Dynamic Properties of Methyl(trimethylphosphane)nickel Complexes Containing (2-Diphenylphosphanyl)phenylamido Ligands

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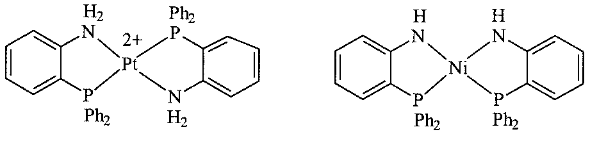
Keywords: Solution dynamics / Nickel / Coordination numbers 4 and 5 / Structure elucidation

P,N-chelates of nickel $NiCl[2\text{-}(Ph_2P)C_6H_4NR](PMe_3)$ (**1**: R = H; **2**: R = $SiMe_3$) have been obtained from $NiCl_2(PMe_3)_2$ and $2\text{-}(Ph_2P)C_6H_4NRLi$. Reaction with MeLi affords methylnickel compounds $NiMe[2\text{-}(Ph_2P)C_6H_4NR](PMe_3)$ (**3**: R = H; **4**: R = Me; **5**: R = $SiMe_3$). By the same route $NiMe[2\text{-}(R^1R^2P)C_6H_4NR](PMe_3)$ (**6**: $R^1 = R^2 = CHMe_2$) was synthesized. Solutions in THF contain *cis* and *trans* isomers of square-planar complexes, and dynamic NMR spectroscopy shows dissociation of trimethylphosphane to be more rapid in the *trans* isomers. In a crystal of **5** the molecular structure is *cis*-**5**. Out of these complexes only **3** and **4** add trimethylphosphane to form pentacoordinate compounds $NiMe[2\text{-}(Ph_2P)C_6H_4NR](PMe_3)_2$ (**7**, **8**) in the crystal as shown by the molecular structure of **7** while in THF equilibria **7** ⇄ *cis*-**1** and **8** ⇄ *cis*-**2** are observed by NMR spectroscopy. The same solution properties are found with $NiMe[2\text{-}(R^1R^2P)C_6H_4NR](PMe_3)_2$ (**9**: $R^1 = CMe_3$, $R^2 = Ph$).

Introduction

A well-known strategy to avoid a bridging coordination mode in transition metal amides is the use of chelating ligands. As a convenient anchoring group the 2-(diphenylphosphanyl) group induces P,N-chelating systems to form five-membered metallacyles. Usually these are derived from 2-(diphenylphosphanyl)aniline which is isoelectronic with P,O-chelating 2-(diphenylphosphanyl)phenol and because of its potential in homogeneous catalysis of olefin reactions merits further investigation. 2-(Diphenylphosphanyl)aniline has been shown by Cooper et al.[1] to form mononuclear bis(chelate) compounds of platinum and nickel acting either as a neutral or as an anionic 4-electron donor (Scheme 1).



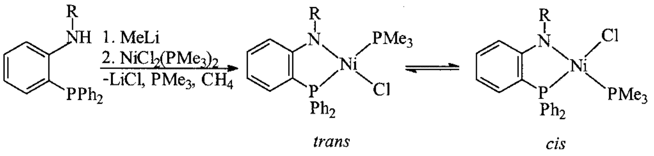
trans-bis(amino)platinum(II) *cis*-bis(amido)nickel(II)

Scheme 1. Square-planar bis(P,N-chelates)

2-(Diphenylphosphanyl)-*N*-methylanilido compounds of rhodium(I) and iridium(I) have been investigated by Dahlenburg et al.,[2] while 2-(diphenylphosphanyl)-*N*,*N*-dimethylaniline in penta- and tetracoordinate complexes of nickel(II) with added Et_2AlCl turns out to be a catalyst in the oligomerization of propene as described by Corain et al.[3]. As a model of a growing alkylmetal chain we have synthesized some methylnickel complexes containing P,N-chelating and trimethylphosphane ligands and report here on molecular structures and dynamic properties in solution.

Results and Discussion

N-Lithiated 2-(diphenylphosphanyl)anilines react with *trans*-$NiCl_2(PMe_3)_2$ [Equation (1)] to afford the chloronickel complexes **1** and **2** as green solids which are sparingly soluble in pentane or ether.



trans *cis*

1: R = H
2: R = $SiMe_3$

(1)

The ^{31}P NMR spectrum obtained from a THF solution of **1** or **2** at 233 K shows four doublet resonances. The pair containing the large P,P coupling is assigned to *trans*-**1** (62%) and *trans*-**2** (66%), while the pair showing the small P,P coupling is due to *cis*-**1** (38%) and *cis*-**2** (34%), respectively. Similar mixtures of isomers have been observed with related cationic palladium complexes.[4]

Added trimethylphosphane accelerates the exchange of ligands but does not alter the green color of these solutions

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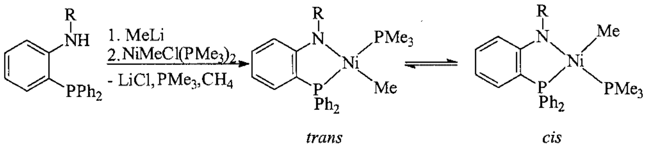
and thereby indicates the absence of a pentacoordinate compound. Addition of a second mol-equiv. of LiMe or use of *trans*-NiMeCl(PMe$_3$)$_2$ as a reactant [Equation (2)] furnishes the corresponding methylnickel compounds.

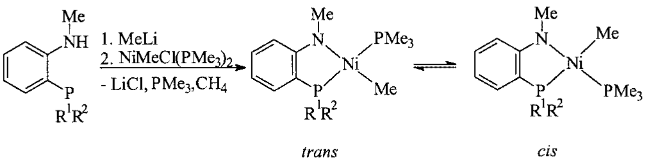


3: R = H
4: R = Me
5: R = SiMe$_3$

(2)

The reaction mixture displays a deep red color, while removal of THF solvent together with 1 mol-equiv. of trimethylphosphane during workup causes a change to orange-yellow, finally yielding orange solids **3−5**. The microcrystalline compounds are highly hygroscopic and under argon decompose above 122 °C, 105 °C, and 83 °C, respectively.

Using 2-(diisopropylphosphanyl)-*N*-methylaniline in a similar synthesis [Equation (3)] affords red crystals of **6** that decompose above 104 °C. NMR spectra of THF solutions of **3−6** again each display a double set of the expected resonances which are assigned to *cis* and *trans* isomers. In particular, NiCH$_3$ protons opposite to the chelating ^{31}P donor resonate between δ = −0.82 and −0.77 ppm with unresolved *trans* coupling ($_{cis}{}^3J_{P,H}$ = 4.5−6.1 Hz) while for those opposite to the amide donor at δ = −0.04(3) ppm a doublet of doublets pattern is observed ($^3J_{P,H}$ = 3.8−4.1 Hz). In toluene solution the *trans* isomers are observed as the dominant species (> 95%).



6: R^1 = R^2 = isopropyl

(3)

The ^{31}P NMR spectra in THF show a large coordination chemical shift of the chelate-P nucleus by 52 ppm to low field and a resonance for the coordinated trimethylphosphane ligand at δ ≈ −2 ppm. Surprisingly, the *cis* and *trans* isomers show different behavior at variable temperatures. Only the *cis* isomers continue to display a doublet of doublets ($^2J_{P,P}$ ≈ 30 Hz) between 298 and 213 K (Figure 1) while the large *trans* coupling ($^2J_{P,P}$ ≈ 300 Hz) is attained in the low-temperature limit. Upon warming, both doublet resonances of *trans*-**3−6** collapse to singlets caused by incipient dissociation of trimethylphosphane. Therefore, the slightly shifted broad singlet at δ = −5 ppm (298 K) must be regarded as an average of rapidly exchanging free and coordinated trimethylphosphane which also involves the pentacoordinate species (see below).

