

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

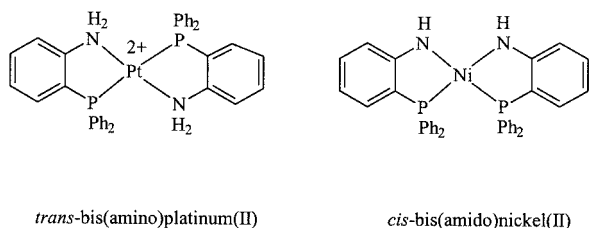
P,N-chelates of nickel $\text{NiCl}[\text{2}-(\text{Ph}_2\text{P})\text{C}_6\text{H}_4\text{NR}](\text{PMe}_3)$ (**1**: R = H; **2**: R = SiMe₃) have been obtained from $\text{NiCl}_2(\text{PMe}_3)_2$ and $\text{2}-(\text{Ph}_2\text{P})\text{C}_6\text{H}_4\text{NRLi}$. Reaction with MeLi affords methylnickel compounds $\text{NiMe}[\text{2}-(\text{Ph}_2\text{P})\text{C}_6\text{H}_4\text{NR}](\text{PMe}_3)$ (**3**: R = H; **4**: R = Me; **5**: R = SiMe₃). By the same route $\text{NiMe}[\text{2}-(\text{R}^1\text{R}^2\text{P})\text{C}_6\text{H}_4\text{NR}](\text{PMe}_3)$ (**6**: R¹ = R² = CHMe₂) 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 $\text{NiMe}[\text{2}-(\text{Ph}_2\text{P})\text{C}_6\text{H}_4\text{NR}](\text{PMe}_3)_2$ (**7**, **8**) in the crystal as shown by the molecular structure of **7** while in THF equilibria **7** $\rightleftharpoons$ *cis*-**1** and **8** $\rightleftharpoons$ *cis*-**2** are observed by NMR spectroscopy. The same solution properties are found with $\text{NiMe}[\text{2}-(\text{R}^1\text{R}^2\text{P})\text{C}_6\text{H}_4\text{NR}](\text{PMe}_3)_2$ (**9**: R¹ = CMe₃, R² = Ph).

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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 metallacycles. 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).



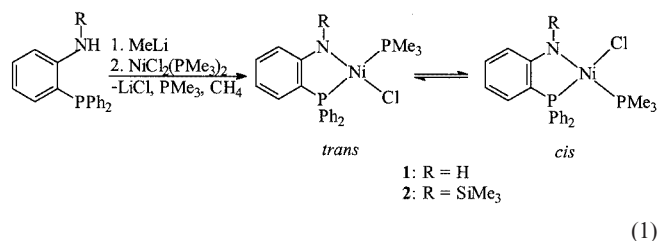
Scheme 1. Square-planar bis(P,N-chelates)

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 Et₂AlCl 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*- $\text{NiCl}_2(\text{PMe}_3)_2$ [Equation (1)] to afford the chloronickel complexes **1** and **2** as green solids which are sparingly soluble in pentane or ether.

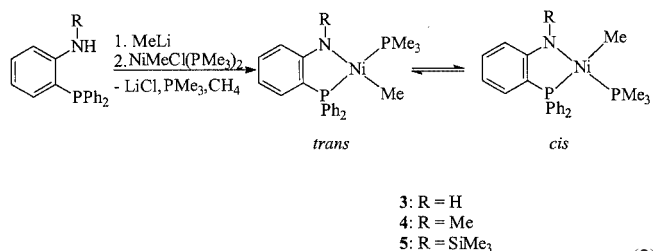


The ³¹P NMR spectrum obtained from a THF solution of **1** or **2** at 233 K shows four doublet resonances. The pair containing the large P,P coupling is assigned to *trans*-**1** (62%) and *trans*-**2** (66%), while the pair showing the small P,P coupling is due to *cis*-**1** (38%) and *cis*-**2** (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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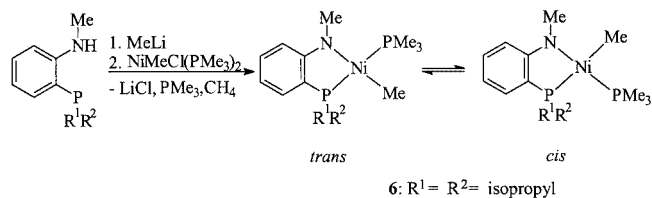
and thereby indicates the absence of a pentacoordinate compound. Addition of a second mol-equiv. of LiMe or use of *trans*-NiMeCl(PMe₃)₂ as a reactant [Equation (2)] furnishes the corresponding methylnickel compounds.



(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, NiCH₃ protons opposite to the chelating ³¹P donor resonate between $\delta = -0.82$ and -0.77 ppm with unresolved *trans* coupling (*cis* ³*J*_{P,H} = 4.5–6.1 Hz) while for those opposite to the amide donor at $\delta = -0.04(3)$ ppm a doublet of doublets pattern is observed (³*J*_{P,H} = 3.8–4.1 Hz). In toluene solution the *trans* isomers are observed as the dominant species (> 95%).



