

Fluxional and Rigid (Trimethylphosphane)cobalt Complexes Containing Chelating (2-Diphenylphosphanyl)anilido Ligands

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Keywords: Chelates / Cobalt / P ligands / Structure elucidation

2-(Diphenylphosphanyl)anilines ($P^{\wedge}NHR$) eliminate methane upon reaction with $[CoMe(PMe_3)_4]$ forming the complexes $[Co(\eta^2-P^{\wedge}NR)(PMe_3)_3]$ (**1**: $R = H$; **2**: $R = Me$) and $[Co(\eta^2-P^{\wedge}NR)(PMe_3)_2]$ (**3**: $R = Me$). Reaction with HCl gives $[CoCl(\eta^1-P^{\wedge}NHR)(PMe_3)_2]$ (**4**: $R = H$; **5**: $R = Me$) and reaction with CO or olefin gives $[Co(\eta^2-P^{\wedge}NR)(CO)(PMe_3)_2]$ (**6**: $R = H$; **7**: $R = Me$) and $[Co(\eta^2-P^{\wedge}NR)(olefin)(PMe_3)_2]$ (**8**: $R = H$, olefin = C_2H_4 ; **9**: $R = Me$, olefin = C_2H_4 ; **10**: $R = Me$, olefin = C_3H_6), respectively. No catalytic transformation of the olefins was observed. Oxidation by iodomethane yields a cobalt(II) compound $[CoI(\eta^2-P^{\wedge}NR)(PMe_3)_2]$ (**11**: $R = Me$). By treating

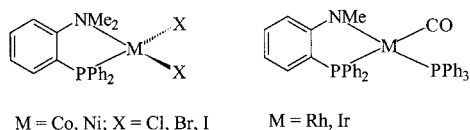
2-(diphenylphosphanyl)aniline with $[CoMe_2(PMe_3)_3]$ a methylcobalt(II) complex $[CoMe(\eta^2-P^{\wedge}NR)(PMe_3)_2]$ (**12**: $R = H$) is obtained, while an excess of the aniline produces $[Co(\eta^2-P^{\wedge}NR)_2]$ (**13**: $R = H$; **14**: $R = Me$) or $[Co(\eta^2-P^{\wedge}NR)_2(PMe_3)]$ (**15**: $R = H$; **16**: $R = Me$). The methylcobalt(III) complexes *mer-trans*- $[CoI Me_2(\eta^2-P^{\wedge}NR)(PMe_3)_2]$ were obtained from $LiP^{\wedge}NR$ and $[CoCl Me_2(PMe_3)_3]$. Dynamic ^{31}P NMR spectra and the structures of complexes **3**, **6**, **12**, and **13** are discussed.

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Introduction

Molecular derivatives of 2-(diphenylphosphanyl)aniline are well known as P,N-chelating ligands for the late transition metals,^[1] and palladium(II), in particular, has been extensively investigated regarding certain aspects of homogeneous catalysis. Examples of first-row transition metals in early studies by Venanzi et al.^[2] are molecular dihalides of cobalt and nickel (high-spin) which have a tetrahedral coordination geometry.

Formulae A



Vaska-type square-planar complexes of rhodium(I) and iridium(I) containing 2-(diphenylphosphanyl)-*N*-methyl-anilido ligands have been investigated by Dahlenburg et al.,^[3] and examples of a μ^2 -bridging coordination mode of the 2-(diphenylphosphanyl)anilido ligand have been found in triangular clusters of ruthenium^[4] and osmium.^[5]

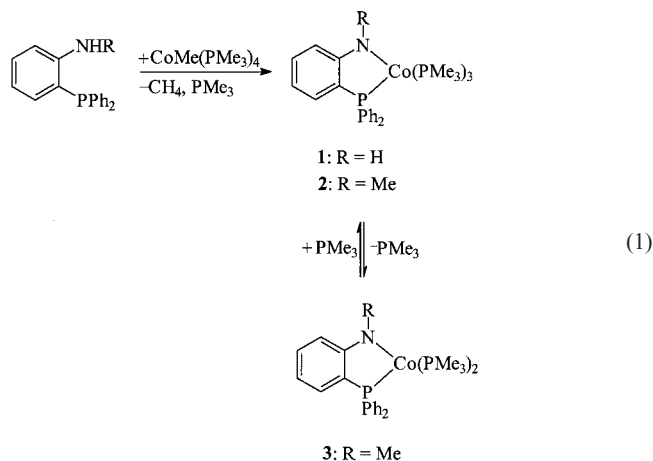
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Here we describe the synthesis and structural properties of some novel mononuclear complexes of cobalt(I) and their transformation by oxidative addition reactions including an unexpected cyclometallation reaction.

