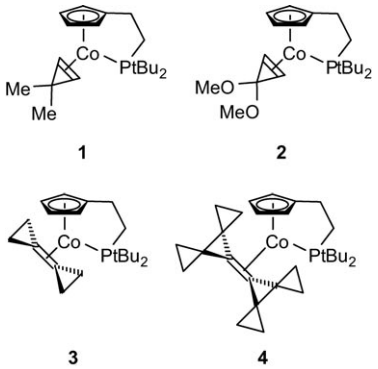
Dedicated to Professor Ekkehard Winterfeldt on the occasion of his 75th birthday

Abstract: The first cyclopentadienylalkylphosphane nickel chelate complexes are reported. The anionic ligand obtained by reaction of spiro[2.4]hepta-4,6-diene with lithium di-*tert*-butylphosphide was treated with $NiCl_2$ to yield [η^5:κ^1-(di-*tert*-butylphosphanylethyl)cyclopentadienyl]chloronickel(II). From this complex, some acetonitrile-stabilized cationic complexes were obtained by reaction with the respective silver salts in acetonitrile. Methyl- and alkynylnickel chelates were prepared by reaction of the chloronickel complex with methyllithium and by copper-mediated coupling with terminal alkynes, respectively. Some of the complexes prepared were investigated by X-ray crystallography or cyclic voltammetry. The alkynylnickel chelates undergo cycloaddition reactions with ethoxycarbonylisothiocyanate or tetracyanoethylene, and the cyclobutenes obtained undergo ring opening to the corresponding dienes. The study includes an NMR spectroscopic investigation of the two conformers of one of these dienes.

Keywords: chelates · cycloaddition · cyclopentadienyl ligands · nickel · phosphane ligands

Introduction

Cyclopentadienyl (Cp) and phosphane ligands are among the most-popular ligands in organometallic chemistry. These ligands are combined in cyclopentadienylalkylphosphane complexes, in which the cyclopentadienyl and phosphane ligands are separated by an alkyl chain; electronic interaction between them is thus unlikely.[1] As a consequence of chelate formation with tethers of appropriate length, the Cp ligand system loses its ability to rotate almost freely around the Cp–metal axis, which is usually a given in Cp complexes. Furthermore, such chelate complexes show enhanced stability relative to the corresponding unchelated analogues. This makes possible the formation of stable complexes with unusual ligands, such as cyclopropene and cyclopropenone acetal complexes **1** and **2**,[2,3] methylenecyclopropane and bi-



1 **2**

3 **4**

cyclopropylidene complexes **3**,[4,5] as well as spirocyclopropane derivatives such as **4**[5] with the cobalt chelate system, which has been investigated in our group for some time.

The importance of cyclopentadienylalkylphosphane chelate complexes is underlined by the fact that, after an initial period of reports describing their synthesis and structural

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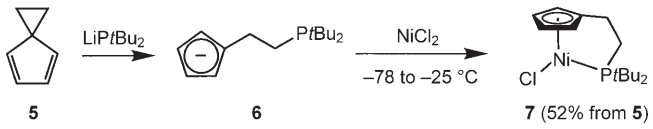
characterization,[1] an increasing number of reports about stoichiometric as well as catalytic reactions has appeared.[6–25]

Cyclopentadienylalkylphosphane chelate complexes of the vast majority of transition metals have been reported, and the field has been comprehensively reviewed in 2000.[1] However, until now no nickel complexes of this type have been published. Recently, Zargarian and co-workers reported some attempts in this direction with closely related indenyl ligands, which, however, remained unsuccessful.[26] Cyclopentadienylnickel and corresponding indenyl complexes deserve interest for their applications as catalysts in the polymerization of *para*-diethynylbenzene derivatives,[27,28] phenylethyne,[29,30] and styrene,[31] in the oligomerization of phenylsilane,[32] as hydrosilylation catalysts[33–35] because of their properties in nonlinear optics,[36,37] and as substrates in the synthesis of polymetallic complexes.[38] In catalytic reactions of cyclopentadienylphosphane nickel complexes, a vacant coordination site is usually generated by decomplexation of the electroneutral phosphane ligand. However, this also limits the stability of these complexes as, once the phosphane ligand is dissociated, the vacant coordination site has to be occupied to stabilize the complex. In this context, cyclopentadienylalkylphosphane chelates may be advantageous, because the phosphane after decomplexation retains the possibility of efficient recomplexation owing to the chelate nature of the complexes. Herein we report the synthesis, structures, and some reactions of the first cyclopentadienylalkylphosphane nickel chelate complexes.

Results and Discussion

Cyclopentadienylnickel (CpNi) complexes are usually prepared either by ligand exchange of nickelocene ([Cp_2Ni]) with complexes such as [$(Ph_3P)_2NiCl_2$] to afford two equivalents of [$CpNiCl(PPh_3)$][39] or by treatment of the cyclopentadienyl anion with nickel halides.[40] For the synthesis of cyclopentadienylalkylphosphane nickel chelates, we decided to use the second procedure, because the (di-*tert*-butylphosphanyl)ethylcyclopentadienyl anion (**6**) is readily accessible from spiro[2.4]hepta-4,6-diene (**5**)[41] by nucleophilic ring opening[42] upon treatment with lithium di-*tert*-butylphosphide. We prefer the di-*tert*-butylphosphanyl derivative because earlier work with related cobalt complexes showed that this substitution pattern leads to high yields and good crystallization properties of the chelate complexes.[43–45]



5 **6** **7** (52% from **5**)

Treatment of **6** with an excess of anhydrous nickel(II) chloride afforded the chloronickel chelate **7** as a deep-red solid in 52% yield (from **5**). Complex **7** is the first representative of the cyclopentadienylalkylphosphane nickel chelate complexes.

Complex **7** was characterized spectroscopically. The molecular-ion peak at $m/z = 330$ (76%) in the mass spectrum confirms the monomeric nature of **7** and indicates that indeed one ligand molecule is coordinated, thus excluding the possibility of the formation of a nickelocene derivative. The base peak at $m/z = 182$ corresponds to the cyclopentadienylethylphosphane nickel cation formed by dissociation of the chloro ligand and two isobutene fragments from the *tert*-butyl substituents. The ^{31}P NMR signal at 92.9 ppm indicates chelate formation by complexation of the phosphane tether.[1] The symmetry of the molecule is reflected in the ^1H NMR spectrum by one signal for both *tert*-butyl substituents and by the AA′BB′ splitting pattern for the cyclopentadienyl protons. All other analytical data including elemental analysis are in full accord with the assigned structure. Unfortunately, attempts to obtain crystals suitable for crystal-structure analysis failed.

Complexes with weakly nucleophilic ligands such as triflate may give access to the respective cationic complexes. In some triflate complexes, the triflate ion is the uncomplexed counterion of the complex cation; however, there is a very limited number of CpNi complexes in which the triflate ion is bound to the nickel atom by one of its oxygen atoms. These few examples include some related indenyl complexes reported by Zargarian and co-workers, two of which were structurally characterized,[46] and (pentamethylcyclopentadienyl)(triphenylphosphanyl)nickel triflate reported by Andersen, Bergman, and co-workers, which has not been structurally characterized.[47,48] The possibility of facile displacement of the triflate ligand led us to treat chloro complex **7** with 1.5 equivalents of silver triflate in dichloromethane. After 3 h at 25 °C, triflate complex **8** was obtained as a reddish-brown solid in 56% yield. This compound was much less stable in solution than **7**, thus disallowing the acquisition of NMR spectra. The IR data obtained were not very diagnostic; however, the mass spectrum showed the molecular-ion peak at $m/z = 444$ (20%). Fragmentation of the triflate ligand gave a peak at $m/z = 295$

Abstract in Urdu:

(سائیکلوپینٹا ڈائینائل الکائیل فاسفین) نکل کیلیٹ کمپلیکسز چھاپے جانے والے اپنی نوعیت کے پہلے کمپلیکسز ہیں۔ منفی چارج رکھنے والا لیگینڈ جو سپائرو[4.2]ہیپٹا-6,4-ڈائین اور لیتھیم ڈائی-ٹرٹری-بیوٹائیلفاسفائیڈ کا حاصل ہے۔ کونکل کلورائیڈ سے ملا کر کلورو کمپلیکس **7** بنایا گیا۔ **7** کو مختلف آسیٹونائٹرائل میں مختلف چاندی کے نمکیات سے ملا کر مثبت چارج والے کمپلیکسز بنائے گئے۔ میتھائل اور الکائینائیل کے پیچیدہ مالیکیولز کو حاصل کرنے کے لیے کاپر ٹیل انگیز کی موجودگی میں سرے والی الکائینز سے عمل کرایا گیا۔ کچھ پیچیدہ مالیکیولز کی ایکسرے تصاویر حاصل کی گئیں۔ الکائینائیل نکل کمپلیکسز کا استھا کسی کاربونائیل آئیسوتھائیوسائنیٹ یا ٹیرٹ ائسائینو استھائلین سے عمل کرایا گیا حاصل ہونے والی سائیکلو بیوٹینز کے رنگ ٹوٹ کر ڈائینز حاصل ہوئیں۔ اس تحقیق میں ڈائینز **24** کے دو کنفرمر کا این ایم آر تجزیہ (رپورٹ) بھی شامل ہے۔

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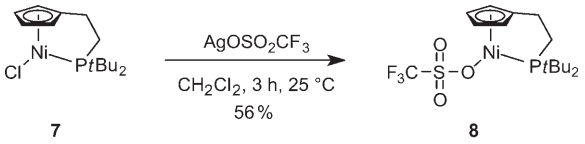


(9 %). As for **7**, the base peak was observed at $m/z = 182$ for the core unit of the chelate system. Crystallization of **8** was effected at −20 °C by dissolving the compound in a small amount of dichloromethane layered with hexane. Despite the poor quality of the single-crystal X-ray analysis, it is presented here (Figure 1) because, with the differences between

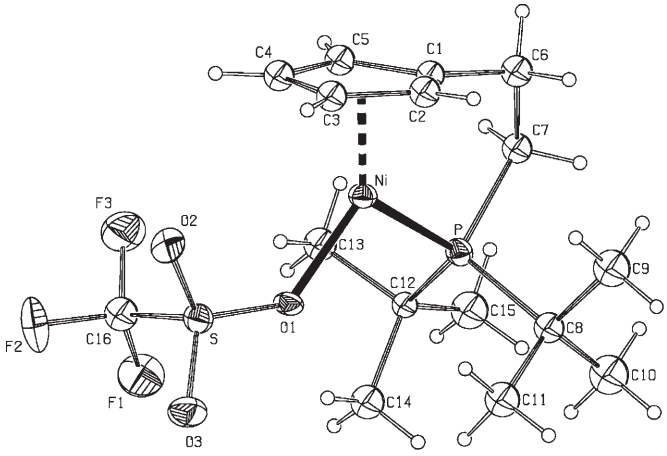
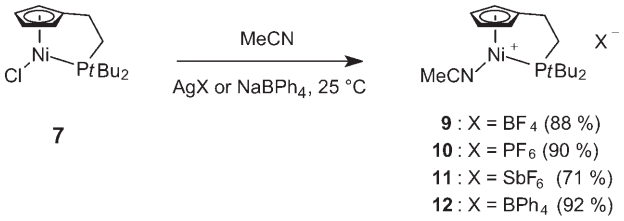


Figure 1. Structure of **8** in the crystal. Selected bond lengths (pm) and angles (°): Ni–O1 195.1(9), Ni–C1 202.8(13), Ni–C2 212.5(15), Ni–C3 213.0(15), Ni–C4 215.8(14), Ni–C5 211.7(14), Ni–P 218.1(5), C1–C2 142(2), C2–C3 139(2), C3–C4 142(2), C4–C5 136(2), C1–C5 142(2); O1–Ni–P 101.3(3), O1 < C− > S–C16 102.4(8), C1–C6–C7 110.7(12), C6–C7–P 109.1(10), C7–P–Ni 102.9(5).

the Cp and indenyl complexes taken into account, it is the first structural analysis of a CpNi complex with a coordinated triflate ligand.

The X-ray analysis confirms the assigned structure. The conformation shown is asymmetric. The analysis suffers from a dynamic or static disorder of the (di-*tert*-butylphosphanyl)ethylene moiety at the Cp ring. Such disorder is frequently observed in structures of cyclopentadienylalkylphosphane complexes.[1] Furthermore, the triflate ligand adopts a quasi-gauche conformation with respect to the S–O1 bond, with a dihedral angle C16–S–O1–Ni of 90.1°. As no NMR data could be obtained, it remains unclear if this asymmetry exists only in the solid state or also in solution. The Ni–O1 distance corresponds to that observed in other nickel–triflate complexes.[46] As in many cyclopentadienylalkylphosphane chelate complexes,[1] C1 is located closer to the metal atom than the other Cp carbon atoms.