(3)

The ³¹P 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 $\delta \approx -2$ ppm. Surprisingly, the *cis* and *trans* isomers show different behavior at variable temperatures. Only the *cis* isomers continue to display a doublet of doublets (²*J*_{P,P} $\approx$ 30 Hz) between 298 and 213 K (Figure 1) while the large *trans* coupling (²*J*_{P,P} $\approx$ 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 $\delta = -5$ ppm (298 K) must be regarded as an average of rapidly exchanging free and coordinated trimethylphosphane which also involves the penta-coordinate 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

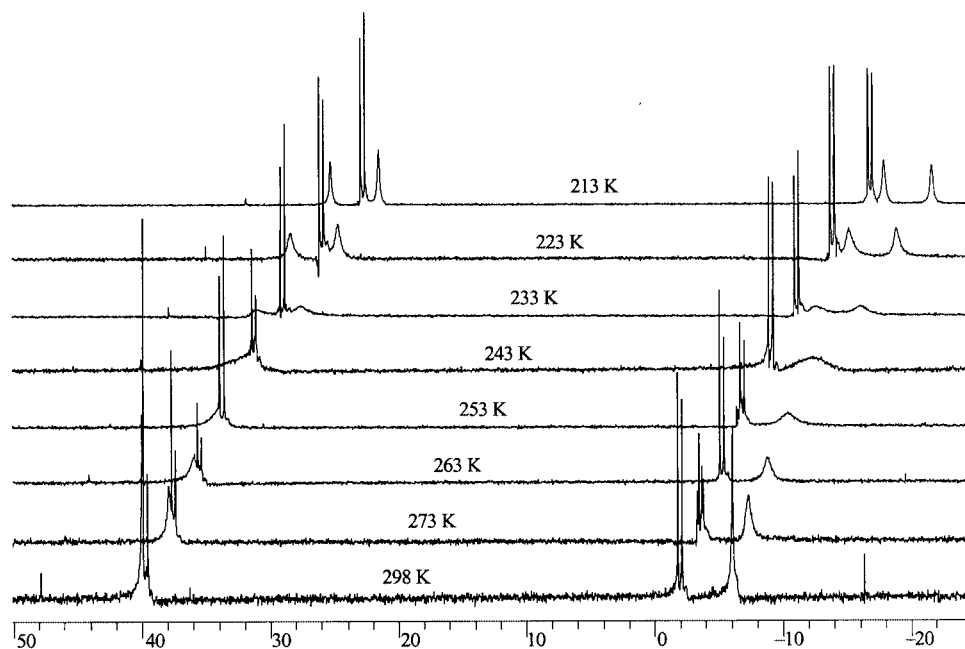


Figure 1. ³¹P NMR spectra of **3** (THF, 213–298 K)

larger *trans* influence of the NiMe group relative to the amide donor. The Me₃Si group is clearly oriented above the plane of the metallacycle.

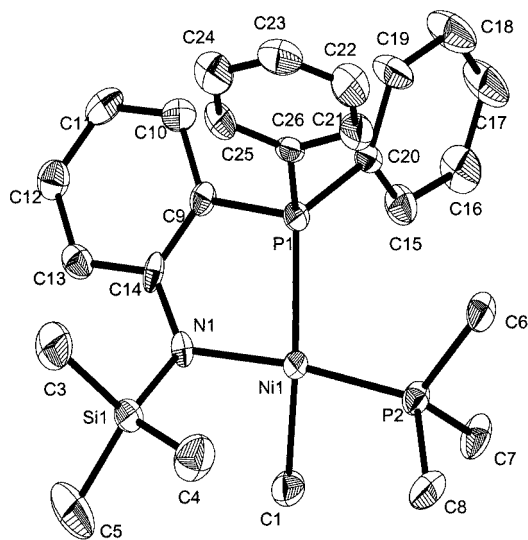


Figure 2. Molecular structure of *cis*-**5** (ORTEP plot with hydrogen atoms omitted); selected bond lengths [Å] and angles [°]: Ni–C1 1.971(11), Ni–N 1.956(8), Ni–P1 2.219(3), Ni–P2 2.124(3), P1–C9 1.814(10), C9–C14 1.387(15), C14–N 1.367(14), N–Si 1.731(8), N–Ni–P2 170.0(3), N–Ni–P1 84.0(3), C1–Ni–P1 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 NiMe₂(PMe₃)₂ and NiMe₂(PMe₃)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 ³¹P 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 PPh₂ 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.

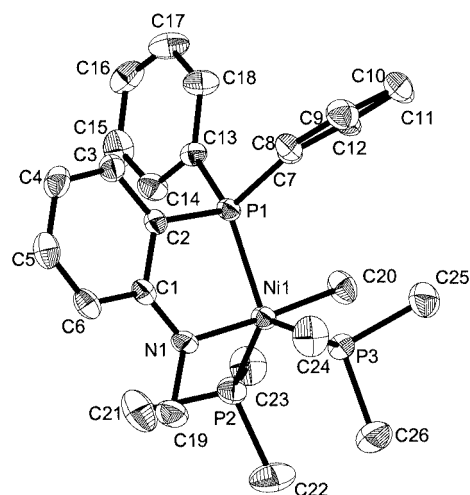
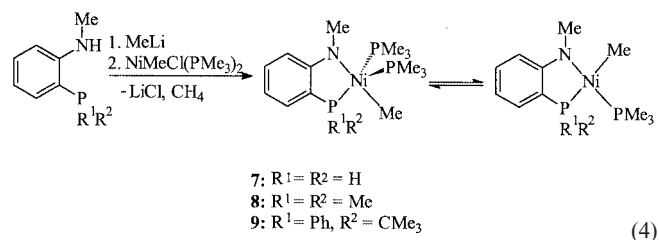