Single crystals of **5** obtained from pentane when subject to an X-ray diffraction experiment were shown to consist of *cis*-**5** (Figure 2). The unit cell contains two molecules that differ mainly in the rotational position of a phenyl substituent. The nickel atom is located in a square-planar arrangement of ligand functions. Bond lengths C−Ni and N−Ni are as usual[5] but opposite N,P and C,P donor atoms deviate from linearity by 10 and 20°, respectively. The chelate bond Ni−P1 is by 8 pm longer than Ni−P2 due to the

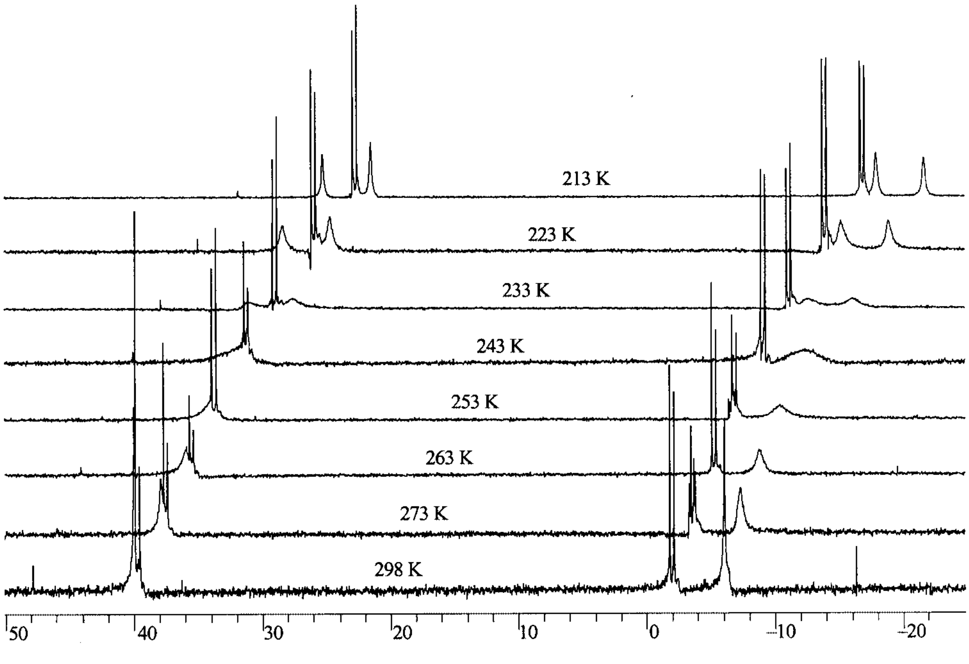


Figure 1. ^{31}P NMR spectra of **3** (THF, 213−298K)

larger *trans* influence of the NiMe group relative to the amide donor. The Me_3Si group is clearly oriented above the plane of the metallacycle.

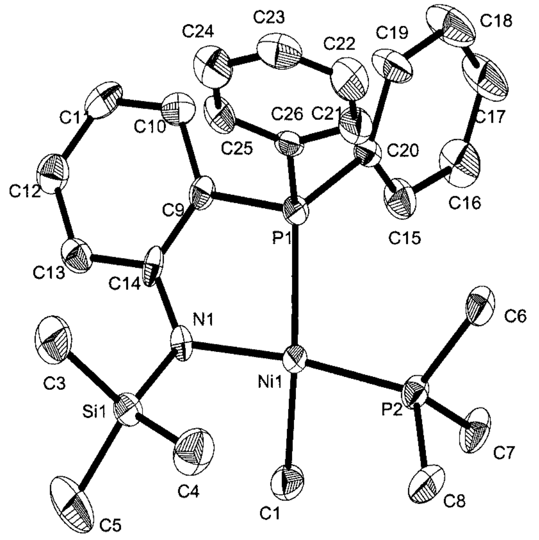


Figure 2. Molecular structure of *cis*-**5** (ORTEP plot with hydrogen atoms omitted); selected bond lengths [Å] and angles [°]: Ni−C1 1.971(11), Ni−N 1.956(8), Ni−P1 2.219(3), Ni−P2 2.124(3), P1−C9 1.814(10), C9−C14 1.387(15), C14−N 1.367(14), N−Si 1.731(8); N−Ni−P2 170.0(3), N−Ni−P1 84.0(3), C1−Ni−P1 160.8(4), N−Ni−C1 91.6(4), P1−Ni−P2 102.26(11), C1−Ni−P2 84.9(4), C9−P1−Ni 96.3(3), C14−N−Ni 117.6(6), Si−N−Ni 115.8(5), C14−N−Si 123.6(6)

Added trimethylphosphane makes **3** and **4** better soluble in pentane and causes a deep red color. Upon cooling, dark red crystals of **7** and **8** are isolated that show an even better thermal stability than their parent complexes reminding one of the pair $NiMe_2(PMe_3)_2$ and $NiMe_2(PMe_3)_3$.[6] Only **6** does not change color under these conditions and is recovered unchanged. Analytical and spectroscopic data are consistent with pentacoordinate compounds **7** and **8**. In solution dissociation of the ligands is excessive, and in ^{31}P NMR experiments a low-temperature limit of ligand motions was only attained with **7** revealing the coordination geometry. A doublet at $\delta = -16$ ppm (2 P) for trimethylphosphane and a triplet at $\delta = 23$ ppm for the PPh_2 group with $^2J_{P,P} = 192$ Hz are consistent with all three phosphorus donor atoms in equatorial sites leaving methyl and amide groups in axial positions of a trigonal bipyramid.

The molecular structure (Figure 3) confirms the configuration of **7** as derived from spectroscopic data. The nickel atom is centered in a trigonal bipyramid with axial C and N and three equatorial P donor atoms. Bond lengths are not notably different from those in *cis*-**5**, and the chelate bite angle [P1−Ni−N 85.60(13)°] is only slightly larger than in *cis*-**5** [P1−Ni−N 84.0(3)°]. A difference is recognized in a trigonal-planar arrangement of bonds to N in **7** (sum of angles 359.7°) as compared with a more pyramidal geometry in *cis*-**5** (sum of angles 357.0°). Interestingly, the sum of internal angles in the metallacycle of **7** (539.7°) is closer to the value of a regular pentagon (540°) than in *cis*-**5** (530.0°) suggesting a better fit of the former and a slight thermodynamic advantage for the pentacoordinate complex molecule.

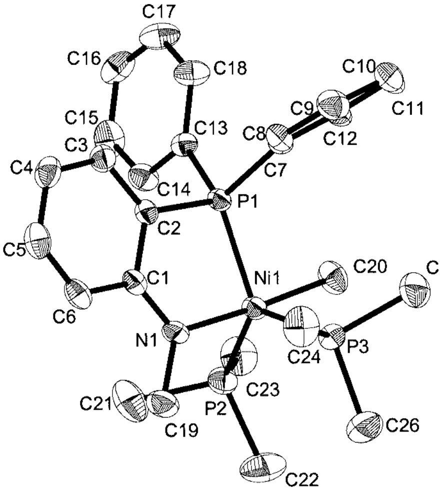
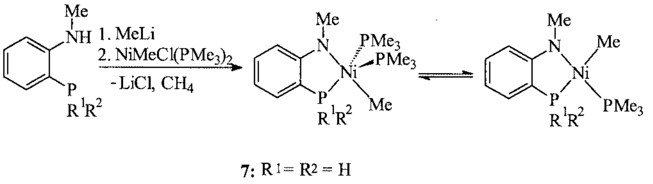


Figure 3. Molecular structure of **7** (ORTEP plot with hydrogen atoms omitted); selected bond lengths [Å] and angles [°]: Ni−C20 1.996(6), Ni−N 1.974(4), Ni−P1 2.202(2), Ni−P2 2.224(2), Ni−P3 2.253(2), N−C1 1.452(6), N−C19 1.452(6), C1−C2 1.423(7); N−Ni−C20 176.7(3), P1−Ni−P2 125.90(6), P1−Ni−P3 110.71(6), P2−Ni−P3 123.36(7), P1−Ni−N 85.60(13), P1−Ni−C20 91.1(2), Ni−N−C1 120.9(3), C1−N−C19 116.5(4), Ni−N−C19 122.3(3)

A prochiral P-donor function was introduced using 2-[*tert*-butyl(phenyl)phosphanyl]-*N*-methylaniline as a prechelate reactant [Equation (4)]. The red crystals of pentacoordinate **9** are highly soluble in pentane and under argon decompose above 115 °C.