Results and Discussion

2-(Diphenylphosphanyl)anilines react with $[CoMe(PMe_3)_4]$ [Equation (1)] with the elimination of methane to afford the pentacoordinate cobalt(I) complexes **1** and **2** as brown solids that are freely soluble in pentane or diethyl ether.



Complex **1** forms dark brown crystals, while **2** is obtained as a solid wax, in moderate yield, from pentane containing excess trimethylphosphane. When dissociation of ligands is favoured, by applying fresh solvent or warming solid **2** in vacuo, a gradual transformation to the tetracoordinate complex **3** is achieved which eventually forms small red brown rods that are highly air-sensitive but thermally stable up to 135 °C. The observed magnetic susceptibility ($\mu_{\text{eff}}/\mu_{\text{B}} = 2.97$) is typical for tetrahedral complexes of cobalt(I).

Complexes **1** and **2** show a characteristic pattern of ^{31}P NMR signals: a doublet of triplets at $\delta = 52$ ppm for the chelating P nucleus, which experiences a coordination chemical shift of $\delta = 70$ ppm, a doublet of doublets at $\delta = -7$ ppm for two isochronic P nuclei and a doublet of triplets at $\delta = 28$ ppm for a third trimethylphosphane P nucleus (Figure 1).

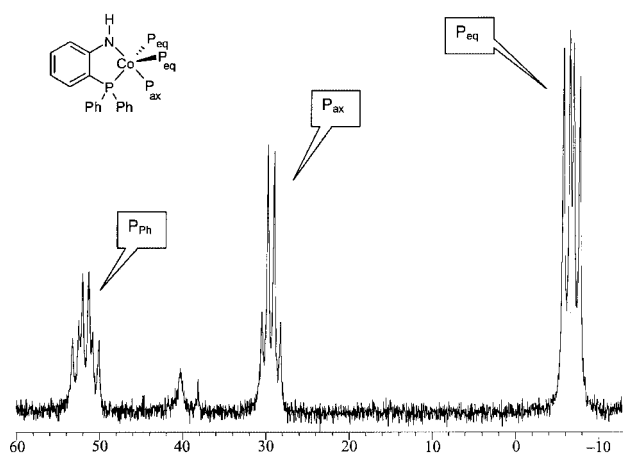


Figure 1. ^{31}P NMR spectrum of **1** (81 MHz, $[\text{D}_8]\text{THF}$, 233 K)

The values of the coupling constants ($J = 99$ and 61 Hz) fall in the range expected for the angles $\text{P}-\text{Co}-\text{P}$ ($90-110^\circ$) and suggest a trigonal-bipyramidal coordination geometry with two trimethylphosphane groups in equatorial positions.

In the molecular structure of **3** (Figure 2) a tetrahedral coordination geometry is confirmed by the angles $\text{P}-\text{Co}-\text{P}$ ($108-109^\circ$). The chelate bite angle $\text{P1}-\text{Co}-\text{N}$ [$86.34(8)^\circ$] is slightly larger than that found in a related pentacoordinate nickel(II) complex,^[6] and the sum of the internal angles in the metallacycle (539.9°) equals that of a regular pentagon; N coordination to the cobalt(I) ion (16 valence electrons) [$\text{Co}-\text{N}$ 1.926(2) Å] is found to be a normal distance,^[7] and remarkably, the sum of the angles at the nitrogen atom (359.9°) indicates planarity as is the case in the nickel complex (18 valence electrons).

Reactions

Ethereal HCl protonates the N donor and one of the trimethylphosphane groups, thereby opening the chelate ring in **1** or **2** while retaining the Ph_2P donor group and generat-