Figure 3. Molecular structure of **7** (ORTEP plot with hydrogen atoms omitted); selected bond lengths [Å] and angles [°]: Ni–C20 1.996(6), Ni–N 1.974(4), Ni–P1 2.202(2), Ni–P2 2.224(2), Ni–P3 2.253(2), N–C1 1.452(6), N–C19 1.452(6), C1–C2 1.423(7), N–Ni–C20 176.7(3), P1–Ni–P2 125.90(6), P1–Ni–P3 110.71(6), 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 prechelatant [Equation (4)]. The red crystals of pentacoordinate **9** are highly soluble in pentane and under argon decompose above 115 °C.



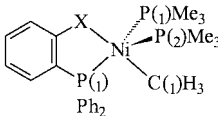
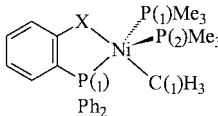
One bulky alkyl substituent in the 2-(phosphanyl) group does not interfere with the reversible uptake of trimethylphosphane. With **9** we have not been able to isolate a 16-VE species in an analytically pure state.

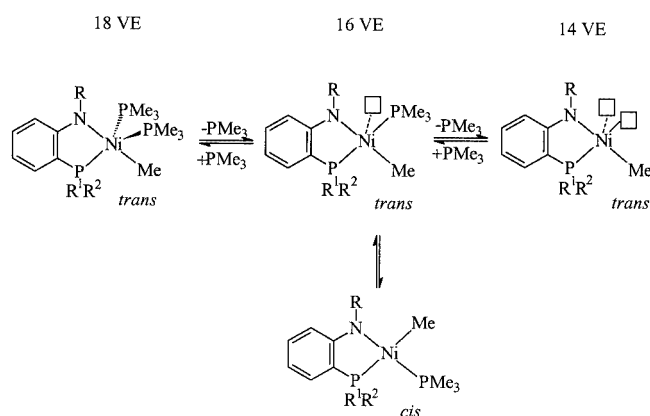
A close structural relationship between **8** and [2-(di-phenylphosphanyl)phenolato-*O,P*]methylbis(trimethylphosphane)nickel^[7] is found in agreement with expectation for isoelectronic molecules (Table 1).

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 lengths [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 NiCl₂(PMe₃)₂, Ni-MeCl(PMe₃)₂,^[6] 2-(diphenylphosphanyl)aniline,^[9] 2-(diphenylphosphanyl)-N-methylaniline, 2-(diisopropylphosphanyl)aniline^[10] and 2-[*tert*-butyl(phenyl)phosphanyl]-N-methylaniline.^[11] IR: Nujol mulls between KBr discs, Bruker spectrophotometer type FRA