7: $R^1 = R^2 = H$
8: $R^1 = R^2 = Me$
9: $R^1 = Ph$, $R^2 = CMe_3$

(4)

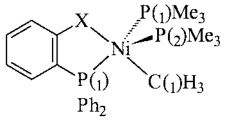
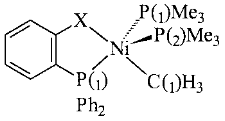
One bulky alkyl substituent in the 2-(phosphanyl) group does not interfere with the reversible uptake of trimethylphosphane. With **9** we have not been able to isolate a 16-VE species in an analytically pure state.

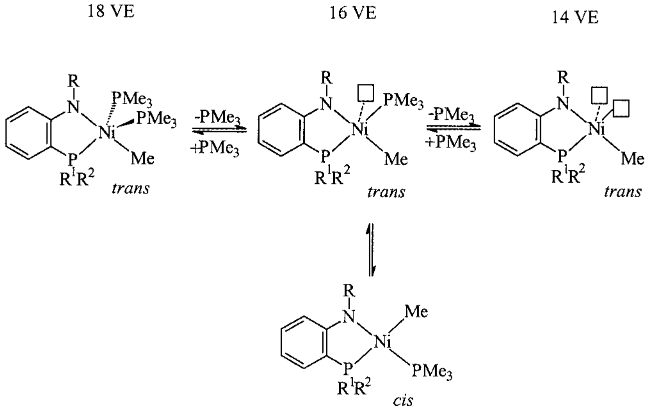
A close structural relationship between **8** and [2-(diphenylphosphanyl)phenolato-*O*,*P*]methylbis(trimethylphosphane)nickel[7] is found in agreement with expectation for isoelectronic molecules (Table 1).

Ligand mobility in P,N-chelates of nickel appears to be generally higher than in P,O-chelates, but only the first dissociation step (Scheme 2) could be demonstrated by experiment.

While removal of the second trimethylphosphane ligand was achieved with P,O-chelating ligands by formation of μ_2-

Table 1. Structural relations between isoelectronic P,O and P,N compounds of nickel(II)

	 X = O[7]	 X = NMe (**8**)
Selected bond lenghts [pm]:		
Ni−C(1)	198.1(5)	199.6(6)
Ni−P(1)	219.1(2)	220.2(2)
Ni−P(2)	224.5(2)	225.3(2)
Ni−P(3)	222.4(2)	222.4(2)
Ni−X	198.4(3)	197.4(4)
Selected bond angles [°]:		
X−Ni−C(1)	177.7(2)	176.7(3)
X−Ni−P(1)	86.35(10)	85.60(13)
P(1)−Ni−P(3)	125.16(6)	125.90(6)
P(1)−Ni−P(2)	114.02(6)	110.71(6)
P(3)−Ni−P(2)	120.71(7)	123.36(7)
Σ five-membered metallacycle [°]:	538.8	539.7



Scheme 2. Dynamic coordination in methylnickel P,N-chelates

O-bridged dinuclear complexes,[8] our attempts to remove the last trimethylphosphane ligand from the metal atom by favoring a bridging coordination mode of the amide function met with thermal decomposition (in boiling toluene). However, this result does not exclude a 14-electron species as an intermediate providing still another vacant coordination site for substrate binding.

Therefore, the tetracoordinate complexes **3−5** as prime candidates were examined with respect to catalytic activity in ethene oligomerization under otherwise same conditions as with the isoelectronic and highly active P,O-chelates.[7] A toluene solution (80 mL) containing 0.1 mmol of complex was kept in a steel autoclave under 50 bar of ethene at 80 °C. No drop of pressure was observed within 12 h which corresponds with no activity.

Conclusion

Methyl(trimethylphosphane)nickel complexes of P,N-chelating 2-(phosphanyl)anilines can be smoothly synthesized from convenient starting compounds as thermally stable materials. Solution dynamics of ligand motions and solvent-dependent equilibria of square-planar *cis* and *trans* isomers are novel and characteristic properties when compared with isoelectronic P,O-chelates. Rapid addition and dissociation of trimethylphosphane exclusively involve equatorial positions of a trigonal bipyramid with axial methyl and N-donor groups. Replacing an oxygen by a nitrogen donor atom in five-membered metallacycles of nickel brings about gross electronic changes whereby catalytic activity in oligomerization of ethene is completely lost. A coarse tuning by electronic effects of substituents attached to the metallacycle would be necessary to recover such activity.

Experimental Section

General Procedures and Materials: All air-sensitive and volatile materials were handled using standard vacuum techniques and were kept under argon. Microanalyses: Kolbe Microanalytical Laboratory, Mülheim/Ruhr, FRG. Melting points/decomposition temperatures: Sealed capillaries, uncorrected values. Chemicals (Merck/Schuchardt) were used as purchased. Literature methods were applied in the preparation of NiCl$_2$(PMe$_3$)$_2$, NiMeCl(PMe$_3$)$_2$,[6] 2-(diphenylphosphanyl)aniline,[9] 2-(diphenylphosphanyl)-*N*-methylaniline, 2-(diisopopylphosphanyl)aniline[10] and 2-[*tert*-butyl(phenyl)phosphanyl]-*N*-methylaniline.[11] IR: Nujol mulls between KBr discs, Bruker spectrophotometer type FRA

106. ^{1}H and ^{13}C NMR spectra (300 MHz and 75 MHz, respectively) were recorded with a Bruker ARX-300 spectrometer, ^{31}P NMR spectra (81 MHz) with a Bruker AM-200 instrument. ^{13}C and ^{31}P resonances were obtained with broad-band proton decoupling.

2-(Diphenylphosphanyl)-*N*-(trimethylsilyl)aniline: 2-(Diphenylphosphanyl)aniline (1.20 g, 4.32 mmol) in diethyl ether (80 mL) was combined with 1.6 M BuLi solution in hexane (2.7 mL, 4.32 mmol) and kept at 20 °C for 30 min. Chlorotrimethylsilane (470 mg, 4.32 mmol) was added, and after 16 h, LiCl was filtered off and the solution concentrated to a volume of 40 mL. Cooling to 4 °C afforded white crystals. Yield 1.10 g (73%); m.p. 76−77 °C. ^{1}H NMR (300 MHz, [D$_8$]THF): δ = 0.01 (s, 9 H, SiCH$_3$), 4.30 (d, $^{4}J_{\mathrm{P,H}}$ = 9.3 Hz, 1 H, NH), 6.45 (dt, ^{3}J = 7.6, ^{4}J = 0.7 Hz, 1 H, CH), 6.65 (m, 2 H, CH), 7.01 (dt, ^{3}J = 6.5, ^{4}J = 1.5 Hz, 2 H, CH), 7.13−7.20 (m, 10 H, CH) ppm. ^{13}C NMR (75 MHz, [D$_8$]THF): δ = −1.89 (s, CH$_3$), 114.7 (s, CH), 116.9 (d, $^{4}J_{\mathrm{P,C}}$ = 2.2 Hz, CH), 120.9 (d, $^{3}J_{\mathrm{P,C}}$ = 5.6 Hz, C), 127.4 (s, CH), 127.6 (d, $^{2}J_{\mathrm{P,C}}$ = 7.8 Hz, CH), 129.1 (s, CH), 132.5 (d, $^{1}J_{\mathrm{P,C}}$ =18.7 Hz, CH), 133.7 (d, $^{3}J_{\mathrm{P,C}}$ = 5.5 Hz, C), 135.1 (d, $^{2}J_{\mathrm{P,C}}$ = 7.7 Hz, C), 150.1 (d, $^{1}J_{\mathrm{P,C}}$ = 19.5 Hz, CH) ppm. ^{31}P NMR (81 MHz, [D$_8$]THF): δ = −10 (s) ppm. C$_{21}$H$_{24}$NPSi (349.5): calcd. C 72.17, H 6.92, N 4.01; found C 72.45, H 6.63, N 3.95.