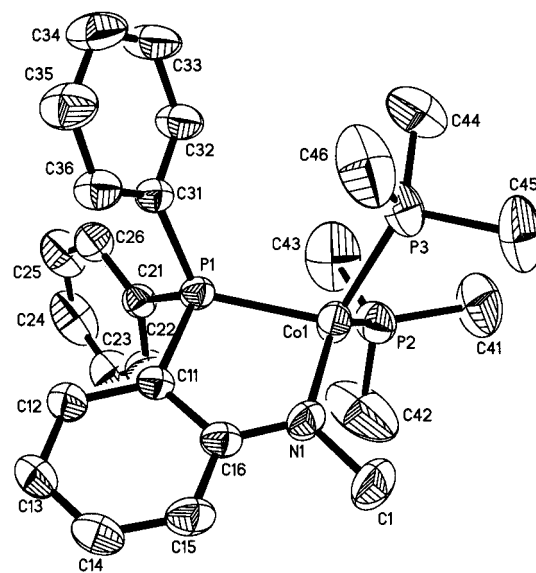
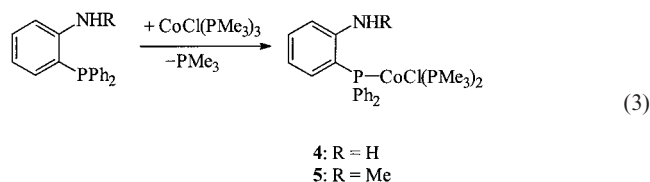
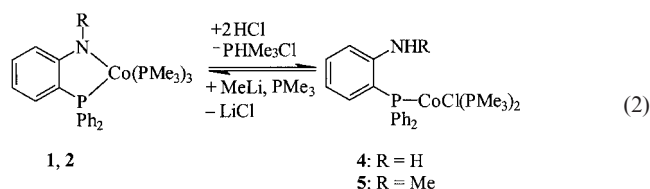


Figure 2. Molecular structure of **3** (ORTEP plot with hydrogen atoms omitted); selected bond lengths [Å] and angles [$^\circ$]: $\text{Co}-\text{N1}$ 1.926(2), $\text{Co}-\text{P1}$ 2.2374(9), $\text{Co}-\text{P2}$ 2.2243(10), $\text{Co}-\text{P3}$ 2.2473(12), $\text{P1}-\text{C11}$ 1.815(3), $\text{C11}-\text{C16}$ 1.426(4), $\text{C16}-\text{N1}$ 1.363(4); $\text{N1}-\text{Co}-\text{P1}$ $86.34(8)$, $\text{N1}-\text{Co}-\text{P2}$ $128.00(9)$, $\text{N1}-\text{Co}-\text{P3}$ $118.97(9)$, $\text{C1}-\text{N1}-\text{Co}$ $121.3(2)$, $\text{C16}-\text{N1}-\text{Co}$ $122.24(18)$, $\text{C1}-\text{N1}-\text{C16}$ $116.4(3)$, $\text{P1}-\text{Co}-\text{P2}$ $108.58(4)$, $\text{P1}-\text{Co}-\text{P3}$ $107.87(4)$, $\text{P2}-\text{Co}-\text{P3}$ $103.64(4)$, $\text{Co}-\text{P1}-\text{C11}$ $98.72(9)$, $\text{P1}-\text{C11}-\text{C16}$ $114.4(2)$

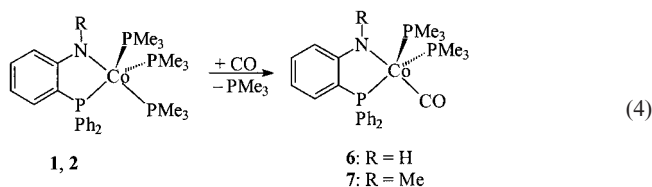
ing the tetracoordinate complexes **4** and **5** [Equation (2)]. The process can be reversed by treating the compound with methyllithium. In a most convenient synthesis $\text{CoCl}(\text{PMe}_3)_3$ is treated with the appropriate 2-(diphenylphosphanyl)aniline [Equation (3)].



Complexes **4** and **5** form green solids that are insoluble in pentane, highly soluble in THF, and are best recrystallised from diethyl ether. IR spectra in the $\nu(\text{NH})$ region show the expected number of bands at 3404 and 3318 cm^{-1} (**4**) that are close to those of 2-(diphenylphosphanyl)aniline.

A band occurring at 3332 cm^{-1} (**5**) is shifted by 30 cm^{-1} with respect to 2-(diphenylphosphanyl)-*N*-methylaniline indicating an intramolecular hydrogen bond $\text{N}-\text{H}\cdots\text{Cl}$ in **5**.

The values of the magnetic susceptibilities (**4**: $\mu_{\text{eff}}/\mu_{\text{B}} = 3.29$; **5**: $\mu_{\text{eff}}/\mu_{\text{B}} = 3.25$) are consistent for tetrahedral high-spin complexes.^[8] Under 1 bar of CO **1** and **2** smoothly form monocarbonyl complexes [Equation (4)].