Another ligand that dissociates particularly easily is acetonitrile. To gain access to cationic, possibly catalytically active nickel chelates, we became interested in a replacement of the chloro ligand in **7** by acetonitrile. Acetonitrile complexes **9**–**12** were easily obtained as green solids in high yields by treatment of **7** with an excess of the respective

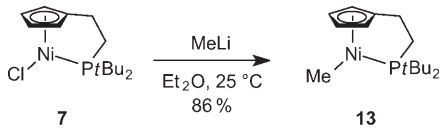


silver salts or sodium tetraphenylborate. The acetonitrile complexes are more air-stable than chloro complex **7**: they could be handled in air for 2–3 h. In solution, however, decomposition started after 30 min. We attribute the stability of the complexes to the presence of the phosphane tether. A similar nonchelate indenyl complex was described as relatively unstable.[49]

Complexes **9**–**12** were characterized spectroscopically. Besides the ^{1}H NMR signals of the (di-*tert*-butylphosphanyl)-ethylcyclopentadienylnickel fragment, the signals of the acetonitrile methyl protons were observed as singlets at around 2.50 ppm for **9**–**11** and at 2.22 ppm for **12**; the corresponding ^{13}C NMR signals for the acetonitrile methyl groups appeared in the range 3.3–3.7 ppm. The ^{31}P NMR signals of **9**–**12** were recorded at around 106 ppm, which is in accord with a coordinated di-*tert*-butylphosphanyl ligand.[1] The positive-ion ESI mass spectra of all four complexes show the base peak at $m/z = 336$, which corresponds to the $[(CpCH_2CH_2PtBu_2)Ni(MeCN)]^+$ cation.

Having prepared some cyclopentadienylalkylphosphane nickel chelates with heteroatomic or acetonitrile ligands, we became interested in the preparation of representatives with nickel–carbon bonds. We considered this challenging because we did not succeed in the preparation of related cobalt complexes previously.

When nickel chelate **7** was treated with methyllithium in diethyl ether at 25 °C, a color change from dark purple to dark brown was observed. Celite filtration and subsequent crystallization from hexane at −20 °C afforded methylnickel chelate **13** as a green solid in 86 % yield. Complex **13** is



rather stable and can be handled as a solid in air for some time. This complex was fully characterized; the significant features are the ^{1}H and ^{13}C NMR signals for the methyl group bound to nickel, which appear at −1.07 and −43.5 ppm, respectively. Coordination of the di-*tert*-butylphosphanylethyl tether was confirmed by the ^{31}P NMR signal at 90.0 ppm. The low-resolution mass spectrum clearly shows the molecular-ion peak at $m/z = 310$ (40 %). The crys-

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tals of **13** obtained were suitable for X-ray crystal-structure analysis (Figure 2).

As in similar cobalt complexes,[2–4,10,11,23,44,45,50] the ethylene bridge C6–C7 adopts a staggered conformation. The

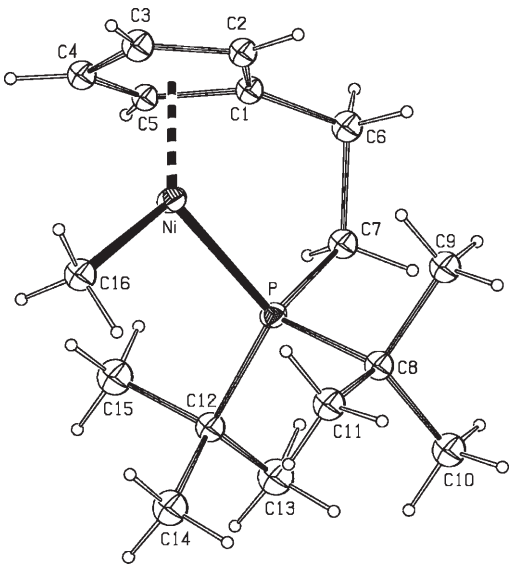


Figure 2. Structure of **13** in the crystal. Selected bond lengths (pm), bond angles (°), and torsion angles (°): Ni–C1 209.9(11), Ni–C2 213.2(10), Ni–C3 211.0(11), Ni–C4 210.4(10), Ni–C5 215.2(10), Ni–C16 197.2(11), Ni–P 214.5(4), C1–C2 137.7(13), C1–C5 144.9(12), C2–C3 141.4(13), C3–C4 140.9(13), C4–C5 132.7(14); C1–Ni–C16 166.6(5), C1–C6–C7 111.4(9), C16–Ni–P 104.6(4), C7–P–Ni 102.6(3); C1–C6–C7–P –35(1), C7–P–Ni–C16 170.3(5).

bond between the nickel atom and the methyl group (Ni–C16) is in the range of other cyclopentadienylmethylnickel complexes.[51]

To introduce more highly functionalized substituents, the synthesis of alkynylnickel chelates was envisaged. According to the method of Sonogashira, Hagihara, and co-workers,[52] chloride **7** was treated with phenylethyne or 4-methylphenylethyne. After stirring at 25 °C for 14 h and purification of the product by column chromatography, alkynyl chelates **14** and **15** were obtained as deep-brown solids in 58 and 91 % yield, respectively. Compared to the 72 % obtained by Bruce et al. in their synthesis of (cyclopentadienyl)(phenylethynyl)(triphenylphosphanyl)nickel(II),[53] the yield for **15** is excellent.

Alkynyl chelates **14** and **15** were characterized spectroscopically. In their IR spectra, the alkynyl vibration bands were observed at 2090 and 2086 cm^{-1}, respectively. The alkynyl carbon atoms bound to nickel showed ^{13}C NMR signals at 90.3 (**14**) and 88.0 ppm (**15**) with $^{2}J_{C,P}$ coupling constants of 33.9 and 34.0 Hz, respectively, indicating coordination of the phosphane tether. ^{13}C NMR signals of the alkynyl carbon atoms not bound to nickel were observed at 117.1 (**14**) and 117.0 ppm (**15**) with a small $^{3}J_{C,P}$ coupling of 1.7 Hz for **14**. The ^{31}P NMR signals at 104.8 (**14**) and 104.5 ppm (**15**) are also in full accord with phosphane-side-arm coordination. The mass spectra of both compounds clearly show the respective molecular-ion peaks. Recrystallization of **15** from hexane at −20 °C gave deep-brown crystals suitable for X-ray structure analysis (Figure 3).

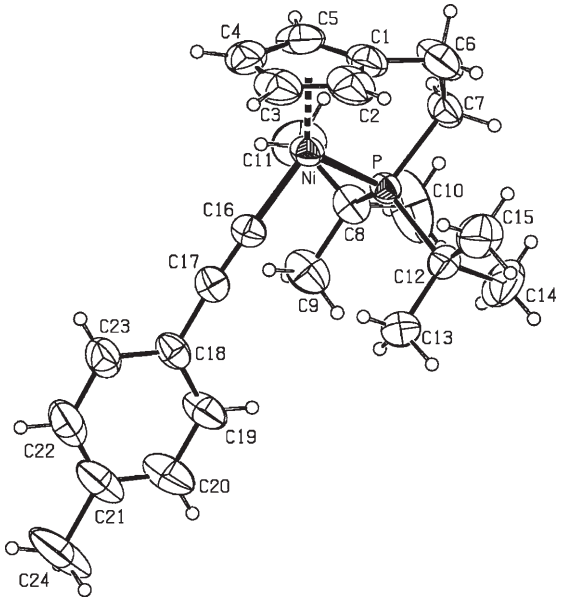
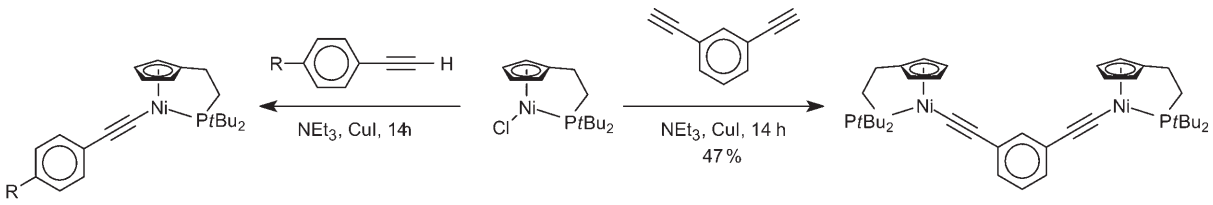


Figure 3. Structure of **15** in the crystal. Selected bond lengths (pm), bond angles (°), and torsion angles (°): C1–C2 140.7(7), C1–C5 143.7(7), C2–C3 136.0(7), C3–C4 139.9(7), C4–C5 139.2(6), C16–C17 120.7(5), Ni–C1 203.4(4), Ni–C2 212.3(5), Ni–C3 211.5(4), Ni–C4 214.3(4), Ni–C16 184.1(4), Ni–P 214.4(1); Ni–C16–C17 176.8(3), C16–C17–C18 174.3(4), C16–Ni–P 99.43(11), C1–C6–C7 113.0(4); C1–C6–C7–P –30(1), C7–P–Ni–C16 177.7(2).

The structure of **15** resembles very much that of **13**. Significant differences were found for the Ni–C16 bond length (197.2(11) pm in **13**, 184.1(4) pm in **15**), thus reflecting the differences in hybridization at C16. Unlike in **13**, the bond lengths in the Cp ring of **15** do not differ significantly; however, most of them are longer than the corresponding ones



14 : R = H (58 %)
15 : R = Me (91 %)

7

16

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in **13**. The acetylide ligand shows slight nonlinearity, which is possibly due to the steric bulk of the di-*tert*-butylphosphanyl ligand.

Next, two equivalents of chloro chelate **7** was treated with 1,3-diethynylbenzene under the same reaction conditions used in the synthesis of **14** and **15**. After the usual workup, dichelate **16** was obtained in 47% yield, corresponding to an average yield per step of 68%. The spectroscopic data of **16** resemble those of **14** and **15**, and the molecular-ion peak was observed in the ESI mass spectrum at $m/z = 715$ (19%). Phosphane-tether coordination was confirmed by a ^{31}P NMR signal at 105.2 ppm and by observation of a $^{2}J_{P,C}$ coupling constant of 33.8 Hz for the alkynyl carbon atoms bound to nickel.

Besides the spectroscopic characterization of chloride **7**, methyl complex **13**, and alkynyl chelates **15** and **16**, these complexes were also investigated by cyclic voltammetry (CV). Representative cyclic voltammograms are shown in Figures 4–7, and the data are given in Table 1.

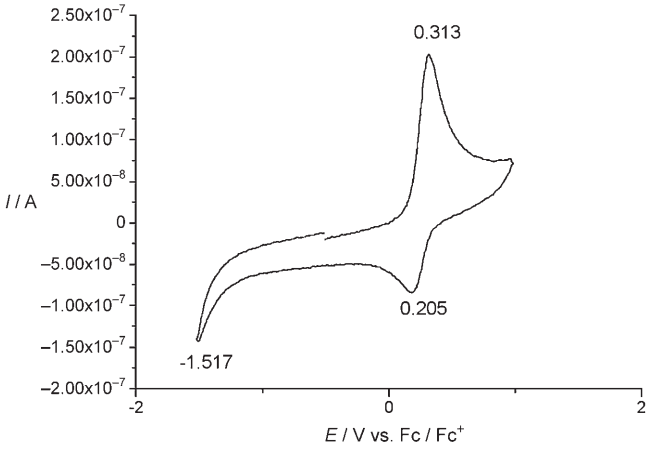


Figure 4. Cyclic voltammogram of chloro chelate **7** (0.1 $V s^{-1}$, $T = 20$ °C, $c = 1.0$ mmol L^{-1}, $c_{TBAHFP} = 0.2$ mol L^{-1}, one scan, dichloromethane). TBAHFP = $Bu_4N^+PF_6^-$.