2-[*tert*-Butyl(phenyl)phosphanyl]-*N*-methylaniline: This prechelate ligand was obtained in a procedure given for 2-(diphenylphosphanyl)-*N*-methylaniline[10] starting from *N*-methylaniline and chloro(*tert*-butyl)phenylphosphane. Yield 52%, yellow oil; b.p. 189−190 °C/7 mbar. IR (Nujol, 4000−400 cm^{-1}): ṽ = 3349 vs (νN−H), 3052 m, 2926 m (νH−C=), 2810 (νNC−H), 1587 s, 1569 s (νC=C), 1518 s, 1454 s, 1435 s, 1419 m, 1312 m (δ$_{\mathrm{as}}$PCH), 1289 m (δ$_{\mathrm{s}}$PCH), 1165 m, 1089 w, 1046 w, 1029 vw, 999 vw, 912 vw, 746 vs, 729 w, 698 vs (γC−H), 515 m, 496 m, 482 m. ^{31}P NMR (81 MHz, CD$_2$Cl$_2$, 296 K): δ = −16 (s) ppm.

Chloro[2-(diphenylphosphanyl)anilido-*N*,*P*](trimethylphosphane)nickel (1): 2-(Diphenylphosphanyl)aniline (750 mg, 2.70 mmol) in 50 mL of THF was combined at −70 °C with 1.6 M MeLi in diethyl ether (1.7 mL, 2.70 mmol), and this solution was added dropwise at −70 °C to NiCl$_2$(PMe$_3$)$_2$ (762 mg, 2.70 mmol) in 50 mL of THF causing the red color to turn green. The mixture was warmed to 20 °C and concentrated to dryness in vacuo. The solid residue was extracted with three 80-mL portions of diethyl ether through a glass-sinter disc (G3) and the green solution cooled to 4 °C to afford green crystals. Yield 710 mg (59%); m.p. 95−96 °C (dec.). IR (Nujol): ṽ = 3377 cm^{-1} (N−H). ^{1}H NMR (200 MHz, [D$_8$]THF, 233 K): *cis*-**1** (63%): δ = 1.07 (d, $^{2}J_{\mathrm{P,H}}$ = 10.1, 9 H, PCH$_3$), 3.65 (s, 1 H, NH), 5.91 (m, 1 H, CH), 6.22 (m, 1 H, CH), 6.67 (m, 1 H, CH), 7.15 (m, 1 H, CH), 7.45−7.55 (m, 6 H, CH), 7.82−7.86 (m, 4 H, CH); *trans*-**1** (37%): δ = 1.33 (d, $^{2}J_{\mathrm{P,H}}$ = 10.0 Hz, 9 H, PCH$_3$), 4.59 (s, 1 H, NH), 6.10 (m, 1 H, CH), 6.37 (m, 1 H, CH), 6.67 (m, 1 H, CH), 7.01 (m, 1 H, CH), 7.15 (m, 1 H, CH), 7.31 (m, 1 H, CH), 7.55−7.59 (m, 6 H, CH), 7.98−8.07 (m, 4 H, CH) ppm. ^{31}P NMR (81 MHz, [D$_8$]THF, 233 K): *cis*-**1** (63%): δ = −9 (d, $^{2}J_{\mathrm{P,P}}$ = 89 Hz, 1 P, PCH$_3$), 52 (d, $^{2}J_{\mathrm{P,P}}$ = 89 Hz, 1 P, PC$_6$H$_5$); *trans*-**1** (37%): δ = −9 (d, $^{2}J_{\mathrm{P,P}}$ = 347 Hz, 1 P, PCH$_3$), 31 (d, $^{2}J_{\mathrm{P,P}}$ = 347 Hz, 1 P, PC$_6$H$_5$) ppm. C$_{21}$H$_{24}$ClNNiP$_2$ (445.0): calcd. C 56.49, H 5.42, N 3.14; found C 56.68, H 5.50, N 3.05.

Chloro[2-(diphenylphosphanyl)-*N*-(trimethylsilyl)anilido-*N*,*P*](trimethylphosphane)nickel (2): 2-(Diphenylphosphanyl)-*N*-(trimethylsilyl)aniline (840 mg, 2.40 mmol) in 50 mL of THF was combined at −70 °C with 1.6 M MeLi in diethyl ether (1.5 mL, 2.40 mmol), and this solution was added as above to NiCl$_2$(PMe$_3$)$_2$ (677 mg, 2.40 mmol) in 50 mL of THF causing the red color to turn green. The mixture was warmed to 20 °C, stirred for 3 h, and concentrated to dryness in vacuo. The residue was extracted with three 80-mL portions of diethyl ether and the green solution cooled to 4 °C to afford green rectangular crystals. Yield 745 mg (60%); m.p. 108−109 °C (dec.). ^{1}H NMR (200 MHz, [D$_8$]THF, 233 K): *cis*-**2** (66%): δ = 0.02 (s, 9 H, SiCH$_3$), 1.06 (d, $^{2}J_{\mathrm{P,H}}$ = 9.2 Hz, 9 H, PCH$_3$), 5.93 (m, 1 H, CH), 6.23 (m, 1 H, CH), 6.71 (m, 2 H, CH), 6.83 (m, 2 H, CH), 7.41−7.49 (m, 6 H, CH), 7.76−7.85 (m, 4 H, CH); *trans*-**2** (34%): δ = 0.06 (s, 9 H, SiCH$_3$), 1.39 (d, $^{2}J_{\mathrm{P,H}}$ = 11.1 Hz, 9 H, PCH$_3$), 6.15 (m, 1 H, CH), 6.40 (m 1 H, CH), 7.05 (m, 2 H, CH), 7.49−7.58 (m, 6 H, CH), 8.00−8.02 (m, 4 H, CH) ppm. ^{31}P NMR (81 MHz, [D$_8$]THF, 233 K): *cis*-**2** (66%): δ = −8 (d, $^{2}J_{\mathrm{P,P}}$ = 88 Hz, 1 P, PCH$_3$), 52 (d, $^{2}J_{\mathrm{P,P}}$ = 88 Hz, 1 P, PC$_6$H$_5$); *trans*-**2** (34%): δ = −9 (d, $^{2}J_{\mathrm{P,P}}$ = 348 Hz, 1 P, PCH$_3$), 32 (d, $^{2}J_{\mathrm{P,P}}$ = 348 Hz, 1 P, PC$_6$H$_5$) ppm. C$_{24}$H$_{32}$ClNNiP$_2$Si (517.1): calcd. C 55.57, H 6.22, N 2.70, P 11.94; found C 55.18, H 5.78, N 2.66, P 11.95.