106. ^1H 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. ^1H NMR (300 MHz, $[\text{D}_8]\text{THF}$): δ = 0.01 (s, 9 H, SiCH_3), 4.30 (d, $^4J_{\text{P,H}}$ = 9.3 Hz, 1 H, NH), 6.45 (dt, 3J = 7.6, 4J = 0.7 Hz, 1 H, CH), 6.65 (m, 2 H, CH), 7.01 (dt, 3J = 6.5, 4J = 1.5 Hz, 2 H, CH), 7.13–7.20 (m, 10 H, CH) ppm. ^{13}C NMR (75 MHz, $[\text{D}_8]\text{THF}$): δ = –1.89 (s, CH_3), 114.7 (s, CH), 116.9 (d, $^4J_{\text{P,C}}$ = 2.2 Hz, CH), 120.9 (d, $^3J_{\text{P,C}}$ = 5.6 Hz, C), 127.4 (s, CH), 127.6 (d, $^2J_{\text{P,C}}$ = 7.8 Hz, CH), 129.1 (s, CH), 132.5 (d, $^1J_{\text{P,C}}$ = 18.7 Hz, CH), 133.7 (d, $^3J_{\text{P,C}}$ = 5.5 Hz, C), 135.1 (d, $^2J_{\text{P,C}}$ = 7.7 Hz, C), 150.1 (d, $^1J_{\text{P,C}}$ = 19.5 Hz, CH) ppm. ^{31}P NMR (81 MHz, $[\text{D}_8]\text{THF}$): δ = –10 (s) ppm. $\text{C}_{21}\text{H}_{24}\text{NPSi}$ (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 prechelat 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}): $\tilde{\nu}$ = 3349 vs (N-H), 3052 m, 2926 m (vH-C), 2810 (vNC-H), 1587 s, 1569 s (vC=C), 1518 s, 1454 s, 1435 s, 1419 m, 1312 m (δ_{asPCH}), 1289 m (δ_{sPCH}), 1165 m, 1089 w, 1046 w, 1029 vw, 999 vw, 912 vw, 746 vs, 729 w, 698 vs ($\gamma\text{C-H}$), 515 m, 496 m, 482 m. ^{31}P NMR (81 MHz, CD_2Cl_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 $\text{NiCl}_2(\text{PMe}_3)_2$ (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): $\tilde{\nu}$ = 3377 cm^{-1} (N–H). ^1H NMR (200 MHz, $[\text{D}_8]\text{THF}$, 233 K): *cis*-1 (63%): δ = 1.07 (d, $^2J_{\text{P,H}}$ = 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, $^2J_{\text{P,H}}$ = 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, $[\text{D}_8]\text{THF}$, 233 K): *cis*-1 (63%): δ = –9 (d, $^2J_{\text{P,P}}$ = 89 Hz, 1 P, PCH_3), 52 (d, $^2J_{\text{P,P}}$ = 89 Hz, 1 P, PC_6H_5); *trans*-1 (37%): δ = –9 (d, $^2J_{\text{P,P}}$ = 347 Hz, 1 P, PCH_3), 31 (d, $^2J_{\text{P,P}}$ = 347 Hz, 1 P, PC_6H_5) ppm. $\text{C}_{21}\text{H}_{24}\text{ClNNiP}_2$ (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 $\text{NiCl}_2(\text{PMe}_3)_2$ (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.). ^1H NMR (200 MHz, $[\text{D}_8]\text{THF}$, 233 K): *cis*-2 (66%): δ = 0.02 (s, 9 H, SiCH_3), 1.06 (d, $^2J_{\text{P,H}}$ = 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, $^2J_{\text{P,H}}$ = 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, $[\text{D}_8]\text{THF}$, 233 K): *cis*-2 (66%): δ = –8 (d, $^2J_{\text{P,P}}$ = 88 Hz, 1 P, PCH_3), 52 (d, $^2J_{\text{P,P}}$ = 88 Hz, 1 P, PC_6H_5); *trans*-2 (34%): δ = –9 (d, $^2J_{\text{P,P}}$ = 348 Hz, 1 P, PCH_3), 32 (d, $^2J_{\text{P,P}}$ = 348 Hz, 1 P, PC_6H_5) ppm. $\text{C}_{24}\text{H}_{32}\text{ClNNiP}_2\text{Si}$ (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 $\text{NiMeCl}(\text{PMe}_3)_2$ (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): $\tilde{\nu}$ = 3348 cm^{-1} (N–H). ^1H NMR (300 MHz, $[\text{D}_8]\text{THF}$): *cis*-3 (60%): δ = –0.07 (dd, $^3J_{\text{P,H}}$ = 4.1, $^{\text{cis}}J_{\text{P,H}}$ = 8.8 Hz, 3 H, NiCH_3), 1.29 (d, $^2J_{\text{P,H}}$ = 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, 3J = 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, $^3J_{\text{P,H}}$ = 6.1 Hz, 3 H, NiCH_3), 1.09 (d, $^2J_{\text{P,H}}$ = 8.6 Hz, 9 H, PCH_3), 3.06 (s, 1 H, NH), 5.88 (dd, 3J = 7.0, 4J = 1.4 Hz, 1 H, CH), 5.91 (dd, 3J = 8.2, $^4J_{\text{P,H}}$ = 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, $[\text{D}_8]\text{THF}$, 296 K): *cis*-3 (60%): δ = 4.2 (dd, $^2J_{\text{P,C}}$ = 33.8, $^2J_{\text{P,C}}$ = 62.6 Hz, NiCH_3), 12.6 (d, $^1J_{\text{P,C}}$ = 21.9 Hz, PCH_3), 108.8 (d, $^3J_{\text{P,C}}$ = 6.2 Hz, C-2), 115.9 (d, $^2J_{\text{P,C}}$ = 9.5 Hz, *m*-C), 128.9 (d, $^2J_{\text{P,C}}$ = 9.3 Hz, *p*-C), 130.2 (s, C-5), 134.1 (d, $^2J_{\text{P,C}}$ = 11.4 Hz, *o*-C), 134.3 (s, C-3), 134.7 (s, *i*-C), 134.9 s, C-6), 171.4 (d, $^2J_{\text{P,C}}$ = 31.0 Hz, NC-1); *trans*-3 (40%): δ = –16.8 (d, $^2J_{\text{P,C}}$ = 24.1 Hz, NiCH_3), 16.3 (d, $^1J_{\text{P,C}}$ = 28.9 Hz, PCH_3), 110.4 (d, $^3J_{\text{P,C}}$ = 5.6 Hz, C-2), 114.8 (d, $^3J_{\text{P,C}}$ = 3.0 Hz, C-5), 128.9 (d, $^2J_{\text{P,C}}$ = 8.6 Hz, *m*-C), 130.4 (s, *p*-C), 132.6 (d, $^2J_{\text{P,C}}$ = 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, $^2J_{\text{P,C}}$ = 32.7 Hz, NC-1) ppm. ^{31}P NMR (81 MHz, $[\text{D}_8]\text{THF}$): *cis*-1 (60%, 193 K): δ = –2 (d, $^2J_{\text{P,P}}$ = 27 Hz, 1 P, PCH_3), 40 (d, $^2J_{\text{P,P}}$ = 27 Hz, 1 P, PC_6H_5); *trans*-3 (40%, 193 K): δ = –2 (d, $^2J_{\text{P,P}}$ = 303 Hz, 1 P, PCH_3), 40 (d, $^2J_{\text{P,P}}$ = 303 Hz, 1 P, PC_6H_5); *cis*-1 (60%, 296 K): δ = –2 (d, $^2J_{\text{P,P}}$ = 25 Hz, 1 P, PCH_3), 40 (d, $^2J_{\text{P,P}}$ = 25 Hz, 1 P, PC_6H_5); *trans*-3 (40%, 296 K): δ = –5 (s, 1 P, PCH_3), 37 (s, 1 P, PC_6H_5) ppm. $\text{C}_{22}\text{H}_{27}\text{NNiP}_2$ (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 $-70\text{ }^{\circ}\text{C}$ to $\text{NiMeCl}(\text{PMe}_3)_2$ (870 mg, 3.32 mmol) in 80 mL of diethyl ether. The orange-red mixture was warmed to $20\text{ }^{\circ}\text{C}$, filtered, and concentrated to dryness in vacuo. The resulting solid was washed with 5 mL of pentane and dried at $20\text{ }^{\circ}\text{C}$ 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. $122\text{--}124\text{ }^{\circ}\text{C}$ (dec.). ^1H NMR (300 MHz, $[\text{D}_8]\text{THF}$): *cis*-**4** (88%): $\delta = 0.13$ (m, 3 H, NiCH_3), 1.15 (d, $^2J_{\text{P,H}} = 6.9$ 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%): $\delta = -0.77$ (m, 3 H, NiCH_3), 1.05 (d, $^2J_{\text{P,H}} = 8.9$ Hz, 9 H, PCH_3), 2.80 (s, NCH_3) ppm. ^{13}C NMR (75.4 MHz, $[\text{D}_8]\text{THF}$, 296 K): *cis*-**4**: $\delta = 4.9$ (m, NiCH_3), 14.5 (d, $^1J_{\text{P,C}} = 30.6$ Hz, PCH_3), 35.2 (s, NCH_3), 108.4 (s, C-2), 108.7 (s, C-5), 127.1 (d, $^1J_{\text{P,C}} = 16.9$ Hz, *m*-C), 127.4–131.1 (m, C-3/C-4), 131.7 (d, $^1J_{\text{P,C}} = 26.7$ Hz, *o*-C), 132.2 (d, $^2J_{\text{P,C}} = 12.1$ Hz, *p*-C), 153.6 (s, C-6) ppm. ^{31}P NMR (81 MHz, $[\text{D}_8]\text{THF}$, 233 K): *cis*-**4** (88%): $\delta = -1$ (d, $^2J_{\text{P,P}} = 32$ Hz, 1 P, PCH_3), 38 (d, $^2J_{\text{P,P}} = 32$ Hz, 1 P, PC_6H_5); *trans*-**4** (12%): $\delta = -9$ (d, $^2J_{\text{P,P}} = 329$ Hz, 1 P, PCH_3), 34 (d, $^2J_{\text{P,P}} = 329$ Hz, 1 P, PC_6H_5) ppm. $\text{C}_{22}\text{H}_{27}\text{NNiP}_2$ (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 $-70\text{ }^{\circ}\text{C}$ with 1.6 M MeLi in diethyl ether (1.5 mL, 2.40 mmol), and to the fluorescent solution was added at $-70\text{ }^{\circ}\text{C}$ solid $\text{NiMeCl}(\text{PMe}_3)_2$ (620 mg, 2.37 mmol) to form a deep red mixture. The mixture was warmed to $20\text{ }^{\circ}\text{C}$, 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 $-27\text{ }^{\circ}\text{C}$ to afford deep orange crystals of **5** (732 mg). Yield 62%; m.p. $83\text{--}84\text{ }^{\circ}\text{C}$ (dec.). ^1H NMR (300 MHz, $[\text{D}_8]\text{THF}$): *cis*-**5** (58%): $\delta = -0.01$ (dd, $^3J_{\text{P,H}} = 3.8$ Hz, $^3J_{\text{P,H}} = 8.8$ Hz, 3 H, NiCH_3), 0.09 (s, 9 H, SiCH_3), 1.09 (d, $^2J_{\text{P,H}} = 4.1$ 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%): $\delta = 0.82$ (d, $^3J_{\text{P,H}} = 4.5$ Hz, 3 H, NiCH_3), 0.07 (s, 9 H, SiCH_3), 1.08 (d, $^2J_{\text{P,H}} = 8.6$ Hz, 9 H, PCH_3), 5.88 (m, 1 H, CH), 6.19 (dd, $^3J = 8.0$, $^4J = 4.7$ 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, $[\text{D}_8]\text{THF}$): *cis*-**5** (58%): $\delta = 1.6$ (s, SiCH_3), 4.2 (m, NiCH_3), 12.7 (d, $^1J_{\text{P,C}} = 21.9$ Hz, PCH_3), 110.8 (s, C-2), 115.9 (s, C-5), 129.3 (d, $^2J_{\text{P,C}} = 9.2$ Hz, *m*-C), 133.2–134.6 (s, C-1, *o*-C, *p*-C), 135.0 (s, C-6), 172.3 (d, $^2J_{\text{P,C}} = 31.5$ Hz, NC-1); *trans*-**5** (42%): $\delta = -16.9$ (d, $^2J_{\text{P,C}} = 24.9$ Hz, NiCH_3), 1.9 (s, SiCH_3), 16.1 (d, $^1J_{\text{P,C}} = 25.9$ Hz, PCH_3), 111.2 (d, $^3J_{\text{P,C}} = 6.1$ Hz, C-2), 114.8 (s, C-5), 129.0 (s, C-3), 130.5 (d, $^2J_{\text{P,C}} = 18.7$ Hz, *o*-C), 132.7 (d, $^2J_{\text{P,C}} = 9.8$ Hz, *m*-C), 133.2 (s, *p*-C), 134.1 (d, $^2J_{\text{P,C}} = 11.9$ Hz, *i*-C), 134.7 (s, C-4), 135.2 (s, C-6), 171.2 (d, $^2J_{\text{P,C}} = 30.8$ Hz, NC-1) ppm. ^{31}P NMR (81 MHz, $[\text{D}_8]\text{THF}$, 233 K) *cis*-**5** (58%): $\delta = 1$ (d, $^2J_{\text{P,P}} = 27$ Hz, 1 P, PCH_3), 40 (d, $^2J_{\text{P,P}} = 27$ Hz, 1 P, PC_6H_5); *trans*-**5** (42%): $\delta = -3$ (d, $^2J_{\text{P,P}} = 297$ Hz, 1 P, PCH_3), 40 (d, $^2J_{\text{P,P}} = 297$ Hz, 1 P, PC_6H_5) ppm. $\text{C}_{25}\text{H}_{35}\text{NNiP}_2\text{Si}$ (497.1): calcd. C 62.66, 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 $-70\text{ }^{\circ}\text{C}$ with 1.6 M MeLi in diethyl ether (2.3 mL, 3.50 mmol), and to the yellow fluorescent solution was added solid $\text{NiMeCl}(\text{PMe}_3)_2$ (912 mg, 3.49 mmol). The mixture was warmed to $20\text{ }^{\circ}\text{C}$ and con-