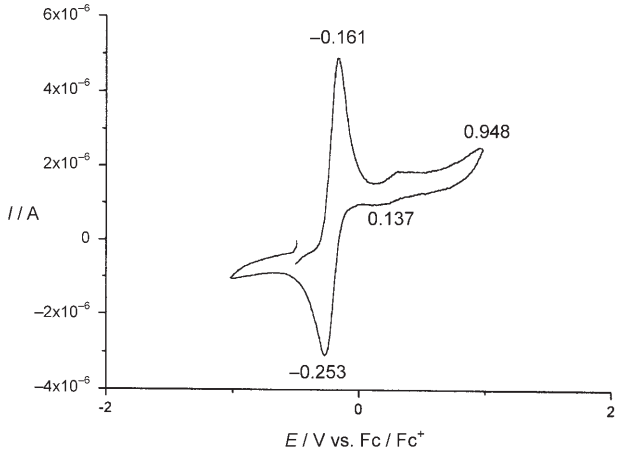


Figure 5. Cyclic voltammogram of methyl complex **13** (0.1 $V s^{-1}$, $T = 20$ °C, $c = 1.0$ mmol L^{-1}, $c_{TBAHFP} = 0.2$ mol L^{-1}, one scan, dichloromethane).

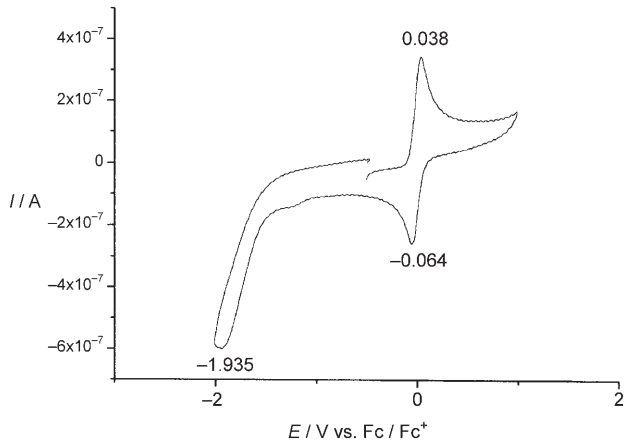


Figure 6. Cyclic voltammogram of alkynyl chelate **15** (0.1 $V s^{-1}$, $T = 20$ °C, $c = 1.0$ mmol L^{-1}, $c_{TBAHFP} = 0.2$ mol L^{-1}, one scan, dichloromethane).

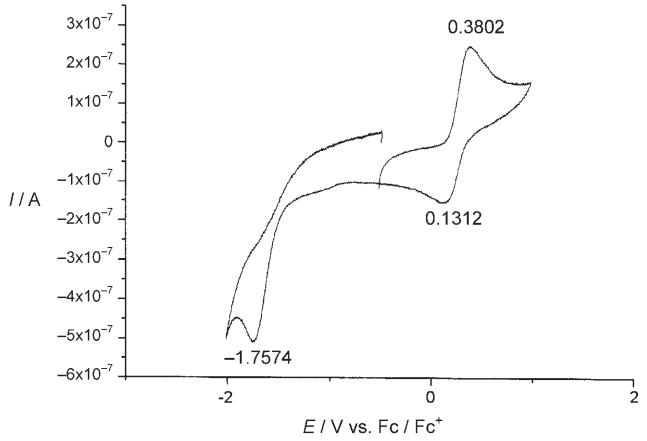


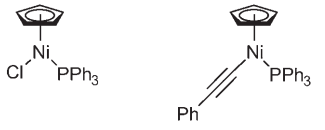
Figure 7. Cyclic voltammogram of alkynyl chelate **16** (0.1 $V s^{-1}$, $T = 20$ °C, $c = 1.0$ mmol L^{-1}, $c_{TBAHFP} = 0.2$ mol L^{-1}, one scan, dichloromethane).

Table 1. Cyclic voltammetry of nickel chelates **7**, **13**, **15**, and **16**.[a]

Complex	E_A [V]	E_C [V]	i_C/i_A
7	0.313	0.205	0.35
13	−0.161	−0.253	0.69
15	0.038	−0.064, −1.935	0.41
16	0.3802	0.1312, −1.7574	0.54

[a] 0.1 $V s^{-1}$, $T = 20$ °C, $c = 1.0$ mmol L^{-1}, $c_{TBAHFP} = 0.2$ mol L^{-1}, one scan, dichloromethane. Potentials are versus Fc/Fc^+. A = anode, C = cathode.

The cyclic voltammogram of chloro complex **7** shows an oxidation at 0.313 V, presumably for the Ni^{II}/Ni^{III} couple. This value differs from that observed by Humphrey and coworkers,[54] who investigated chloronickel(II) complex **17** (0.86 V vs. Ag/AgCl at −50 °C, which corresponds to



17 **18**

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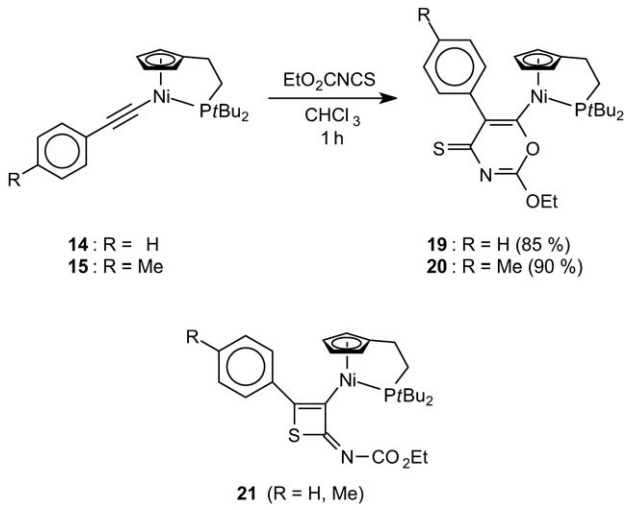
0.435 V vs. Fc/Fc^+), by −0.122 V. The difference presumably reflects the weak π-acceptor behavior of the di-*tert*-butylethyl ligand relative to triphenylphosphane. Manning and co-workers recently observed that a less-electron-rich complex gives a higher oxidation potential.[55] The blocked cyclopentadienyl rotation in **7** relative to **17** may also have some effect. Interestingly, the value for the phenylethynyl complex **18** (0.86 V vs. Ag/AgCl,[54] which corresponds to 0.385 V vs. Fc/Fc^+) differs only slightly from that of **17**, whereas the CV plot of tolylethynyl chelate **15** shows a value much smaller than that of **7** (0.038 vs. 0.313 V). The results of Humphrey and co-workers show a clear correlation between electron withdrawal by the ligand attached to the $CpNi(PPh_3)$ system and the oxidation potentials of the complexes. The relatively large difference in oxidation potential between **7** and **15** begs the question as to why this difference arises. Although the electron-donating methyl group of the tolylethynyl ligand in **15** should cause some decrease in oxidation potential, we feel that this cannot account for the difference of 0.275 V between **7** and **15** as compared to a difference of 0.05 V between **17** and **18**. As the principal difference between **7** and **15** on the one hand and **17** and **18** on the other is the chelate nature of **7** and **15**, a possible answer may be found in the rigidity of complexes **7** and **15** as opposed to **17** and **18**. Furthermore, as evident from the crystal-structure analysis, the cyclopentadienyl ligand in **7** and **15** is bound to the metal in a much less symmetric manner than the unsubstituted Cp ligand in **17** and **18**. These features may cause a change in the HOMO energies, thus affecting the oxidation processes observed by CV.

With respect to the dinuclear chelate complex **16**, it is remarkable that only one oxidation wave was observed. This indicates a HOMO that electronically connects both nickel atoms in spite of the *meta* disubstitution of the benzene ring. If the two nickel atoms were electronically separated, an oxidation wave for each of the $Ni^{II,II} \rightarrow Ni^{II,III}$ and the $Ni^{II,III} \rightarrow Ni^{III,III}$ oxidations should appear.

Metal acetylides are prone to cycloaddition reactions with a variety of unsaturated substrates.[56] Remarkably, there are relatively few reports of nickel acetylides undergoing such reactions; the one by Hong et al.[57] about cycloadditon with ketenes or isocyanates is an example. To check if the cyclopentadienylalkylphosphane chelate complexes prepared are feasible for this reaction, we undertook a brief study of their cycloaddition chemistry.

According to related reactions of ruthenium acetylides,[58] nickel chelates **14** and **15** were treated with 1.2 equivalents of ethoxycarbonylisothiocyanate to give complexes **19** and **20** with a 2-imino-1,3-thiazine-4-thione ligand as orange, moderately air-stable solids in 85 and 90% yield, respectively. Remarkably, the reactions were completed in 1 h, whereas ruthenium acetylides react with formation of an intermediate [2+2] cycloadduct within 1 h, which then undergoes ring expansion to the 2-imino-1,3-thiazine-4-thione system in chloroform a day later. With respect to the corresponding reactions of ruthenium acetylides, 2-iminothietes **21**, which are [2+2] cycloadducts of the acetylides and



ethoxycarbonylisothiocyanate, have to be considered as intermediates in the formation of **19** and **20**. Complex **21** presumably underwent rapid ring opening to a dipolar intermediate, which after electronic reorganization led to **19** and **20** by a subsequent ring-closing reaction. In contrast to the reaction of ruthenium acetylides, intemediates **21** were not observed here.[58]

Complexes **19** and **20** were characterized spectroscopically. The C=S IR absorptions at 1259 cm^{-1} exclude the possibilty of an iminothiete **21**; the C=N absorptions were observed at 1670 and 1669 cm^{-1}, respectively. Unlike the ^1H NMR spectra, which were less diagnostic, the ^{13}C NMR spectra clearly show the C=S signals at 211.7 and 209.1 ppm, respectively. For both compounds, the C=N ^{13}C NMR signal was observed at 160.6 ppm. ^{31}P NMR signals at 101.2 and 101.0 ppm, respectively, confirm the coordination of the phosphane tether to the nickel atom. In the mass spectra, the molecular-ion peaks were observed as the base peaks at $m/z = 528$ and 542, respectively.

[2+2] Cycloadditon reactions of metal acetylides with tetracyanoethene (TCNE) have been carried out for a number of transition metals, including nickel.[59,60] In most cases, the cyclobutenylmetal complexes obtained by [2+2] cycloaddition rapidly undergo electrocyclic ring opening.[61] Only in a limited number of cases (not including nickel complexes) were the cyclobutenylmetal intermediates isolated.[59–67]

Nickel acetylide chelates **14** and **15** were treated with an excess of TCNE over 14 h to afford cross-conjugated dienylnickel chelates **23** and **24** as dark-brown solids in 80 and 79% yield, respectively. Both products are soluble in all common organic solvents and can be handled in air for a limited period of time; after about 2 h some decomposition was observed.

Accordingly, bisacetylide **16** was subjected to the same reaction conditions to give the highly unsaturated cross-conjugated dinuclear complex **25** in 62% yield, which corresponds to the yields for **23** and **24** for the single-step reaction.

Complexes **23**, **24**, and **25** were fully characterized spectroscopically. The nitrile and C=C IR absorptions were ob-

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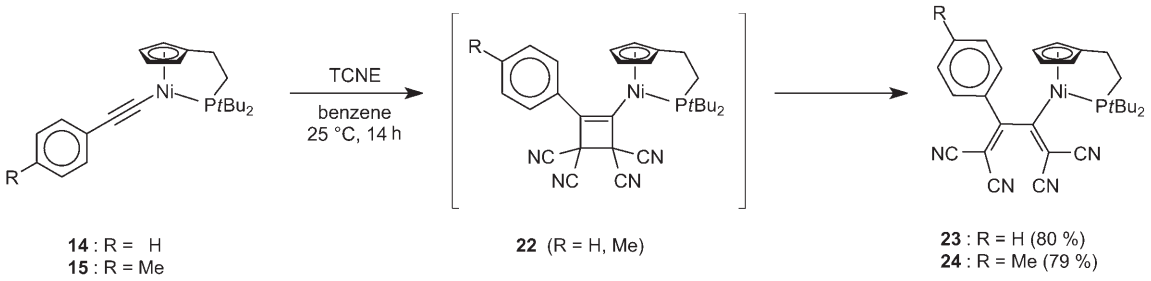