[2-(Diphenylphosphanyl)anilido-*N*,*P*](methyl)(trimethylphosphane)nickel (3): 2-(Diphenylphosphanyl)aniline (910 mg, 3.28 mmol) in 70 mL of diethyl ether was combined at −70 °C with 1.6 M MeLi in diethyl ether (2.1 mL, 3.28 mmol), and this solution was added dropwise at −70 °C to NiMeCl(PMe$_3$)$_2$ (860 mg, 3.28 mmol) in 50 mL of diethyl ether. The mixture was warmed to 20 °C and concentrated to dryness in vacuo. The resulting orange solid was extracted with three 70-mL portions of fresh diethyl ether and the solution concentrated at 20 °C to afford orange crystals of **3** (358 mg). From the mother liquor at −27 °C a light yellow solid (632 mg) was obtained which consisted of **3** only (NMR). Combined yields 990 mg (71%); m.p. 105−106 °C (dec.). IR (Nujol): ṽ = 3348 cm^{-1} (N−H). ^{1}H NMR (300 MHz, [D$_8$]THF): *cis*-**3** (60%): δ = −0.07 (dd, $_{trans}{}^{3}J_{\mathrm{P,H}}$ = 4.1, $_{cis}{}^{3}J_{\mathrm{P,H}}$ = 8.8 Hz, 3 H, NiCH$_3$), 1.29 (d, $^{2}J_{\mathrm{P,H}}$ = 3.6 Hz, 9 H, PCH$_3$), 3.44 (s, 1 H, NH), 5.85 (m, 1 H, CH), 6.64−6.67 (m, 1 H, CH), 6.85 (t, ^{3}J = 6.9 Hz, 1 H, CH), 7.31 (m, 1 H, CH), 7.33−7.36 (m, 6 H, CH), 7.62−7.67 (m, 4 H, CH); *trans*-**3** (40%): δ = −0.82 (d, $^{3}J_{\mathrm{P,H}}$ = 6.1 Hz, 3 H, NiCH$_3$), 1.09 (d, $^{2}J_{\mathrm{P,H}}$ = 8.6 Hz, 9 H, PCH$_3$), 3.06 (s, 1 H, NH), 5.88 (dd, ^{3}J= 7.0, ^{4}J= 1.4 Hz, 1 H, CH), 5.91 (dd, ^{3}J = 8.2, $^{4}J_{\mathrm{P,H}}$ = 5.0 Hz, 1 H, CH), 6.64−6.67 (m, 2 H, CH), 7.36−7.41 (m, 6 H, CH), 7.70−7.77 (m, 4 H, CH) ppm. ^{13}C NMR (75.4 MHz, [D$_8$]THF, 296 K): *cis*-**3** (60%): δ = 4.2 (dd, $^{2}J_{\mathrm{P,C}}$ = 33.8, $^{2}J_{\mathrm{P,C}}$ = 62.6 Hz, NiCH$_3$), 12.6 (d, $^{1}J_{\mathrm{P,C}}$ = 21.9 Hz, PCH$_3$), 108.8 (d, $^{3}J_{\mathrm{P,C}}$ = 6.2 Hz, C-2), 115.9 (d, $^{2}J_{\mathrm{P,C}}$ = 9.5 Hz, *m*-C), 128.9 (d, $^{2}J_{\mathrm{P,C}}$ = 9.3 Hz, *p*-C), 130.2 (s, C-5), 134.1 (d, $^{2}J_{\mathrm{P,C}}$ = 11.4 Hz, *o*-C), 134.3 (s, C-3), 134.7 (s, *i*-C), 134.9 s, C-6), 171.4 (d, $^{2}J_{\mathrm{P,C}}$ = 31.0 Hz, NC-1); *trans*-**3** (40%): δ = −16.8 (d, $^{2}J_{\mathrm{P,C}}$ = 24.1 Hz, NiCH$_3$), 16.3 (d, $^{1}J_{\mathrm{P,C}}$ = 28.9 Hz, PCH$_3$), 110.4 (d, $^{3}J_{\mathrm{P,C}}$ = 5.6 Hz, C-2), 114.8 (d, $^{3}J_{\mathrm{P,C}}$ = 3.0 Hz, C-5), 128.9 (d, $^{2}J_{\mathrm{P,C}}$ = 8.6 Hz, *m*-C), 130.4 (s, *p*-C), 132.6 (d, $^{2}J_{\mathrm{P,C}}$ = 10.2 Hz, *o*-C), 133.2 (s, C-3), 134.7 (s, C-4), 134.9 (s, *i*-C), 135.2 (s, C-6), 169.9 (d, $^{2}J_{\mathrm{P,C}}$ = 32.7 Hz, NC-1) ppm. ^{31}P NMR (81 MHz, [D$_8$]THF): *cis*-**1** (60%, 193 K): δ = −2 (d, $^{2}J_{\mathrm{P,P}}$ = 27 Hz, 1 P, PCH$_3$), 40 (d, $^{2}J_{\mathrm{P,P}}$ = 27 Hz, 1 P, PC$_6$H$_5$); *trans*-**3** (40%, 193 K): δ = −2 (d, $^{2}J_{\mathrm{P,P}}$ = 303 Hz, 1 P, PCH$_3$), 40 (d, $^{2}J_{\mathrm{P,P}}$ = 303 Hz, 1 P, PC$_6$H$_5$); *cis*-**1** (60%, 296 K): δ = −2 (d, $^{2}J_{\mathrm{P,P}}$ = 25 Hz, 1 P, PCH$_3$), 40 (d, $^{2}J_{\mathrm{P,P}}$ = 25 Hz, 1 P, PC$_6$H$_5$); *trans*-**3** (40%, 296 K): δ = −5 (s, 1 P, PCH$_3$), 37 (s, 1 P, PC$_6$H$_5$) ppm. C$_{22}$H$_{27}$NNiP$_2$ (425.1): calcd. C 62.01, H 6.38, N 3.28, P 14.53; found C 61.52, H 6.51, N 3.16, P 14.48.

[2-(Diphenylphosphanyl)-*N*-methylanilido-*N*,*P*](methyl)(trimethylphosphane)nickel (4): 2-(Diphenylphosphanyl)-*N*-methylaniline (970 mg, 3.32 mmol) in 50 mL of diethyl ether was combined at −70 °C with 1.6 M MeLi in diethyl ether (2.2 mL, 3.32 mmol), and this solution was added dropwise at −70 °C to $NiMeCl(PMe_3)_2$ (870 mg, 3.32 mmol) in 80 mL of diethyl ether. The orange-red mixture was warmed to 20 °C, filtered, and concentrated to dryness in vacuo. The resulting solid was washed with 5 mL of pentane and dried at 20 °C in vacuo to afford a yellow solid of **4** (1.18 g). Single orange crystals obtained from toluene were found suitable for X-ray diffraction. Yield 71%; m.p. 122−124 °C (dec.). ^{1}H NMR (300 MHz, $[D_8]THF$): *cis*-**4** (88%): δ = 0.13 (m, 3 H, $NiCH_3$), 1.15 (d, $^{2}J_{P,H}$ = 6.9 Hz, 9 H, PCH_3), 2.60 (s, 3 H, NCH_3), 5.89 (m, 1 H, CH), 6.15 (m, 1 H, CH), 6.62 (m, 1 H, CH), 6.84 (m, 1 H, CH), 7.39 (m, 6 H, CH), 7.59−7.73 (m, 4 H, CH); *trans*-**4** (12%): δ = −0.77 (m, 3 H, $NiCH_3$), 1.05 (d, $^{2}J_{P,H}$ = 8.9 Hz, 9 H, PCH_3), 2.80 (s, NCH_3) ppm. ^{13}C NMR (75.4 MHz, $[D_8]THF$, 296 K): *cis*-**4**: δ = 4.9 (m, $NiCH_3$), 14.5 (d, $^{1}J_{P,C}$ = 30.6 Hz, PCH_3), 35.2 (s, NCH_3), 108.4 (s, C-2), 108.7 (s, C-5), 127.1 (d, $^{1}J_{P,C}$ = 16.9 Hz, *m*-C), 127.4−131.1 (m, C-3/C-4), 131.7 (d, $^{1}J_{P,C}$ = 26.7 Hz, *o*-C), 132.2 (d, $^{2}J_{P,C}$ = 12.1 Hz, *p*-C), 153.6 (s, C-6) ppm. ^{31}P NMR (81 MHz, $[D_8]THF$, 233 K): *cis*-**4** (88%): δ = −1 (d, $^{2}J_{P,P}$ = 32 Hz, 1 P, PCH_3), 38 (d, $^{2}J_{P,P}$ = 32 Hz, 1 P, PC_6H_5); *trans*-**4** (12%): δ = −9 (d, $^{2}J_{P,P}$ = 329 Hz, 1 P, PCH_3), 34 (d, $^{2}J_{P,P}$ = 329 Hz, 1 P, PC_6H_5) ppm. $C_{22}H_{27}NNiP_2$ (425.1): calcd. C 62.76, H 6.64, N 3.18, P 14.07; found C 63.15, H 7.19, N 3.04, P 13.70.