From pentane, red crystals of **6** and **7** are obtained that are thermally stable up to 150 °C. IR spectra contain single $\nu(\text{CO})$ bands of terminal carbonyl ligands (**6**: 1887 cm^{-1} ; **7**: 1906 cm^{-1}) indicating that only one of the possible two isomers is present. The ^{31}P NMR doublet and triplet resonances at characteristic shifts, along with the larger coupling ($J = 97$ Hz) indicate that the carbonyl ligand resides in an axial position. This configuration is also adopted in the

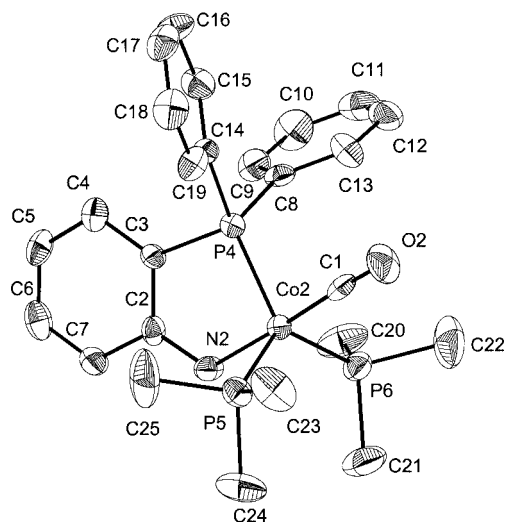
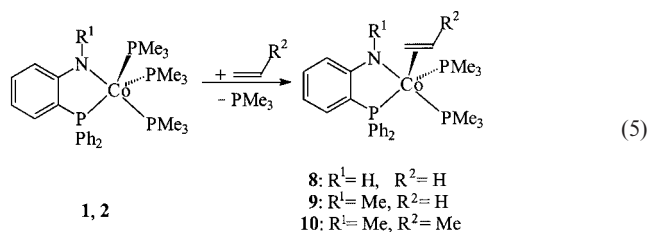


Figure 3. Molecular structure of **6** (ORTEP plot with hydrogen atoms omitted); selected bond lengths [Å] and angles [°]: Co–C1 1.754(14), C1–O2 1.157(15), Co–P4 2.210(3), Co–P5 2.184(3), Co–P6 2.194(3), Co–N2 1.907(9), N2–C2 1.360(14), C2–C3 1.411(15), P4–C3 1.80(1); N2–Co–C1 176.9(5), N2–Co–P4 84.3(3), N2–Co–P5 86.1(3), N2–Co–P6 88.2(3), Co–N2–C2 122.6(8), N2–C2–C3 118.8(9), C2–C3–P4 111.6(8), C3–P4–Co 100.6(4)

crystal, as shown by the molecular structure of **6** (Figure 3).

The carbonyl and amide ligands occupy axial positions with tighter bonding [Co–N = 1.907(9) Å] than that in **3** which arises from a push-pull stabilisation of ligands in *trans* positions [C–Co–N 176.9(5)°]. The chelate bite angle P4–Co–N [84.3(3)°] is only 2° larger than it is in **3**, and the sum of the internal angles in the metallacycle is 537.9°. There is a close structural correspondence between **6** and a related carbonylbis(trimethylphosphane)cobalt(I)(*P,O*-chelate) complex^[9] as can be expected of isoelectronic O and NH donors.

Brown solutions of **1** or **2** in pentane under 1 bar of ethene or propene turn red and upon cooling afford red crystals of monoolefin complexes **8–10** [Equation (5)], in the case of **6** and **7** together with crystals of **3**. No reaction is observed in neat cyclopentene.

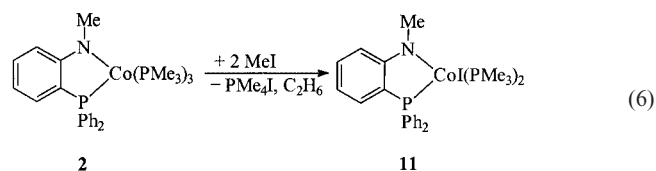


Careful drying under a gas blanket of olefin and manual selection of crystals gives analytically pure samples of **8–10**. All three compounds are solids with low melting points that are sensitive towards heat and oxygen, already releasing olefin at 20 °C in vacuo. As no structural proof has been obtained by X-ray diffraction on single crystals, ^{31}P NMR spectroscopy was used to support pentacoordination in compounds **8–10**. At 193 K ligand mobility is slow enough to reveal the ground-state geometry through a doublet of doublets pattern of three ^{31}P NMR signals (Table 1).