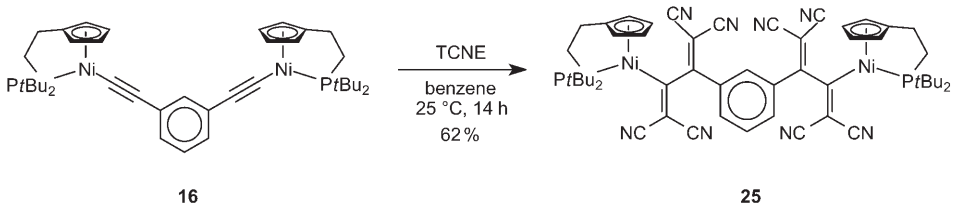

served at 2220 and 1530 cm^{-1}, respectively, and are in full accord with the corresponding values of related complexes. Evidence for the ring-opened structures of **23**–**25** is also provided by the ^{13}C NMR chemical shifts for the dienyl system, which are also in accord with the data of related complexes.[60] ^{31}P NMR signals at 96.1, 95.8, and 96.3 ppm, respectively, account for the coordination of the phosphane side arms. Although the NMR data confirm the assigned structures, there is one point on which the data differ from those of related known compounds. In contrast to our expectation, the ^{1}H and ^{13}C NMR spectra of **23**–**25** show two sets of signals for the *tert*-butyl groups, which indicates the presence of two different species. Furthermore, in both sets of signals the four Cp protons give rise to four different signals, and the *tert*-butyl groups show two signals. This indicates a highly lowered symmetry relative to usual Cp complexes and the cyclopentadienylalkylphosphane chelates prepared earlier by our group. Whereas usual Cp complexes give rise to one cyclopentadienyl resonance, cyclopentadienylalkylphosphane chelates usually show an AA′BB′ splitting pattern for the Cp protons as a result of their symmetry. We therefore explain our results by the presence of two observable conformers. To obtain deeper insight into their conformations, the matter was investigated for **24** by NMR ROESY at 295 and 280 K. There are two sets of signals in the ^{1}H NMR spectra at these two temperatures that belong to two different conformations (integrated ratio of conformers = 6.6:1). The two conformations are in slow exchange at 295 K and below on the NMR timescale as confirmed by chemical-exchange cross-peaks between the two sets of signals in the ROESY spectrum. From the NOE and the exchange cross-peaks of the ROESY spectra, and by taking into account the racemic synthesis, we conclude that four confomers were actually present. These are two pairs of enantiomers (Figure 8), which produced only two sets of signals in the ^{1}H NMR spectra. The presence of four different Cp proton signals indicates that the conformations lack a plane of symmetry through Ni–P–C1. A rotation around the Ni–C12 bond causes the dihedral angle C15–C12–Ni–cen to deviate significantly from 180° (cen = center of the Cp ring).

The relatively large difference in proton chemical shift of the *tert*-butyl substituents in the minor conformer and of the Cp protons in the major conformer are interpreted to be a result of magnetic anisotropy and indicate some proximity of the tolyl substituent to one of the *tert*-butyl substituents in the minor and to some of the Cp protons in the major conformer. This is presumably the result of rotation around either the C12–C13 bond or the Ni–C12 bond (Figure 8). Rotation around both the Ni–C12 and C12–C13 bonds gives enantiomeric confomations, which cannot be differentiated by NMR spectroscopy. Rotation only around C12–C13 gives diastereomeric conformations, which can be differentiated by NMR spectroscopy; rotation around Ni–C12 also gives diastereomeric conformations, but of the other enantiomer. If either of the two rotations took place on the NMR timescale, eight exchange cross-peaks between the Cp protons of the two conformations would occur. The ROESY spectra show only four exchange cross-peaks between the Cp protons of the two conformations. Therefore, only one of the rotations takes place on the NMR timescale. It is not possible to determine by NMR spectroscopy if this is the Ni–C12 or the C12–C13 bond rotation.

Conclusions

The first cyclopentadienylalkylphosphane nickel chelate complexes have been prepared by reaction of the anionic ligand system with nickel(II) chloride and subsequent exchange of the chloro ligand. In this way, stable complexes with nickel–carbon bonds were formed, as well as acetonitrile complexes of the cationic nickel chelate. In some cases, the complexes were characterized crystallographically and by cyclic voltammetry. Alkynylnickel chelates undergo cycloaddition reactions. The complexes prepared are usually more stable than their nonchelated cyclopentadienyl analogues, and the impossibility of rotation around the Cp–Ni axis gives rise to the formation of stable conformers of com-

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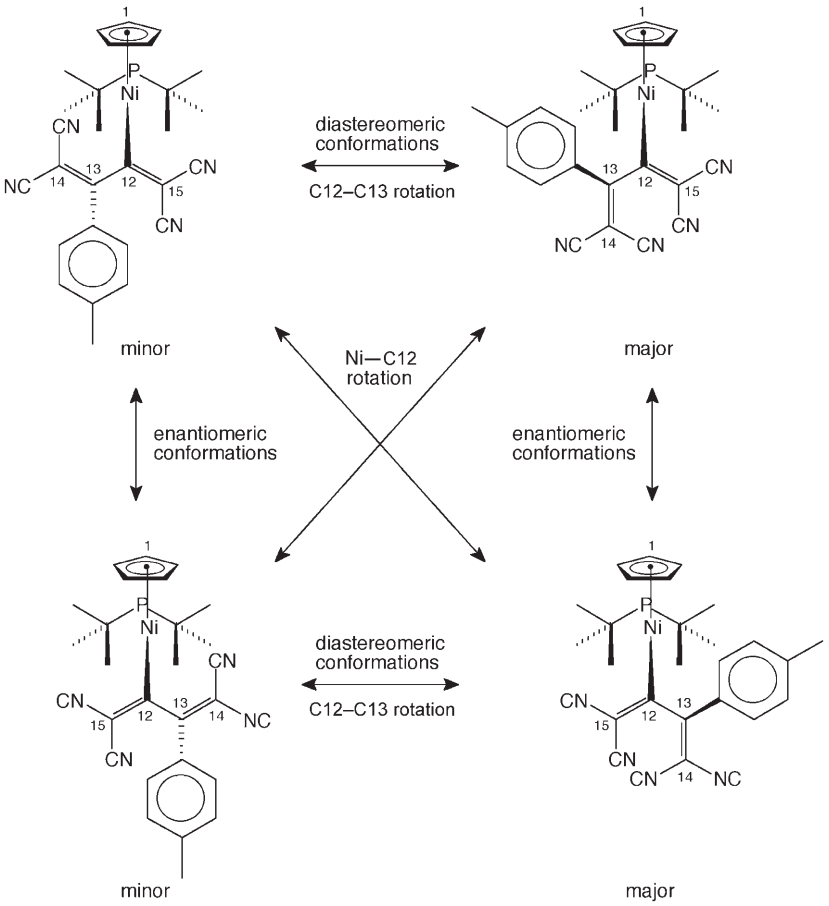

Figure 8. Conformational analysis of **24** based on NMR spectroscopic data.

plex **23**, which were characterized by advanced NMR spectroscopic techniques.

Experimental Section

General

All operations that involved air-sensitive materials were performed under argon by using standard Schlenk techniques. Diethyl ether, THF, benzene, and toluene were dried over and distilled from Na/ or K/benzophenone. Silica gel was heated at reduced pressure and then put under normal pressure in argon. This was repeated five times. Starting materials were either purchased or prepared according to literature procedures. Melting points: Büchi melting-point apparatus, uncorrected. IR spectroscopy: Perkin–Elmer FT 580, FT 1170 (ATR) spectrometers (ATR = attenuated total reflection). ^{1}H NMR spectroscopy: Bruker AVS 200 (200.1 MHz), AVS 400 (400.1 MHz), AVB 500 (500.1 MHz) spectrometers. Chemical shifts are given relative to tetramethylsilane (TMS; 0 ppm) or residual solvent peaks; br = broad, unresolved signal. ^{13}C NMR spectroscopy: Bruker AVS 200 (50.3 MHz), AVS 400 (100.6 MHz) spectrometers. Spectra were obtained with the DEPT and APT techniques. The symbols + and − indicate positive (C, CH_2) and negative phases (CH, CH_3), respectively. Chemical shifts are given relative to TMS (0 ppm) or residual solvent peaks. ^{31}P NMR spectroscopy: ^{1}H-decoupled, Bruker AVS 400 spectrometer (161.9 MHz), 85% aqueous H_3PO_4 as external standard. MS, FAB-MS, HRMS: Finnigan MAT 112, MAT 312, Fisons VG Autospec spectrometers. HRMS (ESI): Micromass LCT with lock–spray ion source combined with Water Alliances 2695 HPLC unit, VG Autospec spectrometer. Elemental analysis: Haeraeus CHN-Rapid instrument.

Syntheses

7: A solution of butyllithium (5.5 mL, 13.8 mmol, 2.5 M in hexane) was slowly added to di-*tert*-butylphosphane[68] (2.0 g, 13.6 mmol) in anhydrous THF (50 mL) at 0 °C to produce a deep-yellow solution. The reaction mixture was warmed slowly to 25 °C and stirred for 14 h. Spiro-[2.4]hepta-4,6-diene (**5**)[41] (1.25 g, 13.6 mmol) was slowly added to the reaction mixture, which became light yellow. The reaction mixture was heated at reflux for 3 h, after which it turned orange-red. Anhydrous $NiCl_2$ (5.2 g, 40.8 mmol) was added at −78 °C, and after 25 min the mixture was allowed to warm to 25 °C over 12 h, during which the reaction mixture turned purple-red. The THF was removed under reduced pressure, and the residue was dissolved in diethyl ether. After filtration through celite, the product was crystallized from diethyl ether to yield [η^5:κ^1-(di-*tert*-butylphosphanylethyl)cyclopentadienyl]-chloronickel(II) (**7**) (2.3 g, 6.9 mmol, 52%) as a deep-purple-red solid. M.p.: 189 °C (decomp.); IR (ATR): $\tilde{\nu}$ = 3077 (w), 2946 (s), 2897 (s), 1645 (w), 1473 (m), 1439 (w), 1389 (m), 1366 (m), 1358 (s), 1302 (w), 1180 (m), 1167 (s), 1064 (w), 1048 (m), 1018 (s), 932 (m), 895 (w), 864 (w), 830 (s), 810 (s), 780 (s), 678 (m), 622 cm^{-1} (w); ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.46 (t, $^3J_{H,H}$ = 7.5 Hz, 2H, 6-H), 1.54 (d, $^3J_{P,H}$ = 13.4 Hz, 18H, $C(CH_3)_3$), 2.18 (dd, $^2J_{P,H}$ = 8.2, $^3J_{H,H}$ = 7.5, 2H, 7-H), 5.87 + 5.43 ppm (AA′BB′, 4H, 2(5)-H, 3(4)-H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ = 25.5 (d, $^2J_{C,P}$ = 3.9 Hz, C6), 30.3 (d, $^2J_{C,P}$ = 3.3 Hz, 6 × CH_3), 34.5 (d, $^1J_{C,P}$ = 21.8 Hz, C7), 34.8 (d, $^1J_{C,P}$ = 14.2 Hz, $C(CH_3)_3$), 96.7 (d, J = 8.1 Hz, C1), 97.5 (d, J = 1.3 Hz, C2(5)), 98.5 ppm (d, J = 5.9 Hz, C3(4)); ^{31}P NMR ($CDCl_3$, 161 MHz): δ = 92.9 ppm (s); MS (70 eV): m/z (%) = 330 (76) $[M]^+$, 295 (3) $[M-Cl]^+$, 274 (3) $[M-C_4H_8]^+$, 239 (78) $[M-C_4H_8Cl]^+$, 238 (25) $[M-C_4H_8-HCl]^+$, 182 (100) $[M-2C_4H_8-HCl]^+$, 136 (29); elemental analysis: calcd (%) for $C_{15}H_{26}PNiCl$ (330.0814): C 54.35, H 7.91; found: C 54.86, H 7.95.

8: A solution of **7** (0.16 g, 0.5 mmol) in dichloromethane (25 mL) was added to a suspension of silver triflate (0.19 g, 0.8 mmol) in dichloromethane (15 mL) at 25 °C. After 3 h of stirring, the reaction mixture was filtered through celite. The solvent was removed under reduced pressure, and the residue was dissolved in dichloromethane (5 mL). The solution was layered with hexane to crystallize the product at −20 °C to yield [η^5:κ^1-(di-*tert*-butylphosphanylethyl)cyclopentadienyl]nickel(II) triflate **8** (0.12 g, 0.3 mmol, 56%) as a reddish-brown solid. Attempts to obtain NMR spectra failed due to decomposition. M.p.: 240 °C (decomp.); IR (ATR): $\tilde{\nu}$ = 2965 (w), 2888 (w), 1470 (w), 1396 (w), 1373 (w), 1260 (s), 1160 (w), 1092 (w), 1022 (s), 936 (w), 867 (w), 795 (s), 687 (w), 663 (m), 636 cm^{-1} (s); MS (70 eV): m/z (%) = 444 (20) $[M]^+$, 295 (9) $[M-CF_3SO_3]^+$, 281 (6) $[M-C_2H_2F_3SO_3]^+$, 238 (75) $[M-C_5H_9F_3SO_3]^+$, 182 (100) $[M-C_9H_{17}F_3SO_3]^+$, 149 (8) $[C_7H_8Ni]^+$, 136 (23); HRMS: m/z calcd for $C_{16}H_{26}O_3F_3PSNi$: 444.0646 $[M]^+$; found: 444.0644.