[2-(Diphenylphosphanyl)-*N*-(trimethylsilyl)anilido-*N*,*P*](methyl)-(trimethylphosphane)nickel (5): 2-(Diphenylphosphanyl)-*N*-(trimethylsilyl)aniline (830 mg, 2.37 mmol) in 80 mL of diethyl ether was combined at −70 °C with 1.6 M MeLi in diethyl ether (1.5 mL, 2.40 mmol), and to the fluorescent solution was added at −70 °C solid $NiMeCl(PMe_3)_2$ (620 mg, 2.37 mmol) to form a deep red mixture. The mixture was warmed to 20 °C, stirred for 1 h, and concentrated to dryness in vacuo. The residue was extracted with two 70-mL portions of diethyl ether and the red solution cooled to −27 °C to afford deep orange crystals of **5** (732 mg). Yield 62%; m.p. 83−84 °C (dec.). ^{1}H NMR (300 MHz, $[D_8]THF$): *cis*-**5** (58%): δ = −0.01 (dd, $_{trans}{}^{3}J_{P,H}$ = 3.8 Hz, $_{cis}{}^{3}J_{P,H}$ = 8.8 Hz, 3 H, $NiCH_3$), 0.09 (s, 9 H, $SiCH_3$), 1.09 (d, $^{2}J_{P,H}$ = 4.1 Hz, 9 H, PCH_3), 5.86 (m, 1 H, CH), 6.55 (m, 1 H, CH), 6.75 (m, 1 H, CH), 7.25 (m, 1 H, CH), 7.31−7.35 (m, 6 H, CH), 7.64−7.70 (m, 4 H, CH); *trans*-**5** (42%): δ = 0.82 (d, $^{3}J_{P,H}$ = 4.5 Hz, 3 H, $NiCH_3$), 0.07 (s, 9 H, $SiCH_3$), 1.08 (d, $^{2}J_{P,H}$ = 8.6 Hz, 9 H, PCH_3), 5.88 (m, 1 H, CH), 6.19 (dd, ^{3}J = 8.0, ^{4}J = 4.7 Hz, 1 H, CH), 6.55−6.63 (m, 1 H, CH), 6.85 (m, 1 H, CH), 7.36−7.41 (m, 6 H, CH), 7.71−7.77 (m, 4 H, CH) ppm. ^{13}C NMR (75.4 MHz, $[D_8]THF$): *cis*-**5** (58%): δ = 1.6 (s, $SiCH_3$), 4.2 (m, $NiCH_3$), 12.7 (d, $^{1}J_{P,C}$ = 21.9 Hz, PCH_3), 110.8 (s, C-2), 115.9 (s, C-5), 129.3 (d, $^{2}J_{P,C}$ = 9.2 Hz, *m*-C), 133.2−134.6 (s, C-1, *o*-C, *p*-C), 135.0 (s, C-6), 172.3 (d, $^{2}J_{P,C}$ = 31.5 Hz, NC-1); *trans*-**5** (42%): δ = −16.9 (d, $^{2}J_{P,C}$ = 24.9 Hz, $NiCH_3$), 1.9 (s, $SiCH_3$), 16.1 (d, $^{1}J_{P,C}$ = 25.9 Hz, PCH_3), 111.2 (d, $^{3}J_{P,C}$ = 6.1 Hz, C-2), 114.8 (s, C-5), 129.0 (s, C-3), 130.5 (d, $^{2}J_{P,C}$ = 18.7 Hz, *o*-C), 132.7 (d, $^{2}J_{P,C}$ = 9.8 Hz, *m*-C), 133.2 (s, *p*-C), 134.1 (d, $^{2}J_{P,C}$ = 11.9 Hz, *i*-C), 134.7 (s, C-4), 135.2 (s, C-6), 171.2 (d, $^{2}J_{P,C}$ = 30.8 Hz, NC-1) ppm. ^{31}P NMR (81 MHz, $[D_8]THF$, 233 K) *cis*-**5** (58%): δ = 1 (d, $^{2}J_{P,P}$ = 27 Hz, 1 P, PCH_3), 40 (d, $^{2}J_{P,P}$ = 27 Hz, 1 P, PC_6H_5); *trans*-**5** (42%): δ = −3 (d, $^{2}J_{P,P}$ = 297 Hz, 1 P, PCH_3), 40 (d, $^{2}J_{P,P}$ = 297 Hz, 1 P, PC_6H_5) ppm. $C_{25}H_{35}NNiP_2Si$ (497.1): calcd. C 6.26, H 7.08, N 2.81, P 12.40; found C 60.36, H 6.75, N 2.78, P 12.15.

[2-(Diisopropylphosphanyl)-*N*-methylanilido-*N*,*P*](methyl)(trimethylphosphane)nickel (6): 2-(Diphenylphosphanyl)-*N*-methylaniline (780 mg, 3.49 mmol) in 50 mL of diethyl ether was combined at −70 °C with 1.6 M MeLi in diethyl ether (2.3 mL, 3.50 mmol), and to the yellow fluorescent solution was added solid $NiMeCl(PMe_3)_2$ (912 mg, 3.49 mmol). The mixture was warmed to 20 °C and concentrated to dryness in vacuo. The resulting orange solid was extracted with two 50-mL portions of pentane, and the combined solutions after repeatedly concentrating and cooling to −27 °C afforded red crystals of **6** (751 mg). Yield 58%; m.p. 104−105 °C (dec.). ^{1}H NMR (300 MHz, $[D_8]THF$, 296 K): *trans*-**6** (78%): δ = −0.65 (d, $^{3}J_{P,H}$ = 9.1 Hz, 3 H, $NiCH_3$), 1.00 (d, $^{2}J_{P,H}$ = 3.6 Hz, 18 H, PCH_3), 2.67 (s, 3 H, NCH_3), 5.82 (m, 1 H, CH), 5.89 (d, ^{3}J = 7.2 Hz, 1 H, CH), 6.57−6.63 (m, 2 H, CH), 7.22−7.27 (m, 6 H, CH), 7.46− 7.48 (m, 4 H, CH); *cis*-**6** (22%): δ = −0.07 (dd, $_{trans}{}^{3}J_{P,H}$ = 3.7, $_{cis}{}^{3}J_{P,H}$ = 6.5 Hz, 3 H, $NiCH_3$), 1.00 (br. s, 9 H, PCH_3), 2.48 (s, 3 H, NCH_3). ^{1}H NMR (300 MHz, $[D_8]$toluene): *trans*-**6** (> 98%): δ = 0.33 (dd, $^{3}J_{P,H}$ = 4.1 and 8.2 Hz, 3 H, $NiCH_3$), 1.00 (d, $^{2}J_{P,H}$ = 6.2 Hz, 9 H, PCH_3), 1.24 (br. d, $^{3}J_{P,H}$ = 7.1 Hz, 6 H, $PCHCH_3$), 1.28 (br. d, $^{3}J_{P,H}$ = 7.1 Hz, 6 H, $PCHCH_3$), 2.34 (m, 2 H, PCH), 2.98 (s, 3 H, NCH_3), 6.40 (t, ^{3}J = 7.1 Hz, 1 H, CH), 6.49 (dd, ^{3}J = 8.4, ^{4}J = 2.2 Hz, 1 H, CH), 7.12 (t, ^{3}J = 7.4 Hz, 1 H, CH), 7.31 (dt, ^{3}J = 7.1, $^{4}J_{P,H}$ = 1.4 Hz, 1 H, CH) ppm. ^{13}C NMR (75.4 MHz, $[D_8]THF$, 296 K): *trans*-**6**: δ = −14.3 (d, $^{2}J_{P,C}$ = 16.8 Hz, $NiCH_3$), 16.7 (d, $^{1}J_{P,C}$ = 7.6 Hz, PCH_3), 44.4 (s, N*C*H_3), 108.5 (s, C-2), 110.4 (d, $^{2}J_{P,C}$ = 12.5 Hz, 5-C), 128.9 (d, $^{2}J_{P,C}$ = 8.6 Hz, *m*-C), 129.4−131.9 (m, *p*-C/C-3), 133.3 (d, $^{2}J_{P,C}$ = 11.5 Hz, *o*-C), 134.4 (d, $^{2}J_{P,C}$ = 12.4 Hz, C-4), 135.3 (s, *i*-C), 139.8 (s, C-6) ppm. ^{31}P NMR (81 MHz, $[D_8]THF$, 193 K): *trans*-**6** (78%): δ = −11 (d, $^{2}J_{P,P}$ = 326 Hz, 1 P, PCH_3), 45 (d, $^{2}J_{P,P}$ = 297 Hz, 1 P, $PCHCH_3$); *cis*-**1** (22%): δ = −1 (d, $^{2}J_{P,P}$ = 25 Hz, 1 P, PCH_3), 45 (d, $^{2}J_{P,P}$ = 25 Hz, 1 P, $PCHCH_3$) ppm. ^{31}P NMR (81 MHz, $[D_8]$toluene): *trans*-**6** (> 98%): δ = −18 (d, $^{2}J_{P,P}$ = 327 Hz, 1 P, PCH_3), 40 (d, $^{2}J_{P,P}$ = 327 Hz, 1 P, $PCHCH_3$) ppm. $C_{17}H_{33}NNiP_2$ (371.1): calcd. C 54.87, H 8.94, N 3.76, P 16.65; found C 54.88, H 8.83, N 3.71, P 16.70.