Table 1. ^{31}P NMR spectroscopic data (81 MHz, $[\text{D}_8]\text{THF}$, 193 K) for (olefin)cobalt compounds **8–10** [δ in ppm, J in Hz]

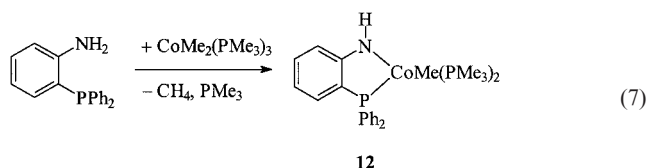
	$\delta(\text{P}_{\text{Ph}})$		$\delta(\text{P}_{\text{ax}})$		$\delta(\text{P}_{\text{eq}})$	
	$^2J(\text{P}_{\text{Ph}}\text{P}_{\text{eq}})$	$^2J(\text{P}_{\text{Ph}}\text{P}_{\text{ax}})$	$^2J(\text{P}_{\text{ax}}\text{P}_{\text{Ph}})$	$^2J(\text{P}_{\text{ax}}\text{P}_{\text{eq}})$	$^2J(\text{P}_{\text{eq}}\text{P}_{\text{Ph}})$	$^2J(\text{P}_{\text{eq}}\text{P}_{\text{ax}})$
8	61 (dd)		23 (dd)		3 (dd)	
	34	30	30	52	34	52
9	61 (dd)		23 (dd)		3 (dd)	
	36	32	32	56	36	56
10	61 (dd)		22 (dd)		3 (dd)	
	38	30	30	52	38	52

^{31}P nuclei of axial and equatorial trimethylphosphane groups are coupled with an equatorial chelating ^{31}P nucleus leaving an equatorial position for the olefin ligand. Reaction of **2** with iodomethane [Equation (6)] – oxidative substitution of a trimethylphosphane group and quaternisation – takes an unexpected course.



Black crystals of an iodocobalt(II) complex **11** are obtained from diethyl ether. Elemental analysis shows that the cobalt atom has lost the initial methylmetal function and is coordinated to five ligands. Accordingly, the magnetic susceptibility ($\mu_{\text{eff}}/\mu_{\text{B}} = 2.09$) is as expected for a pentacoordin-

ate cobalt (d^7) compound.^[10] A corresponding methylcobalt(II) complex **12** is obtained by reaction of 2-(diphenylphosphanyl)aniline with $\text{CoMe}_2(\text{PMe}_3)_3$ [Equation (7)].



The black crystals of **12** are freely soluble in pentane and are thermally even more stable than **11**. The magnetic susceptibility ($\mu_{\text{eff}}/\mu_{\text{B}} = 1.65$) is at the lower end of that expected for a trigonal-bipyramidal configuration of the Co atom (d^7 , 17 valence electrons).^[10] While no solution structure of **12** could be derived from spectroscopic data, the molecular structure was revealed by X-ray diffraction (Figure 4).

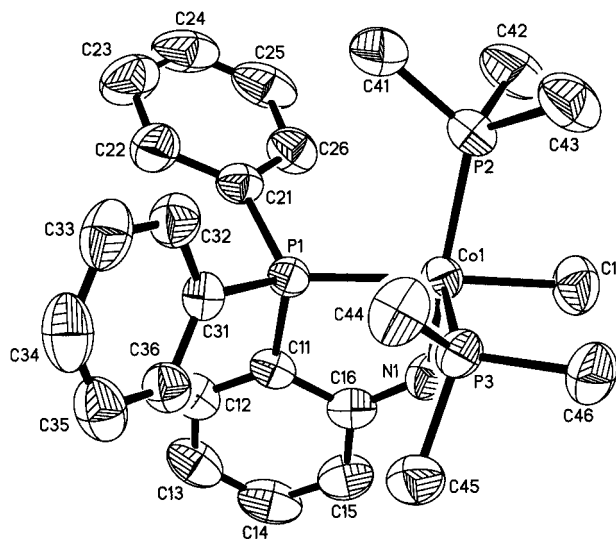
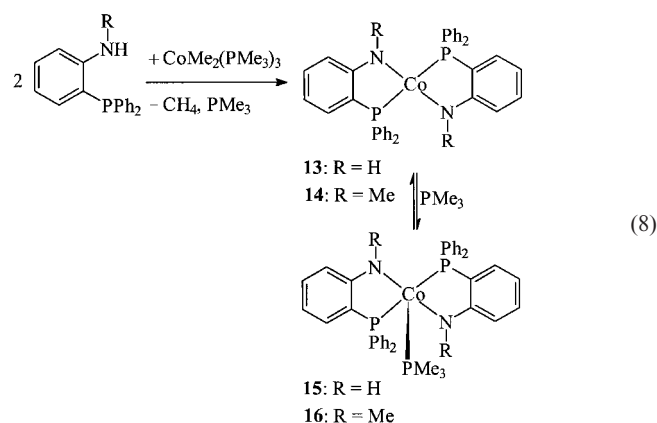