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9: A solution of **7** (0.10 g, 0.3 mmol) and silver tetrafluoroborate (0.09 g, 0.5 mmol) in acetonitrile (5 mL) was stirred for 1 h at 25 °C. After removal of the acetonitrile under reduced pressure, the residue was dissolved in dichloromethane (20 mL) and filtered through celite. Dichloromethane was removed under reduced pressure, and the residue was washed with diethyl ether (2×30 mL) to yield [η^5:κ^1-(di-*tert*-butylphosphanylethyl)cyclopentadienyl](acetonitrile)nickel(II) tetrafluoroborate (**9**) (0.12 g, 0.3 mmol, 88%) as a green solid. M.p.: 179 °C (decomp.); IR (ATR): $\tilde{\nu}$= 2962 (w), 2917 (w), 2360 (w), 2224 (w), 2193 (w), 2173 (s), 2145 (w), 2100 (w), 2090 (w), 2026 (w), 2011 (w), 1986 (w), 1964 (s), 1479 (s), 1262 (w), 1102 (w), 1085 (m), 1022 (m), 807 (s), 655 cm^{-1} (s); ^{1}H NMR ([D$_6$]acetone, 400 MHz): δ=1.52 (d, $^3J_{P,H}$=14.0 Hz, 18H, C(CH$_3$)$_3$), 1.84 (m, 2H, 6-H), 2.49 (s, 3H, NCCH$_3$), 2.67 (m, 2H, 7-H), 5.73+6.15 ppm (AA′BB′, 4H, 2(5)-H, 3(4)-H); ^{13}C NMR ([D$_6$]acetone, 100 MHz): δ=3.3 (s, NC*C*H$_3$), 25.9 (d, $^2J_{C,P}$=2.2 Hz, C6), 28.8 (d, $^2J_{C,P}$=3.6 Hz, C(*C*H$_3$)$_3$), 34.9 (d, $^1J_{C,P}$=25.1 Hz, C7), 35.3 (d, $^1J_{C,P}$=15.6 Hz, *C*(CH$_3$)$_3$), 97.5 (d, $J_{C,P}$=4.6 Hz, C3(4)), 98.6 (d, $J_{C,P}$=1.9 Hz, C2(5)), 106.5 (d, $J_{C,P}$=10.0 Hz, C1), 131.6 ppm (s, CN); ^{31}P NMR ([D$_6$]acetone, 161 MHz): δ=106.0 ppm (s); MS (70 eV): *m*/*z* (%)=423 (2) [*M*]$^+$, 422 (12) [*M*−H]$^+$, 295 (4) [*M*−CH$_3$CNBF$_4$]$^+$, 274 (3) [*M*−C$_4$H$_8$]$^+$, 238 (18) [*M*−CH$_3$CNBF$_4$−C$_4$H$_9$]$^+$, 182 (52) [M−2C$_4$H$_8$−CH$_3$CNBF$_4$]$^+$, 136 (9), 57 (100); HRMS (ESI, acetonitrile): *m*/*z* calcd for C$_{17}$H$_{29}$NPNi: 336.1391 [*M*]$^+$; found: 336.1400.

10: A solution of **7** (0.100 g, 0.3 mmol) and silver hexafluorophosphate (0.092 g, 0.4 mmol) in acetonitrile (5 mL) was stirred for 1 h at 25 °C. After removal of the acetonitrile under reduced pressure, the residue was dissolved in dichloromethane (20 mL) and filtered through celite. The dichloromethane was removed under reduced pressure, and the residue was washed with diethyl ether (2×30 mL) to yield [η^5:κ^1-(di-*tert*-butylphosphanylethyl)cyclopentadienyl](acetonitrile)nickel(II) hexafluorophosphate (**10**) (0.130 g, 0.3 mmol, 90%) as a dark-green solid. M.p.: 230 °C (decomp.); IR (ATR): $\tilde{\nu}$=2982 (w), 2917 (w), 2366 (w), 2231 (w), 2219 (w), 2166 (s), 2142 (w), 2075 (w), 2016 (w), 1953 (w), 1925 (w), 1910 (w), 1476 (m), 1371 (w), 1102 (w), 1085 (m), 1022 (m), 832 (s), 739 (w), 655 cm^{-1} (s); ^{1}H NMR ([D$_6$]acetone, 400 MHz): δ=1.52 (d, $^3J_{P,H}$= 14.0 Hz, 18H, C(CH$_3$)$_3$), 1.83 (m, 2H, 6-H), 2.48 (s, 3H, NCC*H*$_3$), 2.66 (m, 2H, 7-H), 5.72+6.14 ppm (AA′BB′, 4H, 2(5)-H, 3(4)-H);^{13}C{^{1}H} NMR ([D$_6$]acetone, 100 MHz): δ=3.3 (s, NC*C*H$_3$), 25.9 (d, $^2J_{C,P}$=2.1 Hz, C6), 28.9 (d, $^2J_{C,P}$=3.6 Hz, CH$_3$), 34.9 (d, $^1J_{C,P}$=25.0 Hz, C7), 35.3 (d, $^1J_{C,P}$=15.8 Hz, *C*(CH$_3$)$_3$), 97.6 (d, $J_{C,P}$=4.4 Hz, C3(4)), 98.6 (d, $J_{C,P}$=1.7 Hz, C2(5)), 106.5 (d, $J_{C,P}$=9.8 Hz, C1), 131.6 ppm (s, CN); ^{31}P NMR ([D$_6$]acetone, 161 MHz): δ=106.0 ppm (s); MS (ESI, acetonitrile): *m*/*z* (%)=462 (9) [*M*−PF$_6$+Rb+CH$_3$CN]$^+$, 385 (2) [*M*−PF$_6$+H$_2$O+CH$_3$O]$^+$, 336 (100) [*M*−PF$_6$]$^+$, 296 (5) [*M*+H−CH$_3$CNPF$_6$]$^+$, 294 (6) [*M*−H−CH$_3$CNPF$_6$]$^+$, 144 (100) [PF$_6$]$^-$; HRMS (ESI): *m*/*z* calcd for C$_{17}$H$_{29}$NPNi: 336.1391 [*M*]$^+$; found: 336.1389; *m*/*z* calcd for PF$_6$: 144.9642 [*M*]$^-$; found: 144.9646.

11: A solution of **7** (0.10 g, 0.30 mmol) and silver hexafluoroantimonate (0.13 g, 0.4 mmol) in acetonitrile (5 mL) was stirred for 1 h at 25 °C. After removal of the acetonitrile under reduced pressure, the residue was dissolved in dichloromethane (20 mL) and filtered through celite. The dichloromethane was removed under reduced pressure, and the residue was washed with diethyl ether (2×30 mL) to yield [η^5:κ^1-(di-*tert*-butylphosphanylethyl)cyclopentadienyl](acetonitrile)nickel(II) hexafluoroantimonate (**11**) (0.12 g, 0.21 mmol, 71%) as a dark-green solid. M.p.: 237 °C (decomp.); IR (ATR): $\tilde{\nu}$=2965 (w), 2888 (w), 2345 (w), 2207 (w), 2052 (w), 2039 (m), 1978 (w), 1478 (w), 1464 (w), 1393 (w), 1360 (w), 1261 (w), 1179 (w), 1093 (s), 1023 (w), 937 (w), 833 (m), 807 (s), 655 cm^{-1} (m); ^{1}H NMR ([D$_6$]acetone, 400 MHz): δ=1.52 (d, $^3J_{P,H}$=13.9 Hz, 18H, C(CH$_3$)$_3$), 1.84 (m, 2H, 6-H), 2.50 (d, $^5J_{P,H}$=0.6 Hz, 3H, NCC*H*$_3$), 2.67 (m, 2H, 7-H), 5.71+6.14 ppm (AA′BB′, 4H, 2(5)-H, 3(4)-H); ^{13}C{^{1}H} NMR ([D$_6$]acetone, 100 MHz): δ=3.7 (s, C10), 26.2 (d, $^2J_{C,P}$= 2.4 Hz, C6), 29.2 (d, $^2J_{C,P}$=3.6 Hz, CH$_3$), 35.3 (d, $^1J_{C,P}$=25.2 Hz, C7), 35.7 (d, $^1J_{C,P}$=15.6 Hz, *C*(CH$_3$)$_3$), 97.9 (d, $J_{C,P}$=4.6 Hz, C3(4)), 99.0 (d, $J_{C,P}$= 1.9 Hz, C2(5)), 106.8 (d, $J_{C,P}$=9.7 Hz, C1), 131.9 ppm (s, C9); ^{31}P NMR ([D$_6$]acetone, 161 MHz): δ=106.0 ppm (s); MS (ESI, acetonitrile): *m*/*z* (%)=462 (6) [*M*−SbF$_6$+Rb+CH$_3$CN]$^+$, 385 (1) [*M*−SbF$_6$+H$_2$O+CH$_3$O]$^+$, 336 (100) [*M*−SbF$_6$]$^+$, 296 (5) [*M*+H−CH$_3$CNSbF$_6$]$^+$, 294 (8) [*M*−H−CH$_3$CNSbF$_6$]$^+$, 234 (100) [SbF$_6$]$^-$; HRMS (ESI, acetonitrile): *m*/*z* calcd for C$_{17}$H$_{29}$NPNi: 336.1391 [*M*]$^+$, found: 336.1397; *m*/*z* calcd for SbF$_6$: 234.8942 [*M*]$^-$, found: 234.8946.

12: A solution of **7** (0.10 g, 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 under reduced pressure, the residue was dissolved in dichloromethane (20 mL) and filtered through celite. Dichloromethane was removed under reduced pressure, and the residue was washed with diethyl ether (2×30 mL) to yield [η^5:κ^1-(di-*tert*-butylphosphanylethyl)cyclopentadienyl](acetonitrile)nickel(II) tetraphenylborate (**12**) (0.18 g, 0.3 mmol, 92%) as a light-green solid. M.p.: 167 °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 cm^{-1} (m); ^{1}H NMR ([D$_6$]acetone, 400 MHz): δ=1.49 (d, $^3J_{P,H}$=13.9 Hz, 18H, C(CH$_3$)$_3$), 1.76 (m, 2H, 6-H), 2.22 (s, 3H, NCC*H*$_3$), 2.58 (m, 2H, 7-H), 5.63+6.08 (AA′BB′, 4H, 2(5)-H, 3(4)-H), 6.79 (dd, $^3J_{H,H}$=7.2, 7.1 Hz, 4H, *p*-H), 6.92–6.96 (m, 8H, *o*-H), 7.33–7.36 ppm (m, 8H, *m*-H); ^{13}C NMR ([D$_6$]acetone, 100 MHz): δ= 3.5 (s, NC*C*H$_3$), 26.2 (d, $^2J_{C,P}$=2.3 Hz, C6), 29.2 (d, $^2J_{C,P}$=3.4 Hz, C-(*C*H$_3$)$_3$), 35.3 (d, $^1J_{C,P}$=25.2 Hz, C7), 35.7 (d, $^1J_{C,P}$=15.8 Hz, *C*(CH$_3$)$_3$), 97.9 (d, $J_{C,P}$=4.5 Hz, C3(4)), 98.9 (d, $J_{C,P}$=1.7 Hz, C2(5)), 106.8 (d, $J_{C,P}$= 9.8 Hz, C1), 131.8 (s, CN), 122.2 (d, $^4J_{B,C}$=0.6 Hz, *p*-C), 125.9 (dd, $^3J_{B,C}$= 2.7 Hz, *m*-C), 136.9 (dd, $^2J_{B,C}$=1.5, 1.2 Hz, *o*-C), 164.6 ppm (four-line m, $^1J_{B,C}$=49.2 Hz, *ipso*-C); ^{31}P NMR ([D$_6$]acetone, 161 MHz): δ=106.0 ppm (s); MS (ESI, acetonitrile): *m*/*z* (%)=462 (7) [*M*−BPh$_4$+Rb+CH$_3$CN]$^+$, 385 (1) [*M*−BPh$_4$+H$_2$O+CH$_3$O]$^+$, 336 (100) [*M*−BPh$_4$]$^+$, 319 (100) [BPh$_4$]$^-$, 295 (6) [*M*−CH$_3$CNBPh$_4$]$^+$, 294 (10) [*M*−H−CH$_3$CNBPh$_4$]$^+$; HRMS (ESI acetonitrile): *m*/*z* calcd for C$_{17}$H$_{29}$NPNi: 336.1391 [*M*]$^+$; found: 336.1386; *m*/*z* calcd for C$_{24}$H$_{20}$B: 319.1658 [*M*]$^-$; found: 319.1669.