centrated 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 $-27\text{ }^{\circ}\text{C}$ afforded red crystals of **6** (751 mg). Yield 58%; m.p. $104\text{--}105\text{ }^{\circ}\text{C}$ (dec.). ^1H NMR (300 MHz, $[\text{D}_8]\text{THF}$, 296 K): *trans*-**6** (78%): $\delta = -0.65$ (d, $^3J_{\text{P,H}} = 9.1$ Hz, 3 H, NiCH_3), 1.00 (d, $^2J_{\text{P,H}} = 3.6$ Hz, 18 H, PCH_3), 2.67 (s, 3 H, NCH_3), 5.82 (m, 1 H, CH), 5.89 (d, $^3J = 7.2$ 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%): $\delta = -0.07$ (dd, $^3J_{\text{P,H}} = 3.7$, $^3J_{\text{P,H}} = 6.5$ Hz, 3 H, NiCH_3), 1.00 (br. s, 9 H, PCH_3), 2.48 (s, 3 H, NCH_3). ^1H NMR (300 MHz, $[\text{D}_8]\text{toluene}$): *trans*-**6** (> 98%): $\delta = 0.33$ (dd, $^3J_{\text{P,H}} = 4.1$ and 8.2 Hz, 3 H, NiCH_3), 1.00 (d, $^2J_{\text{P,H}} = 6.2$ Hz, 9 H, PCH_3), 1.24 (br. d, $^3J_{\text{P,H}} = 7.1$ Hz, 6 H, PCHCH_3), 1.28 (br. d, $^3J_{\text{P,H}} = 7.1$ Hz, 6 H, PCHCH_3), 2.34 (m, 2 H, PCH), 2.98 (s, 3 H, NCH_3), 6.40 (t, $^3J = 7.1$ Hz, 1 H, CH), 6.49 (dd, $^3J = 8.4$, $^4J = 2.2$ Hz, 1 H, CH), 7.12 (t, $^3J = 7.4$ Hz, 1 H, CH), 7.31 (dt, $^3J = 7.1$, $^4J_{\text{P,H}} = 1.4$ Hz, 1 H, CH) ppm. ^{13}C NMR (75.4 MHz, $[\text{D}_8]\text{THF}$, 296 K): *trans*-**6**: $\delta = -14.3$ (d, $^2J_{\text{P,C}} = 16.8$ Hz, NiCH_3), 16.7 (d, $^1J_{\text{P,C}} = 7.6$ Hz, PCH_3), 44.4 (s, NCH_3), 108.5 (s, C-2), 110.4 (d, $^2J_{\text{P,C}} = 12.5$ Hz, *5*-C), 128.9 (d, $^2J_{\text{P,C}} = 8.6$ Hz, *m*-C), 129.4–131.9 (m, *p*-C/C-3), 133.3 (d, $^2J_{\text{P,C}} = 11.5$ Hz, *o*-C), 134.4 (d, $^2J_{\text{P,C}} = 12.4$ Hz, C-4), 135.3 (s, *i*-C), 139.8 (s, C-6) ppm. ^{31}P NMR (81 MHz, $[\text{D}_8]\text{THF}$, 193 K): *trans*-**6** (78%): $\delta = -11$ (d, $^2J_{\text{P,P}} = 326$ Hz, 1 P, PCH_3), 45 (d, $^2J_{\text{P,P}} = 297$ Hz, 1 P, PCHCH_3); *cis*-**1** (22%): $\delta = -1$ (d, $^2J_{\text{P,P}} = 25$ Hz, 1 P, PCH_3), 45 (d, $^2J_{\text{P,P}} = 25$ Hz, 1 P, PCHCH_3) ppm. ^{31}P NMR (81 MHz, $[\text{D}_8]\text{toluene}$): *trans*-**6** (> 98%): $\delta = -18$ (d, $^2J_{\text{P,P}} = 327$ Hz, 1 P, PCH_3), 40 (d, $^2J_{\text{P,P}} = 327$ Hz, 1 P, PCHCH_3) ppm. $\text{C}_{17}\text{H}_{33}\text{NNiP}_2$ (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 $-70\text{ }^{\circ}\text{C}$ with 1.6 M MeLi in diethyl ether (1.8 mL, 2.92 mmol), and this solution was added dropwise at $-70\text{ }^{\circ}\text{C}$ to $\text{NiMeCl}(\text{PMe}_3)_2$ (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 $-5\text{ }^{\circ}\text{C}$ for 10 min. Yield 790 mg of **7** (54%); m.p. $110\text{--}111\text{ }^{\circ}\text{C}$ (dec.). IR (Nujol): $\tilde{\nu} = 3361\text{ cm}^{-1}$ (N–H). ^1H NMR (300 MHz, $[\text{D}_8]\text{THF}$, 296 K): *trans*-**7** (66%): $\delta = -0.75$ (d, $^3J_{\text{P,H}} = 8.6$ Hz, 3 H, NiCH_3), 1.00 (d, $^2J_{\text{P,H}} = 3.6$ Hz, 18 H, PCH_3), 2.78 (NH 3,44s, 1 H, NH), 5.86 (m, 1 H, CH), 6.19 (dd, $^3J = 6.2$, $^4J = 1.6$ 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%): $\delta = -0.06$ (m, 3 H, NiCH_3), 1.00 (d, $^2J_{\text{P,H}} = 3.6$ 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, $[\text{D}_8]\text{THF}$, 296 K): *trans*-**7**: $\delta = -14.1$ (m, NiCH_3), 16.7 (d, $^1J_{\text{P,C}} = 7.2$ Hz, PCH_3), 45.1 (s, NCH_3), 108.5–135.4 (s, 10 C) ppm. ^{31}P NMR (81 MHz, $[\text{D}_8]\text{THF}$, 233 K): *trans*-**7** (66%): $\delta = -26$ (br. s, 2 P, PCH_3), 27 (br. s, 1 P, PC_6H_5); *cis*-**7** (34%): $\delta = -1$ (d, $^2J_{\text{P,P}} = 26$ Hz, 1 P, PCH_3), 39 (d, $^2J_{\text{P,P}} = 26$ Hz, 1 P, PC_6H_5) ppm. $\text{C}_{25}\text{H}_{35}\text{NNiP}_3$ (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 $-70\text{ }^{\circ}\text{C}$ with $\text{NiMe}_2(\text{PMe}_3)_3$ (920 mg, 2.90 mmol) in 80 mL of diethyl ether. Warming to $20\text{ }^{\circ}\text{C}$ 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 $-27\text{ }^{\circ}\text{C}$ 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 $\text{NiMeCl}(\text{PMe}_3)_2$ (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. $117\text{--}119^{\circ}\text{C}$ (dec.). ^1H NMR (300 MHz, $[\text{D}_8]\text{THF}$, 296 K): *trans*-**8** (79%): $\delta = -0.74$ (d, $^3J_{\text{P,H}} = 10.1$ Hz, 3 H, NiCH_3), 1.02 (d, $^2J_{\text{P,H}} = 4.8$ Hz, 18 H, PCH_3), 1.24 (d, $^2J_{\text{P,H}} = 12.6$ 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, $^4J_{\text{P,H}} = 5.0$, $^3J = 8.5$ 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%): $\delta = -0.07$ (dd, $^3J_{\text{P,H}} = 4.2$, $^3J_{\text{P,H}} = 8.2$ Hz, 3 H, NiCH_3), 1.12 (d, $^2J_{\text{P,H}} = 4.8$ Hz, 9 H, PCH_3), 1.47 (d, $^2J_{\text{P,H}} = 13.2$ 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, $^4J_{\text{P,H}} = 5.2$, $^3J = 8.2$ 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, $[\text{D}_8]\text{THF}$, 296 K): *trans*-**8**: $\delta = -14.4$ (d, $^2J_{\text{P,C}} = 14.5$ Hz, NiCH_3), 16.3 (d, $^2J_{\text{P,C}} = 6.9$ Hz, PCH_3), 29.1 (d, $^1J_{\text{P,C}} = 5.8$ Hz, CCH_3), 36.3 (d, $^2J_{\text{P,C}} = 11.9$ Hz, CCH_3), 44.6 (s, NCH_3), 107.5 (s, C-2), 110.1 (s, C-5), 110.7 (d, $^2J_{\text{P,C}} = 10.8$ Hz, *o*-C), 127.9 (s, C-3), 128.5 (d, $^3J_{\text{P,C}} = 6.8$ Hz, *p*-C), 131.8 (s, C-4), 132.8 (d, $^3J_{\text{P,C}} = 8.4$ Hz, *m*-C), 133.9 (s, *i*-C), 134.8 (s, C-6), 170.5 (m, NC-1) ppm. ^{31}P NMR (81 MHz, $[\text{D}_8]\text{THF}$, 233 K): *trans*-**8** (79%): $\delta = -16$ (d, $^2J_{\text{P,P}} = 181$ Hz, 2 P, PCH_3), 31 (t, $^2J_{\text{P,P}} = 181$ Hz, 1 P, PC_6H_5); *cis*-**8** (21%): $\delta = -1$ (d, $^2J_{\text{P,P}} = 29$ Hz, 1 P, PCH_3), 57 (d, $^2J_{\text{P,P}} = 29$ Hz, 1 P, PC_6H_5) ppm. $\text{C}_{26}\text{H}_{38}\text{NNiP}_3$ (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 $\text{NiClMe}(\text{PMe}_3)_2$ (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. $115\text{--}117^{\circ}\text{C}$ (dec.). ^1H NMR (300 MHz, $[\text{D}_8]\text{THF}$, 296 K): *trans*-**9** (79%): $\delta = -0.74$ (d, $^3J_{\text{P,H}} = 10.1$ Hz, 3 H, NiCH_3), 1.02 (d, $^2J_{\text{P,H}} = 4.8$ Hz, 18 H, PCH_3), 1.24 (d, $^2J_{\text{P,H}} = 12.6$ 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, $^4J_{\text{P,H}} = 5.0$, $^3J = 8.5$ 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%): $\delta = -0.07$ (dd, $^3J_{\text{P,H}} = 4.2$ Hz, $^3J_{\text{P,H}} = 8.2$ Hz, 3 H, NiCH_3), 1.12 (d, $^2J_{\text{P,H}} = 4.8$ Hz, 9 H, PCH_3), 1.47 (d, $^2J_{\text{P,H}} = 13.2$ 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, $^4J_{\text{P,H}} = 5.2$, $^3J = 8.2$ 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, $[\text{D}_8]\text{THF}$, 296 K): *trans*-**9**: $\delta = -14.4$ (d, $^2J_{\text{P,C}} = 14.5$ Hz, NiCH_3), 16.3 (d, $^2J_{\text{P,C}} = 6.9$ Hz, PCH_3), 29.1 (d, $^1J_{\text{P,C}} = 5.8$ Hz, CCH_3), 36.3 (d, $^2J_{\text{P,C}} = 11.9$ Hz, CCH_3), 44.6 (s, NCH_3), 107.5 (s, C-2), 110.1 (s, C-5), 110.7 (d, $^2J_{\text{P,C}} = 10.8$ Hz, *o*-C), 127.9 (s, C-3), 128.5 (d, $^3J_{\text{P,C}} = 6.8$ Hz, *p*-C), 131.8 (s, C-4), 132.8 (d, $^3J_{\text{P,C}} = 8.4$ Hz, *m*-C), 133.9 (s, *i*-C), 134.8 (s, C-6), 170.5 (m, NC-1) ppm. ^{31}P NMR (81 MHz, $[\text{D}_8]\text{THF}$, 233 K): *trans*-**9** (79%): $\delta =$