Figure 4. Molecular structure of **12** (ORTEP plot with hydrogen atoms omitted); selected bond lengths [Å] and angles [°]: Co–C1 2.019(3), Co–N1 1.929(2), Co–P1 2.2472(8), Co–P2 2.1858(9), Co–P3 2.2833(8), N1–C16 1.351(3), C16–C11 1.407(4), C11–P1 1.808(3); P1–Co–C1 162.43(10), N1–Co–P2 154.60(7), N1–Co–P3 102.47(7), N1–Co–P1 82.64(7), Co–N1–C16 125.32(18), N1–C16–C11 118.5(2), C16–C11–P1 111.83(19), C11–P1–Co 101.65(9)

The cobalt centre of **12** is located above an almost square plane (P1,P2,C1,N1) with an apical trimethylphosphane group (P3) attached to it at the longest Co–P distance. The void *trans* to P3 is large enough for, although not occupied by, a hydride ligand. This is seen from the IR spectrum where the $\nu(\text{CoH})$ region is empty along with the d^7 valence state of the Co atom. The methyl ligand (C1) is arranged in the opposite position to the chelating P donor (P1) which is different from an otherwise related pentacoordinate methylnickel(II) complex (18 electrons), where it is *trans* to the amide donor.^[6] The chelate bite angle is close to that in

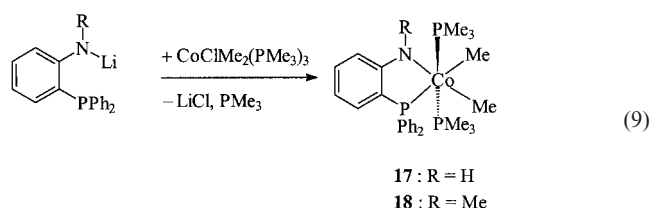
3, and the sum of the internal angles (539.9°) indicates a relaxed metallacycle. Reactivity of the methylmetal function is sufficient to afford bis(P,N)chelate compounds of cobalt(II) [Equation (8)].



The molecular complexes **13** and **14** (15 metal valence electrons) are stable up to 250 and 200 °C, respectively. Only when additional trimethylphosphane is supplied in excess, does it coordinate to afford the pentacoordinate species **15** and **16**. Magnetic susceptibilities (**13**: $\mu_{\text{eff}}/\mu_{\text{B}} = 2.05$; **14**: $\mu_{\text{eff}}/\mu_{\text{B}} = 2.33$; **15**: $\mu_{\text{eff}}/\mu_{\text{B}} = 2.10$; **16**: $\mu_{\text{eff}}/\mu_{\text{B}} = 2.04$) fall in the range expected for tetracoordinate (low-spin)^[9,11] and pentacoordinate^[9,10] cobalt(II) compounds but give no further clue to the configuration of the complexes.

In the molecular structure of **13** (Figure 5) a *trans* square-planar arrangement of ligands is revealed around a cobalt atom sitting in a centre of inversion. The chelate bite angle is normal [P–Co–N $83.6(2)^\circ$] and so are the bond lengths [Co–N 1.858(6), Co–P 2.212(6) Å]. The structure of **13** is the first for this type of bis(*P,N*)chelate cobalt complex, with the *trans* configuration differing from that of isoelectronic *cis*-bis(*P,O*)chelate cobalt compounds.^[9]

In an attempted synthesis of methylcobalt(III) complexes containing chelating 2-(diphenylphosphanyl)anilido ligands no reaction of $\text{CoMe}_3(\text{PMe}_3)_3$ with 2-(diphenylphosphanyl)aniline or 2-(diphenylphosphanyl)-*N*-methylaniline was observed. An alternative route [Equation (9)] afforded the dimethylcobalt(III) compounds **17** and **18**.