13: Methyllithium (0.5 mL, 0.7 mmol, 1.6 M in diethyl ether) was added dropwise to a solution of **7** (0.20 g, 0.6 mmol) in diethyl ether (60 mL) at 25 °C. The reaction mixture turned green. The solution was stirred for 1 h and filtered through celite. After solvent removal under reduced pressure, recrystallization from a saturated solution of hexane at −20 °C yielded [η^5:κ^1-(di-*tert*-butylphosphanylethyl)cyclopentadienyl]methylnickel(II) (**13**) (0.16 g, 0.5 mmol, 86%) as a crystalline solid. M.p.: 182 °C (decomp.); IR (ATR): $\tilde{\nu}$=2945 (w), 2903 (w), 2858 (w), 1457 (w), 1388 (w), 1361 (w), 1304 (w), 1260 (m), 1179 (w), 1166 (w), 1127 (s), 1092 (w), 1088 (s), 1017 (s), 931 (w), 871 (w), 821 (m), 808 (m), 778 (s), 668 (m), 650 (w), 620 cm^{-1} (m); ^{1}H NMR (CDCl$_3$, 200 MHz): δ=−1.07 (d, $^3J_{P,H}$= 3.2 Hz, 3H, CH$_3$Ni), 1.36 (d, $^3J_{P,H}$=12.7 Hz, 18H, C(CH$_3$)$_3$), 1.93 (dt, $^3J_{H,H}$=7.5, 6.9 Hz, 2H, 6-H), 2.36 (dd, $^2J_{P,H}$=7.6 Hz, $^3J_{H,H}$=7.5 Hz, 2H, 7-H), 5.13 (s, 2H, 2(5)-H), 5.70 ppm (s, 2H, 3(4)-H); ^{13}C{^{1}H} NMR (CDCl$_3$, 100 MHz): δ=−43.5 (d, $^2J_{C,P}$=20.3 Hz, CH$_3$Ni), 24.9 (s, C6), 29.4 (s, 2 C-(*C*H$_3$)$_3$), 34.6 (d, $J_{C,P}$=18 Hz, C7), 40.3 (s, *C*(CH$_3$)$_3$), 88.7 (s, C2(5)), 93.9 ppm (s, C3(4)), 97.4 (s, C1); ^{31}P NMR (CDCl$_3$, 161 MHz): δ=90.0 (s) ppm; MS (70 eV): *m*/*z* (%)=310 (40) [*M*]$^+$, 295 (32) [*M*−CH$_3$]$^+$, 268 (32) [*M*−C$_3$H$_6$]$^+$, 254 (21) [*M*−C$_4$H$_8$]$^+$, 239 (29) [*M*−C$_5$H$_{11}$]$^+$, 226 (25) [*M*−C$_6$H$_{12}$]$^+$, 198 (20) [M−2C$_4$H$_8$]$^+$, 183 (42) [M−2C$_4$H$_8$−CH$_3$]$^+$, 162 (62), 138 (32); HRMS: *m*/*z* calcd for C$_{16}$H$_{29}$PNi: 310.1360 [*M*]$^+$; found: 310.1345.

14: Phenyl acetylene (0.17 g, 1.6 mmol) was added dropwise to a suspension of **7** (0.33 g, 1.0 mmol) and CuI (5 mg) in freshly distilled triethylamine (20 mL). The reaction mixture was stirred for 14 h at 25 °C, after which the solvent was removed under reduced pressure. The crude product was extracted with diethyl ether (3×25 mL) and subjected to chromatography (SiO$_2$, petroleum ether/ethyl acetate=10:1) to yield [η^5:κ^1-(di-*tert*-butylphosphanylethyl)cyclopentadienyl](2-phenylethynyl)nickel(II) (**14**) (0.23 g, 0.6 mmol, 58%) as a deep-brown solid. M.p.: 218 °C (decomp.); IR (ATR): $\tilde{\nu}$=3083 (w), 3068 (w), 2944 (s), 2895 (s), 2090 (m) 1652 (w), 1589 (m),1481 (m), 1438 (w), 1390 (m), 1371 (m), 1357 (s), 1306 (w), 1179 (m), 1064 (w), 1037 (m), 1024 (s), 927 (m), 900 (w), 861 (w), 812 (s), 790 (s), 690 (m), 676 cm^{-1} (w); ^{1}H NMR (CDCl$_3$, 400 MHz): δ= 1.51 (d, $^3J_{P,H}$=13.5 Hz, 18H, C(C*H*$_3$)$_3$), 2.01 (dt, 2H, $^3J_{H,H}$=7.5, 7.4 Hz, 6-H), 2.49 (dd, $^2J_{P,H}$=8.5 Hz, $^3J_{H,H}$=7.5, 2H, 7-H), 5.52+5.71 (AA′BB′, 4H, 2(5)-H, 3(4)-H), 6.98 (dd, $^3J_{H,H}$=6.0 Hz, $^4J_{H,H}$=1.2 Hz, 1H, *p*-H), 7.1 (dd, $^3J_{H,H}$=7.8, 7.4 Hz, 2H, *m*-H), 7.2 ppm (dd, $^3J_{HH}$=7.0 Hz, $^4J_{HH}$= 1.3 Hz, 2H, *o*-H); ^{13}C{^{1}H} NMR (CDCl$_3$, 100 MHz): δ=25.6 (d, $^2J_{C,P}$=

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3.6 Hz, C6), 29.4 (d, $^2J_{C,P}$=3.4 Hz, C(CH_3)$_3$), 35.1 (d, $^1J_{C,P}$=16.1 Hz, *C*-(CH_3)$_3$), 39.0 (d, $^1J_{C,P}$=19.5 Hz, C7), 90.3 (d, $^2J_{C,P}$=33.9 Hz, Ni*C*−C), 91.9 (d, *J*=5.6 Hz, C2(5)), 94.7 (d, *J*=1.7 Hz, C3(4), 108.1 (d, *J*=8.2 Hz, C1), 117.1 (d, $^3J_{C,P}$=1.7 Hz, NiC−*C*), 124.3 (s, *p*-C), 127.5 (s, *m*-C), 128.6 (s, *ipso*-C), 131.0 ppm (d, $^5J_{C,P}$=0.6 Hz, *o*-C); ^{31}P NMR ($CDCl_3$, 161 MHz): δ=104.8 ppm (s); MS (70 eV): *m*/*z* (%)=397 (100) [*M*+1]$^+$, 340 (34) [*M*−C_4H_8]$^+$, 282 (28), 284 (47) [*M*−2C_4H_8]$^+$, 238 (31), 206 (15), 180 (10), 182 (37), 160 (11), 136 (14); HRMS (ESI): *m*/*z* calcd for $C_{23}H_{31}PNi$: 397.1595 [*M*−H]$^+$; found: 397.1581.

15: (4-Methylphenyl)ethyne (0.14 g, 1.2 mmol) was added dropwise to a suspension of **7** (0.20 g, 0.6 mmol) and CuI (5 mg) in freshly distilled triethylamine (10 mL). The reaction mixture turned purple-brown. After the mixture was stirred for 14 h, the solvent was evacuated to dryness. The crude product was extracted with diethyl ether (3×25 mL) and subjected to chromatography (SiO_2, petroleum ether/ethyl acetate=10:1) to yield [η^5:κ^1-(di-*tert*-butylphosphanylethyl)cyclopentadienyl]-2-(4-methylphenyl)ethynylnickel(II) (**15**) (0.23 g, 0.6 mmol, 91%) as a deep-brown solid. Part of **15** was recrystallized from hexane at −20°C to give fine crystals suitable for X-ray structure analysis. M.p.: 220°C (decomp.); IR (ATR): $\tilde{\nu}$=2962 (w), 2944 (s), 2895 (s), 2086 (m), 1605 (w), 1503 (m), 1455 (m), 1357 (m), 1259 (s), 1173 (m), 1017 (s), 865 (w), 782 (s), 674 cm^{-1} (m); ^{1}H NMR ($CDCl_3$, 400 MHz): δ=1.50 (d, $^3J_{P,H}$=13.5 Hz, 18H, C(CH_3)$_3$), 2.02 (dt, $^3J_{H,H}$=7.4 Hz, 2H, 6-H), 2.25 (s, 3H, 4-CH_3), 2.48 (dd, $^2J_{P,H}$=8.5 Hz, $^3J_{H,H}$=7.5 Hz, 2H, 7-H), 5.52+5.70 (AA′BB′, 4H, 2(5)-H, 3(4)-H), 6.92 (d, $^3J_{H,H}$=7.9 Hz, 2H, *m*-H), 7.10 ppm (d, $^3J_{H,H}$=8.0 Hz, 2H, *o*-H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ=21.1 (s, 4-CH_3), 25.6 (d, $^2J_{C,P}$=3.7 Hz, C6), 29.4 (d, $^2J_{C,P}$=3.5, C(CH_3)$_3$), 35.1 (d, $^1J_{C,P}$=15.8 Hz, *C*(CH_3)$_3$), 39.0 (d, $^1J_{C,P}$=19.3 Hz, C7), 88.0 (d, $^2J_{C,P}$=34.0 Hz, Ni*C*−C), 91.9 (d, *J*=5.7 Hz, C2(5)), 94.7 (d, *J*=1.8 Hz, C3(4)), 107.9 (d, *J*=8.2 Hz, C1), 117.0 (s, NiC−*C*), 125.9 (s, *ipso*-C), 128.2 (s, *m*-C), 130.9 (d, $^4J_{C,P}$=0.4 Hz, *o*-C), 133.8 ppm (s, *p*-C); ^{31}P NMR ($CDCl_3$, 161 MHz): δ=104.5 ppm (s); MS (ESI, acetonitrile): *m*/*z* (%)=509 (8) [*M*+K+H_2O+CH_3CN]$^+$, 474 (6) [*M*+Na+CH_3CN]$^+$, 411 (12) [*M*+H]$^+$, 336 (100) [*M*−C_9H_7+CH_3CN]$^+$, 294 (5) [*M*−C_9H_6]$^+$, 255 (4) [$C_{13}H_{10}$NiP]$^+$; HRMS (ESI, acetonitrile): *m*/*z* calcd for $C_{24}H_{33}PNi$: 411.1752 [*M*+H]$^+$; found: 411.1767.

16: 1,3-Diethynylbenzene (0.08 g, 0.6 mmol) was added dropwise to a suspension of **7** (0.4 g, 1.2 mmol) and CuI (5 mg) in freshly distilled triethylamine (10 mL). The reaction mixture turned purple-brown. After the mixture was stirred for 14 h, the solvent was removed under reduced pressure until dryness. The crude product was extracted with diethyl ether (3×25 mL) and subjected to chromatography (SiO_2, petroleum ether/ethyl acetate=10:1) to yield 1,3-bis{[η^5:κ^1-(di-*tert*-butylphosphanylethyl)cyclopentadienyl]ethynylnickel(II)}benzene (0.4 g, 0.6 mmol, 47%) as a deep-brown solid. M.p.: 302°C (decomp.); IR (ATR): $\tilde{\nu}$=3081 (w), 3070 (w), 2962 (s), 2870 (s), 2082 (m), 1584 (m),1471 (m), 1435 (w), 1390 (m), 1371 (m), 1357 (m), 1306 (w), 1259 (s), 1179 (m), 1064 (w), 1037 (m), 1016 (s), 911 (m), 900 (w), 865 (w), 798 (s), 733 (m), 687 (m), 675 cm^{-1} (w); ^{1}H NMR ($CDCl_3$, 400 MHz): δ=1.50 (d, $^3J_{P,H}$=13.5 Hz, 36H, 4-CH_3), 2.03 (dt, $^3J_{H,H}$=7.5, 7.4 Hz, 4H, 6(6′)-H), 2.47 (dd, $^2J_{P,H}$=8.5 Hz, $^3J_{H,H}$=7.5 Hz, 4H, 7(7′)-H), 5.51+5.70 (AA′BB′, 8H, 2,2′(5,5′)-H, 3,3′(4,4′)-H), 7.05 (dd, $^3J_{H,H}$=7.6 Hz, 1H, CCH*C*H*C*HC), 7.18 (ddd, $^3J_{H,H}$=7.6, 6.2 Hz, $^4J_{H,H}$=1.4 Hz, 2H, CC*H*CHC*H*C), 7.3 ppm (s, CCHC); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ=25.8 (d, $^2J_{C,P}$=3.6 Hz, C6(6′)), 29.5 (d, $^2J_{C,P}$=3.5, CH_3), 35.3 (d, $^1J_{C,P}$=16.2 Hz, *C*(CH_3)$_3$), 39.2 (d, $^1J_{C,P}$=19.5 Hz, C7(7′)), 92.1 (d, *J*=5.7 Hz, C2,2′(5,5′)), 93.5 (d, $^2J_{C,P}$=33.8 Hz, C9(9′)), 94.9 (d, *J*=1.9 Hz, C3,3′(4,4′)), 108.5 (d, *J*=7.9 Hz, C1(1′)), 116.3 (s, NiC−*C*≡C), 121.3 (s, Ni−C≡C−*C*), 127.6 (s, *C*HCH*C*H), 131.7 (s, CH*C*HCH), 134.6 ppm (s, *C*CHC); ^{31}P NMR ($CDCl_3$, 161 MHz): δ=105.2 ppm (s); MS (ESI, acetonitrile): *m*/*z* (%)=778 (3) [*M*+Na+CH_3CN]$^+$, 715 (19) [*M*+H]$^+$, 539 (4) [*M*−$C_{13}H_{19}$]$^+$, 421 (9) [*M*−$C_{15}H_{24}$NiP]$^+$, 336 (100) [*M*−$C_{25}H_{30}$NiP+CH_3CN]$^+$, 318 (5) [*M*−$C_{23}H_{31}$NiP]$^+$, 255 (11) [$C_{13}H_{10}$NiP]$^+$, 215 (11) [$C_{10}H_7$NiP]$^+$, 102 (3) [C_8H_6]$^+$; HRMS (ESI, acetonitrile): *m*/*z* calcd for $C_{40}H_{56}P_2Ni_2$: 715.2642 [*M*+H]$^+$; found: 715.2663.