[2-(Diphenylphosphanyl)anilido-*N*,*P*](methyl)bis(trimethylphosphane)nickel (7): 2-(Diphenylphosphanyl)aniline (810 mg, 2.92 mmol) in 50 mL of diethyl ether was combined at −70 °C with 1.6 M MeLi in diethyl ether (1.8 mL, 2.92 mmol), and this solution was added dropwise at −70 °C to $NiMeCl(PMe_3)_2$ (763 mg, 2.92 mmol) in 50 mL of diethyl ether. Workup proceeded as with **3**, and crystallization from 70 mL of pentane, containing excess PMe_3 (1.23 g, 16.1 mmol), afforded dark red crystals that were dried in vacuo at −5 °C for 10 min. Yield 790 mg of **7** (54%); m.p. 110−111 °C (dec.). IR (Nujol): $\tilde{\nu}$ = 3361 cm^{-1} (N−H). ^{1}H NMR (300 MHz, $[D_8]THF$, 296 K): *trans*-**7** (66%): δ = −0.75 (d, $^{3}J_{P,H}$ = 8.6 Hz, 3 H, $NiCH_3$), 1.00 (d, $^{2}J_{P,H}$ = 3.6 Hz, 18 H, PCH_3), 2.78 (NH 3,44s, 1 H, NH), 5.86 (m, 1 H, CH), 6.19 (dd, ^{3}J = 6.2, ^{4}J = 1.6 Hz, 1 H, CH), 6.66 (m, 1 H, CH), 6.85 (m, 1 H, CH), 7.30−7.38 (m, 6 H, CH), 7.64−7.74 (m, 4 H, CH); *cis*-**7** (34%): δ = −0.06 (m, 3 H, $NiCH_3$), 1.00 (d, $^{2}J_{P,H}$ = 3.6 Hz, 9 H, PCH_3), 3.44 (s, 1 H, NH), 5.88 (m, 1 H, CH), 6.20 (m, 1 H, CH) ppm. ^{13}C NMR (75.4 MHz, $[D_8]THF$, 296 K): *trans*-**7**: δ = −14.1 (m, $NiCH_3$), 16.7 (d, $^{1}J_{P,C}$ = 7.2 Hz, PCH_3), 45.1 (s, NCH_3), 108.5−135.4 (s, 10 C) ppm. ^{31}P NMR (81 MHz, $[D_8]THF$, 233 K): *trans*-**7** (66%): δ = −26 (br. s, 2 P, PCH_3), 27 (br. s, 1 P, PC_6H_5); *cis*-**7** (34%): δ = −1 (d, $^{2}J_{P,P}$ = 26 Hz, 1 P, PCH_3), 39 (d, $^{2}J_{P,P}$ = 26 Hz, 1 P, PC_6H_5) ppm. $C_{25}H_{35}NNiP_3$ (501.1): calcd. C 59.79, H 7.23, N 2.79, P 18.50; found C 58.80, H 7.39, N 2.74, P 18.33.

[2-(Diphenylphosphanyl)-*N*-methylanilido-*N*,*P*](methyl)bis-(trimethylphosphane)nickel (8). Method a: 2-(Diphenylphosphanyl)-*N*-methylaniline (845 mg, 2.90 mmol) in 70 mL of THF was combined at −70 °C with $NiMe_2(PMe_3)_3$ (920 mg, 2.90 mmol) in 80 mL of diethyl ether. Warming to 20 °C caused evolution of gas and a dark red color. After 3 h, the volatiles were removed in vacuo and the residue was extracted with 70 mL of pentane, containing excess PMe_3 (610 mg, 8.0 mmol). Cooling to −27 °C afforded dark red crystals of **8**: Yield 478 mg (32%). **Method b:** 2-(Diphenylphosphanyl)-*N*-methylaniline (770 mg, 2.64 mmol) in 70 mL of diethyl ether was combined at −70 °C with 1.6 M MeLi in diethyl ether (1.7 mL, 2.64 mmol), and to the yellow fluorescent solution was added NiMeCl(PMe$_3$)$_2$ (690 mg, 2.64 mmol) in 50 mL of diethyl ether. The deep red mixture was warmed to 20 °C and after 3 h concentrated to dryness in vacuo. The resulting solid was worked up as above affording crystals of **8**. Yield 912 mg (67%); m.p. 117−119 °C (dec.). ^{1}H NMR (300 MHz, [D$_8$]THF, 296 K): *trans*-**8** (79%): δ = −0.74 (d, $^3J_{P,H}$ = 10.1 Hz, 3 H, NiCH$_3$), 1.02 (d, $^2J_{P,H}$ = 4.8 Hz, 18 H, PCH$_3$), 1.24 (d, $^2J_{P,H}$ = 12.6 Hz, 9 H, PCH$_3$), 2.66 (s, 3 H, NCH$_3$), 5.95 (t, ^3J = 7.2 Hz, 1 H, CH), 6.12 (dd, $^4J_{P,H}$ = 5.0, ^3J = 8.5 Hz, 1 H, CH), 6.86 (dt, ^3J = 8.1, ^4J = 1.5 Hz, 1 H, CH), 7.22 (dt, ^3J = 7.4, ^4J = 1.5 Hz, 1 H, CH), 7.21−7.29 (m, 3 H, CH), 7.59−7.67 (m, 2 H, CH); *cis*-**8** (21%): δ = −0.07 (dd, $^3J_{P,H}$ = 4.2, $^3J_{P,H}$ = 8.2 Hz, 3 H, NiCH$_3$), 1.12 (d, $^2J_{P,H}$ = 4.8 Hz, 9 H, PCH$_3$), 1.47 (d, $^2J_{P,H}$ = 13.2 Hz, 9 H, PCH$_3$), 2.59 (s, 3 H, NCH$_3$), 5.83 (t, ^3J = 7.1 Hz, 1 H, CH), 6.17 (dd, $^4J_{P,H}$ = 5.2, ^3J = 8.2 Hz, 1 H, CH), 6.41 (dt, ^3J = 8.8, ^4J = 1.5 Hz, 1 H, CH), 6.86 (dt, ^3J = 8.1, ^4J = 1.5 Hz, 1 H, CH), 7.31−7.33 (m, 3 H, CH), 7.70−7.80 (m, 2 H, CH) ppm. ^{13}C NMR (75.4 MHz, [D$_8$]THF, 296 K): *trans*-**8**: δ = −14.4 (d, $^2J_{P,C}$ = 14.5 Hz, NiCH$_3$), 16.3 (d, $^2J_{P,C}$ = 6.9 Hz, PCH$_3$), 29.1 (d, $^1J_{P,C}$ = 5.8 Hz, C*C*H$_3$), 36.3 d $^2J_{P,C}$ = 11.9 Hz, *C*CH$_3$), 44.6 (s, N*C*H$_3$), 107.5 (s, C-2), 110.1 (s, C-5), 110.7 (d, $^2J_{P,C}$ = 10.8 Hz, *o*-C), 127.9 (s, C-3), 128.5 (d, $^3J_{P,C}$ = 6.8 Hz, *p*-C), 131.8 (s, C-4), 132.8 (d, $^3J_{P,C}$ = 8.4 Hz, *m*-C), 133.9 (s, *i*-C), 134.8 (s, C-6), 170.5 (m, NC-1) ppm. ^{31}P NMR (81 MHz, [D$_8$]THF, 233 K): *trans*-**8** (79%): δ = −16 (d, $^2J_{P,P}$ = 181 Hz, 2 P, PCH$_3$), 31 (t, $^2J_{P,P}$ = 181 Hz, 1 P, PC$_6$H$_5$); *cis*-**8** (21%): δ = −1 (d, $^2J_{P,P}$ = 29 Hz, 1 P, PCH$_3$), 57 (d, $^2J_{P,P}$ = 29 Hz, 1 P, PC$_6$H$_5$) ppm. C$_{26}$H$_{38}$NNiP$_3$ (515.2): calcd. C 60.49, H 7.42, N 2.71, P 18.00; found C 60.71, H 7.30, N 2.75, P 18.10.