Highly soluble short orange rods of **17** and **18** are crystallised from pentane and melt at 85 and 89 °C, respectively. Under conditions of low ligand mobility (193 K) the ^{31}P NMR signals recorded as a triplet (1 P) and doublet (2 P) indicate a meridional arrangement of P donor functions in

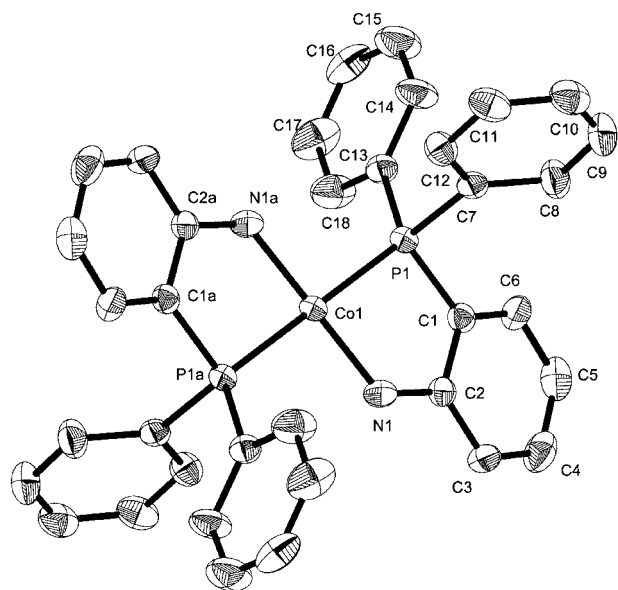
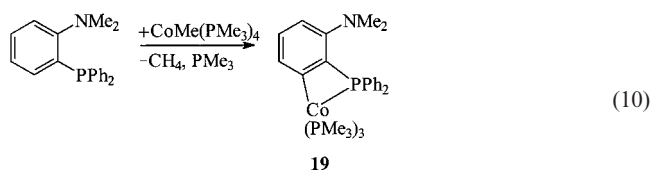


Figure 5. Molecular structure of **13** (ORTEP plot with hydrogen atoms omitted); selected bond lengths [Å] and angles [°]: Co–N1 1.858(6), Co–P1 2.212(2), P1–C1 1.798(8), C1–C2 1.398(10), C2–N1 1.389(9); C2–N1–Co 124.6(5), N1–C2–C1 117.0(7), C2–C1–P1 111.5(6), C1–P1–Co 100.8(3)

octahedral complexes of a low-spin Co (d^6) ion. Complex **15** tends to lose one of the methyl groups since after repeated recrystallisations black crystals of **12** were obtained.

Reactions involving methylcobalt compounds thus far have been directed towards a prechelatate NH function and proceed with the elimination of methane. Surprisingly, $[\text{CoMe}(\text{PMe}_3)_4]$ was found to react smoothly at -70°C with 2-(diphenylphosphanyl)-*N,N*-dimethylaniline. Evolution of gas was observed while heating to 20°C , and eventually dark red crystals of **19** were obtained and found to arise from a cyclometallation reaction [Equation (10)].



The ^{31}P NMR spectrum at 233 K clearly shows the characteristic shifts and coupling pattern of an *ortho*-metallated tris(trimethylphosphane)cobalt complex.^[12] As no further signals are detected, the absence of possible isomers of **19** is confirmed. This unusual result is supported by the ^{13}C NMR spectroscopic data. Only ten resonances of aromatic carbon nuclei were detected whereas eighteen are expected to arise from altogether five available *ortho*-CH groups.

Consequently, a thorough search for isomers of **19** was undertaken. In view of an 80% yield the synthesis was repeated on a larger scale (see Exp. Sect.) to afford 85% of the product, and 270 mg of solid residue could be scrutinised by IR and ^{13}C NMR spectroscopy. Again only the

signals of **19** were detected besides some trimethylphosphane oxide and the well-known marks of silicon grease, which amounts to an estimated regioselectivity of better than 99%.

Complexes of rhodium and iridium, containing 2-(diphenylphosphanyl)-*N,N*-dimethylaniline as a bidentate ligand, have been described,^[13] and no *ortho*-metallation was reported. Clearly, this spontaneous transformation with cobalt and its unexpected absolute selectivity merit further investigation.