19: Ethoxycarbonylisothiocyanate (80 mg, 0.6 mmol, 70 μL) was added to a solution of **14** (0.20 g, 0.5 mmol) in chloroform (10 mL), and the mixture was stirred at 25°C for 2 h. The volume of the solution was reduced to 1 mL, and pentane (30 mL) was added. The solution was then filtered through celite. After solvent removal under reduced pressure, the residue was dried and dissolved in diethyl ether (5 mL). Hexane (5 mL) was layered over the solution to crystallize the product at −20°C; this yielded [η^5:κ^1-(di-*tert*-butylphosphanylethyl)cyclopentadienyl](2-ethoxy-5-phenyl-4-thioxo-4*H*-1,3-oxazin-6-yl)nickel(II) (**19**) (0.27 g, 0.5 mmol, 85%) as an orange solid. M.p.: 154°C (decomp.); IR (ATR): $\tilde{\nu}$=2958 (w), 2903 (w), 2861 (w), 2155 (w), 2087 (w), 1670 (w), 1606 (w), 1523 (w), 1507 (w), 1308 (w), 1259 (s), 1210 (w), 1088 (s), 1016 (s), 865 (w), 791 (w), 694 (w), 673 cm^{-1} (w); ^{1}H NMR ($CDCl_3$, 400 MHz): δ=1.34 (d, $^3J_{P,H}$=13.8 Hz, 18H, C(CH_3)$_3$), 1.35 (t, $^3J_{H,H}$=7.0 Hz, 3H, CH_3CH_2), 2.08 (dt, $^3J_{H,H}$=7.4, 7.2 Hz, 2H, 6-H), 2.52 (dd, $^2J_{P,H}$=8.4 Hz, $^3J_{H,H}$=7.5 Hz, 2H, 7-H), 4.23 (q, $^3J_{H,H}$=7.1 Hz, 2H, CH_2CH_3), 5.33+5.70 (AA′BB′, 4H, 2(5)-H, 3(4)-H), 7.13 (dd, $^3J_{H,H}$=7.4 Hz, 1H, *p*-H), 7.28 (dd, $^3J_{H,H}$=7.5, 7.8 Hz, 2H, *m*-H), 8.21 ppm (d, $^3J_{H,H}$=7.1, $^4J_{H,H}$=1.1 Hz, 2H, *o*-H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ=14.4 (s, CH_3CH_2), 25.5 (d, $^2J_{C,P}$=3.1 Hz, C6), 29.3 (d, $^2J_{C,P}$=4.1 Hz, C(CH_3)$_3$), 34.9 (d, $^1J_{C,P}$=16.1 Hz, *C*(CH_3)$_3$), 39.9 (d, $^1J_{C,P}$=20.5 Hz, C7), 62.5 (s, CH_2CH_3), 91.6 (d, *J*=4.8 Hz, C2(5)), 95.9 (d, *J*=1.4 Hz, C3(4)), 113.0 (d, *J*=8.5 Hz, C1), 124.4 (s, *m*-C), 125.1 (s, *p*-C), 127.6 (s, *o*-C), 134.8 (d, $^4J_{C,P}$=0.7 Hz, *ipso*-C), 150.3 (d, $^3J_{C,P}$=0.9 Hz, NiC−*C*), 160.6 (s, C=N), 165.4 (d, $^2J_{C,P}$=1.7 Hz, NiC−C), 211.7 ppm (d, $^4J_{C,P}$=20.5 Hz, C=S); ^{31}P NMR ($CDCl_3$, 161 MHz): δ=101.2 ppm (s); MS (ESI, acetonitrile): *m*/*z* (%)=583 (84) [*M*−H+H_2O+K]$^+$, 528 (100) [*M*+H]$^+$, 336 (38) [*M*−$C_{12}H_{10}NO_2S$+CH_3CN]$^+$; HRMS (ESI acetonitrile): *m*/*z* calcd for $C_{27}H_{36}NO_2PSNi$: 528.1636 [*M*+H]$^+$; found: 528.1649.

20: Ethoxycarbonylisothiocyanate (34 mg, 0.3 mmol, 30 μL) was added to a solution of **14** (0.10 g, 0.3 mmol) in chloroform (10 mL), and the mixture was stirred for 2 h at 25°C. The volume of the solution was reduced to 1 mL, and pentane (30 mL) was added. The solution was then filtered through celite. After solvent removal under reduced pressure, the residue was dried and dissolved in diethyl ether (5 mL). Hexane (5 mL) was layered over the solution to crystallize [η^5:κ^1-(di-*tert*-butylphosphanylethyl)-cyclopentadienyl][2-ethoxy-5-(4-methylphenyl)-4-thioxo-4*H*-1,3-oxazin-6-yl]nickel(II) (**20**) (0.12 g, 0.2 mmol, 90%) as an orange solid. M.p.: 160°C (decomp.); IR (ATR): $\tilde{\nu}$=2962 (w), 2903 (w), 2859 (w), 2153 (w), 2086 (w), 1669 (w), 1609 (w), 1521 (w), 1505 (w), 1309 (w), 1259 (s), 1209 (w), 1087 (s), 1016 (s), 864 (w), 790 (w), 695 (w), 674 cm^{-1} (w); ^{1}H NMR ($CDCl_3$, 400 MHz): δ=1.31 (d, $^3J_{P,H}$=13.8 Hz, 18H, C(CH_3)$_3$), 1.33 (t, $^3J_{H,H}$=7.1 Hz, 3H, CH_3CH_2), 2.10 (dt, $^3J_{P,H}$=7.4, 7.2 Hz, 2H, 6-H), 2.32 (s, 3H, *p*-CH_3), 2.54 (dd, $^2J_{P,H}$=8.4 Hz, $^3J_{H,H}$=7.5 Hz, 2H, 7-H), 4.23 (q, $^3J_{H,H}$=7.1 Hz, 2H, CH_2CH_3), 5.34+5.72 (AA′BB′, 2×2H, 2(5)-H, 3(4)-H), 7.10+8.10 ppm (AA′BB′, 2×2H, *o*-H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ=14.3 (s, CH_3CH_2), 21.2 (s, *p*-CH_3), 25.5 (d, $^2J_{C,P}$=3.4 Hz, C6), 29.3 (d, $^2J_{C,P}$=3.9 Hz, C(CH_3)$_3$), 34.9 (d, $^1J_{C,P}$=15.9 Hz, *C*(CH_3)$_3$), 39.9 (d, $^1J_{C,P}$=20.5 Hz, C7), 62.4 (s, CH_2CH_3), 91.6 (d, *J*=4.8 Hz, C2(5)), 95.9 (d, *J*=1.5 Hz, C3(4)), 112.9 (d, *J*=8.3 Hz, C1), 124.3 (s, *m*-C), 128.2 (s, *o*-C), 132.1 (s, *p*-C), 134.6 (s, *ipso*-C), 150.5 (s, NiC−*C*), 160.6 (s, C=N), 165.2 (s, Ni*C*−C), 209.1 ppm (d, $^4J_{C,P}$=20.5 Hz, C=S); ^{31}P NMR ($CDCl_3$, 161 MHz): δ=101.0 ppm (s); MS (ESI, acetonitrile): *m*/*z* (%)=597 (16) [*M*−H+H_2O+K]$^+$, 542 (100) [*M*+H]$^+$, 336 (71) [*M*−$C_{13}H_{12}NO_2S$+CH_3CN]$^+$; HRMS (ESI, acetonitrile): *m*/*z* calcd for $C_{28}H_{38}NO_2PSNi$: 542.1793 [*M*+H]$^+$; found: 542.1813.

23: A solution of **14** (0.15 g, 0.4 mmol) and tetracyanoethylene (0.085 g, 0.7 mmol) in benzene (15 mL) was stirred for 14 h at 25°C. After solvent removal under reduced pressure, the reaction mixture was subjected to chromatography (SiO_2, petroleum ether/ethyl acetate=10:1) to yield [η^5:κ^1-(di-*tert*-butylphosphanylethyl)cyclopentadienyl][2-(1,1,4,4-tetracyano-3-phenyl-1,3-butadienyl)]nickel(II) (**23**) (0.16 g, 0.3 mmol, 80%) as a dark-brown solid. M.p.: 180°C; IR (ATR): $\tilde{\nu}$=2962 (w), 2944 (s), 2895 (s), 2219 (s), 1734 (w), 1602 (w), 1531 (m),1501 (w), 1473 (s), 1389 (m), 1365 (m), 1259 (s), 1177 (m), 1015 (s), 932 (w), 902 (w), 806 (s), 736 (w), 668 (m), 641 (w), 630 (w), 614 cm^{-1} (m); major conformer: ^{1}H NMR ($CDCl_3$, 400 MHz): δ=1.39 (d, $^3J_{P,H}$=14.5 Hz, 9H, 3×C(CH_3)$_3$), 1.46 (d, $^3J_{P,H}$=15.1 Hz, 9H, C(CH_3)$_3$), 1.75 (br d, $^3J_{P,H}$=37.0 Hz, 1H, 6-H$_a$), 2.00 (br, 1H, 6-H$_b$), 2.24 (br, 1H, 7-H$_a$), 2.50 (br, 1H, 7-H$_b$), 3.32 (br, 1H, 3(4)-H), 4.71 (br, 1H, 4(3)-H), 4.96 (br, 1H, 2(5)-H), 6.11 (br, 1H, 5(2)-H), 7.28 (br, 2H, 16(20)-H), 7.55 ppm (br, 3H, 17-H, 18(19)-H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ=25.1 (s, C6), 29.4 (s, C(CH_3)$_3$), 29.9 (s, C(CH_3)$_3$), 34.5 (d, $^1J_{C,P}$=15.6 Hz, *C*(CH_3)$_3$), 35.7 (d, $^1J_{C,P}$=14.3 Hz, *C*-

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(CH_3)$_3$), 38.7 (d, $^1J_{C,P}$ = 22.8 Hz, C7), 75.4 (s, C14), 91.7 (s, C2(5)), 94.0 (s, C2(5)), 94.3 (s, C15), 96.9 (s, C3(4)), 100.8 (s, C3(4)), 110.5, 112.8, 115.2, 117.0 (4×CN), 112.9 (s, C1), 126.9 (s, C17(19)), 129.0 (s, C16(20)), 131.3 (s, C13a), 134.6 (s, C18), 180.3 (s, C13), 213.1 ppm (s, C12); ^{31}P NMR ($CDCl_3$, 161 MHz): δ = 96.1 ppm (s); minor conformer: ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.65 (br, 9H, C(CH_3)$_3$), 1.30 (br, 9H, C(CH_3)$_3$), 5.32 (br, 1H, 5(2)-H), 5.65 (br, 1H, 3(4)-H), 5.70 (br, 1H, 4(3)-H), 6.22 ppm (br, 1H, 2(5)-H); MS (ESI, acetonitrile): *m*/*z* (%) = 588 (38) [*M*+Na+CH_3CN]$^+$, 542 (100) [*M*+H_2O]$^+$, 525 (28) [*M*+H]$^+$, 336 (38) [*M*−$C_{14}H_5N_4$+CH_3CN]$^+$; HRMS (ESI, acetonitrile): *m*/*z* calcd for $C_{29}H_{31}N_4PNi$: 525.1718 [*M*+H]$^+$; found: 525.1733.