{2-[*tert*-Butyl(phenyl)phosphanyl]-*N*-methylanilido-*N*,*P*}(methyl)bis(trimethylphosphane)nickel (9): 2-[*tert*-Butyl(phenyl)phosphanyl]-*N*-methylaniline (680 mg, 2.50 mmol) in 80 mL of diethyl ether was treated at − 50 °C whilst stirring with 1.6 M MeLi in diethyl ether (1.6 mL, 2.50 mmol). After warming to 20 °C, the mixture was stirred until evolution of gas had ceased. At − 50 °C this reagent was combined with NiClMe(PMe$_3$)$_2$ (655 mg, 2.50 mmol) in 50 mL of diethyl ether. The mixture was stirred at 20 °C for 3 h and concentrated to dryness in vacuo. The resulting orange solid was extracted with two 50-mL portions of pentane and the solution concentrated at 20 °C to afford short red rods of **9**. Yield 583 mg (47%), m.p. 115−117 °C (dec.). ^{1}H NMR (300 MHz, [D$_8$]THF, 296 K): *trans*-**9** (79%): δ = −0.74 (d, $^3J_{P,H}$ = 10.1 Hz, 3 H, NiCH$_3$), 1.02 (d, $^2J_{P,H}$ = 4.8 Hz, 18 H, PCH$_3$), 1.24 (d, $^2J_{P,H}$ = 12.6 Hz, 9 H, PCH$_3$), 2.66 (s, 3 H, NCH$_3$), 5.95 (t, ^3J = 7.2 Hz, 1 H, CH), 6.12 (dd, $^4J_{P,H}$ = 5.0, ^3J = 8.5 Hz, 1 H, CH), 6.86 (dt, ^3J = 8.1, ^4J = 1.5 Hz, 1 H, CH), 7.22 (dt, ^3J = 7.4, ^4J = 1.5 Hz, 1 H, CH), 7.21−7.29 (m, 3 H, CH), 7.59−7.67 (m, 2 H, CH); *cis*-**9** (21%): δ = −0.07 (dd, ${}_{trans}{}^3J_{P,H}$ = 4.2 Hz, ${}_{cis}{}^3J_{P,H}$ = 8.2 Hz, 3 H, NiCH$_3$), 1.12 (d, $^2J_{P,H}$ = 4.8 Hz, 9 H, PCH$_3$), 1.47 (d, $^2J_{P,H}$ = 13.2 Hz, 9 H, PCH$_3$), 2.59 (s, 3 H, NCH$_3$), 5.83 (t, ^3J = 7.1 Hz, 1 H, CH), 6.17 (dd, $^4J_{P,H}$ = 5.2, ^3J = 8.2 Hz, 1 H, CH), 6.41 (dt, ^3J = 8.8, ^4J = 1.5 Hz, 1 H, CH), 6.86 (dt, ^3J = 8.1, ^4J = 1.5 Hz, 1 H, CH), 7.31−7.33 (m, 3 H, CH), 7.70−7.80 (m, 2 H, CH) ppm. ^{13}C NMR (75.4 MHz, [D$_8$]THF, 296 K): *trans*-**9**: δ = −14.4 (d, $^2J_{P,C}$ = 14.5 Hz, NiCH$_3$), 16.3 (d, $^2J_{P,C}$ = 6.9 Hz, PCH$_3$), 29.1 (d, $^1J_{P,C}$ = 5.8 Hz, C*C*H$_3$), 36.3 (d, $^2J_{P,C}$ = 11.9 Hz, *C*CH$_3$), 44.6 (s, N*C*H$_3$), 107.5 (s, C-2), 110.1 (s, C-5), 110.7 (d, $^2J_{P,C}$ = 10.8 Hz, *o*-C), 127.9 (s, C-3), 128.5 (d, $^3J_{P,C}$ = 6.8 Hz, *p*-C), 131.8 (s, C-4), 132.8 (d, $^3J_{P,C}$ = 8.4 Hz, *m*-C), 133.9 (s, *i*-C), 134.8 (s, C-6), 170.5 (m, NC-1) ppm. ^{31}P NMR (81 MHz, [D$_8$]THF, 233 K): *trans*-**9** (79%): δ = −16 (d, $^2J_{P,P}$ = 181 Hz, 2 P, PCH$_3$), 31 (t, $^2J_{P,P}$ = 181 Hz, 1 P, PC$_6$H$_5$); *cis*-**9** (21%): δ = −1 (d, $^2J_{P,P}$ = 29 Hz, 1 P, PCH$_3$), 57 (d, $^2J_{P,P}$ = 29 Hz, 1 P, PC$_6$H$_5$) ppm. C$_{24}$H$_{42}$NNiP$_3$ (495.2): calcd. C 58.09, H 8.53, N 2.82, P 18.73; found C 58.06, H 8.40, N 2.73, P 18.70.

Crystal Structure Analyses: Crystal data are presented in Table 2. Data collection: Complex *cis*-**5**: A crystal was sealed under argon in a glass capillary and mounted on a Stoe Stadi-4 diffractometer. Reflections were collected (ω-scans) using graphite-monochromated Mo-K_α radiation; absorption corrections based on ψ-scans were applied. The structure was solved by direct and conventional Fourier methods. All non-hydrogen atoms were treated anisotropically, hydrogen atoms were treated with a riding model in idealized positions. The final *wR*2 value is high due to poor crystal quality, but there is no doubt about the space group. Complex **7**: Crystal mounting, data collection, structure solution, and refinement as for *cis*-**5**. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre. Copies of the data [CCDC-186327 (*cis*-**5**) and -186328 (**7**)] can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033, E-mail: deposit@ccdc.cam.ac.uk].

Table 2. Crystal data for compounds *cis*-**5** and **7**

	cis-**5**	**7**
Empirical formula	C$_{25}$H$_{35}$NNiP$_2$Si	C$_{26}$H$_{38}$NNiP$_3$
Formula mass	498.4	516.3
Crystal size [mm]	0.38 × 0.20 × 0.19	0.41 × 0.30 ×0.18
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
a [Å]	10.6570(9)	8.558(3)
b [Å]	18.9000(11)	19.911(10)
c [Å]	26.19900(17)	15.817(7)
β [°]	90.870(5)	93.13(3)
V [Å^3]	5276.32(40)	2726.2(2)
Z	4	4
$D_{calcd.}$ [g/cm^3]	1.255	1.255
μ(Mo-K_α) [mm^{-1}]	0.856	0.843
T [K]	293(2)	293(2)
Data coll. range [°]	5.8 ≤ 2Θ ≤ 50	4.9 ≤ 2Θ ≤ 50
h	$-10 \le h \le 10$	$-8 \le h \le 8$
k	$0 \le k \le 18$	$0 \le k \le 19$
l	$0 \le l \le 25$	$0 \le l \le 15$
No. reflect. measured	13711	8166
No. unique data	4834 (R$_{int}$ = 0.0367)	2535 (R$_{int}$ = 0.0222)
Parameters	541	292
GoF on F^2	1.172	1.163
R_1 [$I \ge 2\sigma(I)$]	0.0727	0.0389
*wR*2 (all data)	0.3110	0.1295

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