-16 (d, $^2J_{\text{P,P}} = 181$ Hz, 2 P, PCH_3), 31 (t, $^2J_{\text{P,P}} = 181$ Hz, 1 P, PC_6H_5); *cis*-**9** (21%): $\delta = -1$ (d, $^2J_{\text{P,P}} = 29$ Hz, 1 P, PCH_3), 57 (d, $^2J_{\text{P,P}} = 29$ Hz, 1 P, PC_6H_5) ppm. $\text{C}_{24}\text{H}_{42}\text{NNiP}_3$ (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 $wR2$ 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**

	<i>cis</i> - 5	7
Empirical formula	$\text{C}_{25}\text{H}_{35}\text{NNiP}_2\text{Si}$	$\text{C}_{26}\text{H}_{38}\text{NNiP}_3$
Formula mass	498.4	516.3
Crystal size [mm]	$0.38 \times 0.20 \times 0.19$	$0.41 \times 0.30 \times 0.18$
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
<i>a</i> [Å]	10.6570(9)	8.558(3)
<i>b</i> [Å]	18.9000(11)	19.911(10)
<i>c</i> [Å]	26.19900(17)	15.817(7)
β [°]	90.870(5)	93.13(3)
<i>V</i> [Å ³]	5276.32(40)	2726.2(2)
<i>Z</i>	4	4
$D_{\text{calcd.}}$ [g/cm ³]	1.255	1.255
$\mu(\text{Mo-}K_{\alpha})$ [mm ⁻¹]	0.856	0.843
<i>T</i> [K]	293(2)	293(2)
Data coll. range [°]	$5.8 \leq 2\theta \leq 50$	$4.9 \leq 2\theta \leq 50$
<i>h</i>	$-10 \leq h \leq 10$	$-8 \leq h \leq 8$
<i>k</i>	$0 \leq k \leq 18$	$0 \leq k \leq 19$
<i>l</i>	$0 \leq l \leq 25$	$0 \leq l \leq 15$
No. reflect. measured	13711	8166
No. unique data	4834 ($R_{\text{int}} = 0.0367$)	2535 ($R_{\text{int}} = 0.0222$)
Parameters	541	292
GoF on F^2	1.172	1.163
R_1 [$I \geq 2\sigma(I)$]	0.0727	0.0389
$wR2$ (all data)	0.3110	0.1295

Acknowledgments

Financial support of this work by the Fonds der Chemischen Industrie is gratefully acknowledged.

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Received May 24, 2002
[I02269]