24: A solution of **15** (0.19 g, 0.5 mmol) and tetracyanoethylene (0.10 g, 0.8 mmol) in benzene (20 mL) was stirred for 14 h at 25 °C. After solvent removal under reduced pressure, the residue was subjected to chromatography (SiO_2, petroleum ether/ethyl acetate = 10:1) to yield [η^5:κ^1-(di-*tert*-butylphosphanylethyl)cyclopentadienyl][2-[1,1,4,4-tetracyano-3-(4-methylphenyl)-1,3-butadienyl]]nickel(II) (**24**) (0.18 g, 0.4 mmol, 79 %) as a dark-brown solid. M.p.: 183 °C; IR (ATR): $\tilde{\nu}$ = 2960 (w), 2940 (s), 2890 (s), 2220 (s), 1733 (w), 1606 (w), 1529 (m), 1504 (w), 1471 (s), 1391 (m), 1361 (m), 1258 (s), 1178 (m), 1014 (s), 934 (w), 904 (w), 806 (s), 739 (w), 667 (m), 642 (w), 630 (w), 614 cm^{-1} (m); major conformation: ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.39 (d, $^3J_{P,H}$ = 14.5 Hz, 9H, C(CH_3)$_3$), 1.46 (d, $^3J_{P,H}$ = 15.1 Hz, 9H, C(CH_3)$_3$), 1.75 (br d, $^3J_{P,H}$ = 37.0 Hz 1H, 6-H_a), 2.00 (br, 1H, 6-H_b), 2.24 (br, 1H, 7-H_a), 2.50 (br, 1H, 7-H_b), 3.32 (br, 1H, 3(4)-H), 4.71 (br, 1H, 4(3)-H), 4.96 (br, 1H, 2(5)-H), 6.11 (br, 1H, 5(2)-H), 7.28 (br, 2H, 16(20)-H), 7.55 ppm (br, 3H, 17-H, 18(19)-H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ = 25.1 (s, C6), 29.4 (s, C(CH_3)$_3$), 29.9 (s, C(CH_3)$_3$), 34.5 (d, $^1J_{C,P}$ = 15.6 Hz, *C*(CH_3)$_3$), 35.7 (d, $^1J_{C,P}$ = 14.3 Hz, *C*-(CH_3)$_3$), 38.7 (d, $^1J_{C,P}$ = 22.8 Hz, C7), 75.4 (s, C14), 91.7 (s, C2(5)), 94.0 (s, C2(5)), 94.3 (s, C15), 96.9 (s, C3(4)), 100.8 (s, C3(4)), 110.5, 112.8, 115.2, 117.0 (4×CN), 112.9 (s, C1), 126.9 (s, C17(19)), 129.0 (s, C16(20)), 131.3 (s, C13a), 134.6 (s, C18), 180.3 (s, C13), 213.1 ppm (s, C12); ^{31}P NMR ($CDCl_3$, 161 MHz): δ = 96.1 ppm (s); minor conformation: ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.65 (br, 9H, C(CH_3)$_3$), 1.30 (br, 9H, C(CH_3)$_3$), 5.32 (br, 1H, 5(2)-H), 5.65 (br, 1H, 3(4)-H), 5.70 (br, 1H, 4(3)-H), 6.22 ppm (br, 1H, 2(5)-H); MS (ESI, acetonitrile): *m*/*z*(%) = 602 (43) [*M*+Na+CH_3CN]$^+$, 556 (100) [*M*+H_2O]$^+$, 539 (29) [*M*+H]$^+$, 336 (29) [*M*−$C_{15}H_7N_4$+CH_3CN]$^+$; HRMS (ESI, acetonitrile): *m*/*z* calcd for $C_{30}H_{33}N_4PNi$: 539.1875 [*M*+H]$^+$; found: 539.1884.

25: A solution of **16** (0.42 g, 0.6 mmol) and tetracyanoethylene (0.35 g, 2.4 mmol) in benzene (15 mL) was stirred at 25 °C for 14 h. After solvent removal under reduced pressure, the residue was subjected to chromatography (SiO_2, petroleum ether/ethyl acetate = 10:1) to yield 1,3-bis[[3-[η^5:κ^1-(di-*tert*-butylphosphanylethyl)cyclopentadienyl]nickel(II)-yl]-1,1,4,4-tetracyano-2-(1,3-butadienyl)]benzene (**25**) (0.35 g, 0.37 mmol, 62 %, mixture of conformers) as a dark-brown solid. M.p.: 320 °C (decomp.); IR (ATR): $\tilde{\nu}$ = 2959 (w), 2940 (s), 2895 (s), 2223 (s), 1729 (w), 1607 (w), 1530 (m),1504 (w), 1471 (s), 1393 (m), 1364 (m), 1257 (s), 1178 (m), 1015 (s), 935 (w), 903 (w), 806 (s), 739 (w), 667 (m), 645 (w), 632 (w), 612 cm^{-1} (m); major conformation: ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.30 (d, $^3J_{P,H}$ = 15.1 Hz, 18H, C(CH_3)$_3$), δ = 1.47 (d, $^3J_{P,H}$ = 15.2 Hz, 18H, C(CH_3)$_3$), 1.72 (br d, $^3J_{P,H}$ = 35.8 Hz, 2H, 6(6′)-H_a), 2.00 (br, 2H, 6(6′)-H_b), 2.30 (br, 2H, 7(7′)-H_a), 2.48 (br, 2H, 7(7′)-H_b), 3.41 (br, 2H, 3,3′-(4,4′)-H), 4.76 (br, 2H, 4,4′(3,3′)-H), 5.00 (br, 2H, 2,2′(5,5′)-H), 6.11 (br, 2H, 5,5′(2,2′)-H), 7.32 (br, 1H, 18-H), 7.53 (br, 2H, 17(19)-H), 7.66 ppm (d, $^3J_{H,H}$ = 6.9 Hz, 1H, 16-H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ = 25.1 (s, C6(6′)), 29.4 (s, C(CH_3)$_3$), 29.9 (s, C(CH_3)$_3$), 34.6 (d, $^1J_{C,P}$ = 15.9 Hz, *C*-(CH_3)$_3$), 35.7 (d, $^1J_{C,P}$ = 15.1 Hz, *C*(CH_3)$_3$), 38.7 (d, $^1J_{C,P}$ = 22.9 Hz, C7(7′)), 76.0 (s, C14(14′)), 92.0 (s, C2,2′(5,5′)), 94.2 (s, C2,2′(5,5′)), 94.8 (s, C15-(15′), 96.5 (s, C3,3′(4,4′)), 100.9 (s, C3,3′(4,4′)), 110.5, 112.6, 115.3, 116.9 (8×CN), 115.4 (s, C1(1′)), 123.4 (s, C13a(13a′)), 127.8 (s, C17(19)), 130.2 (s, C18), 135.9 (s, C16), 178.9 (s, C13(13′)), 212.4 ppm (s, C12(12′)); ^{31}P NMR ($CDCl_3$, 161 MHz): δ = 96.3 ppm (s); minor conformation: ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.72 (br, 18H, C(CH_3)$_3$), 1.30 (br, 18H, C(CH_3)$_3$), 5.25 (br, 1H, 5(2)-H), 5.65 (br, 1H, 3(4)-H), 5.70 (br, 1H, 4(3)-H), 6.21 ppm (br, 1H, 2(5)-H); MS (ESI, acetonitrile): *m*/*z* (%) = 653 (3) [*M*−$C_{16}H_{22}$NNiP]$^+$, 612 (38) [*M*−$C_{18}H_{25}N_2$NiP]$^+$, 566 (100) [*M*−$C_{21}H_{25}N_4$NiP+H_2O]$^+$, 549 (25) [*M*−$C_{21}H_{24}N_4$NiP]$^+$, 336 (31) [*M*−$C_{37}H_{30}N_8$NiP+CH_3CN]$^+$.

Crystallographic Data

8: Empirical formula $C_{16}H_{26}F_3NiO_3PS$, formula weight 445.11 g mol^{-1}, monoclinic, $P2_1/c$ (No. 14), a = 9.431(2), b = 13.919(4), c = 15.115(3) Å, α = 90.00, β = 101.63(3), γ = 90.00°, V = 1943.4(8) Å^3, Z = 4, d_{calcd} = 1.521 g cm^{-3}, F(000) = 928, μ = 1.228 mm^{-1}, crystal size 0.12×0.07×0.03 mm, stoe IPDS area detector diffractometer, T = 300(2) K, λ ($Mo_{K\alpha}$) = 0.71073 Å, θ_{min} = 2.01, θ_{max} = 26.24°, $-11 \le h \le 11$, $-17 \le k \le 17$, $-18 \le l \le 18$, absorption correction: none, extinction correction: none, 15553 reflections collected, unique 3858 (R(int) = 0.5061), observed 508 ($I > 2\sigma$(I), R(int) = 0.052), completeness to θ = 26.2° or 100 %, refinement by full-matrix least-squares on F^2, data 3858, 146 parameters, GOF = 0.451, final R indices ($I > 2\sigma(I)$), $R1$ = 0.3263, $wR2$ = 0.1903, R indices (all data), $R1$ = 0.3263, $wR2$ = 0.1903, largest difference peak/hole 0.24 and −0.36 e Å^{-3}.

13: Empirical formula $C_{16}H_{29}NiP$, formula weight 311.07, hexagonal, $P6_1$ (No. 169), a = 8.967(1), b = 8.967(1), c = 36.131(4) Å, α = 90.00, β = 90.00, γ = 120.00°, V = 2516.0(5) Å^3, Z = 6, d_{calcd} = 1.232 g cm^{-3}, F(000) = 1008, μ = 1.236 mm^{-1}, crystal size 0.25×0.07×0.04 mm, stoe IPDS area detector diffractometer, T = 300(2) K, λ ($Mo_{K\alpha}$) = 0.71073 Å, θ_{min} = 2.62, θ_{max} = 20.95°, $-8 \le h \le 8$, $-8 \le k \le 8$, $-35 \le l \le 35$, completeness to θ = 20.95° or 99 %, absorption correction: none, extinction correction: none, 18505 reflections collected, 793 unique (R(int) = 0.1887), 1745 observed ($I > 2\sigma(I)$), 83 parameters, refinement by full-matrix least-squares on F^2, GOF = 1.141, overall 0.852, final R indices ($I > 2\sigma(I)$): $R1$ = 0.0474, $wR2$ = 0.0707, R indices (all data): $R1$ = 0.1196, $wR2$ = 0.0806, absolute structure parameter 0.06(4), largest difference peak/hole 0.34 and −0.71 e Å^{-3}.

15: Empirical formula $C_{24}H_{33}NiP$, formula weight 411.18 g mol^{-1}, orthorhombic, *Pccn* (No. 56), a = 14.645(3), b = 17.867(4), c = 17.329(5) Å, α = 90.00, β = 90.00, γ = 90.00°, V = 4534.3(19) Å^3, Z = 8, d_{calcd} = 1.205 g cm^{-3}, F(000) = 1760, μ = 0.931 mm^{-1}, crystal size 0.67×0.63×0.52 mm, Stoe IPDS area detector diffractometer, T = 300(2) K, λ ($Mo_{K\alpha}$) = 0.71073 Å, θ_{min} = 2.15, θ_{max} = 24.15°, $-16 \le h \le 16$, $-20 \le k \le 20$, $-19 \le l \le 19$, absorption correction: none, extinction correction: none, 49417 reflections collected, 3555 unique (R(int) = 0.0540), completeness to θ = 24.2 or 99.1 %, refinement by full-matrix least-squares on F^2, data 3555, 235 parameters, GOF = 1.218, final R indices ($I > 2\sigma(I)$): $R1$ = 0.0436, $wR2$ = 0.0952, R indices (all data): $R1$ = 0.0624 , $wR2$ = 0.0984, largest difference peak/hole 0.33 and −0.30 e Å^{-3}.

CCDC-632851 (**8**), -632850 (**13**), and -632849 (**15**) contain the supplementary crystallographic data (without structure factors) for this paper. These data can be obtained free of charge from the Cambridge Crystallography Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk) or at www.cam.ac.uk/data_request/cif.

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