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 $[\text{CoCl}(\text{PMe}_3)_3]$,^[14] $[\text{CoMe}(\text{PMe}_3)_4]$,^[15] $[\text{CoMe}_2(\text{PMe}_3)_3]$,^[10] $[\text{CoClMe}_2(\text{PMe}_3)_3]$,^[16] 2-(diphenylphosphanyl)aniline,^[17] 2-(diphenylphosphanyl)-*N*-methylaniline,^[18] and 2-(diphenylphosphanyl)-*N,N*-dimethylaniline.^[19] 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 NMR resonances were obtained with broad-band proton decoupling. MS: Varian Mat-311 (FD). Magnetic susceptibility data were obtained by the Faraday method, Cahn D 200 torsion balance and Bruker BMN-200/60 magnet system at 1.5 Tesla.

[2-(Diphenylphosphanyl)anilido-*N,P*]tris(trimethylphosphane)cobalt (1).

Method a: 2-(Diphenylphosphanyl)aniline (1202 mg, 3.70 mmol) in diethyl ether (40 mL) was combined with $[\text{CoMe}(\text{PMe}_3)_4]$ (1400 mg, 3.70 mmol) in diethyl ether (40 mL) at -70°C causing the evolution of gas and giving a brown heterogeneous mixture. This was heated to 20°C and stirred for 1 h. The dark solid of **1** was isolated by decanting and washing with cold pentane and dried in vacuo. From the liquor, at 4°C , another 260 mg of black crystals of **1** were obtained. Combined yield 1710 mg (82%). **Method b:** Chloro[2-(diphenylphosphanyl)anilido-*N,P*]bis(trimethylphosphane)cobalt (**4**) (980 mg, 1.87 mmol) and trimethylphosphane (1500 mg, 19.7 mmol) in THF (40 mL) were combined at -70°C with MeLi (1.6 M in diethyl ether (1.2 mL, 1.80 mmol) causing the dark green colour to turn red brown. The mixture was heated to 20°C and stirred for 30 min. The volatiles were removed in vacuo and the residue was extracted with three portions of diethyl ether (80 mL). Fractional crystallisation at 4°C afforded black crystals of **1**. Yield 664 mg (63%); m.p. $118\text{--}119^\circ\text{C}$ (dec.). IR (Nujol): $\tilde{\nu} = 3331\text{ cm}^{-1}$ (N–H). ^1H NMR (300 MHz, $[\text{D}_8]\text{THF}$, 233 K): $\delta = 0.88$ (br. s, 9 H, PCH_3), 1.28 (br. s, 18 H, PCH_3), 2.95 (s, 1 H, NH), 5.69 (t, $^3J = 6.8\text{ Hz}$, 1 H, CH), 6.23 (t, $^3J = 4.9\text{ Hz}$, 1 H, CH), 6.38 (t, $^3J = 7.1\text{ Hz}$, 1 H, CH), 7.06 (t, $^3J = 7.4\text{ Hz}$, 1 H, CH), 7.19–7.25 (m, 6 H, CH), 7.62–7.66 (m, 4 H, CH) ppm. ^{31}P NMR (81 MHz, $[\text{D}_8]\text{THF}$, 233 K): $\delta = -7$ (dd, $^2J_{\text{P,P}} = 99$ and 61 Hz, 2 P, PCH_3), 28 (dt, $^2J_{\text{P,P}} = 61$ and 60 Hz, 1 P, PC_6H_5), 52 (dt, $^2J_{\text{P,P}} = 99$ and 61 Hz, 1 P, PCH_3) ppm. $\text{C}_{27}\text{H}_{42}\text{CoNP}_4$ (563.5): calcd. C 57.55, H 7.51, N 2.49, P 21.99; found C 58.29, H 7.53, N 2.48, P 21.60.

[2-(Diphenylphosphanyl)-*N*-methylanilido-*N,P*]tris(trimethylphosphane)cobalt (2).

Method a: 2-(Diphenylphosphanyl)-*N*-

methylaniline (750 mg, 1.95 mmol) in THF (50 mL) was combined with $\text{CoMe}(\text{PMe}_3)_4$ (740 mg, 1.95 mmol) in THF (50 mL) at 20 °C. The mixture was stirred for 16 h and the solvents were evaporated to dryness in vacuo. The residue was extracted with two portions of pentane (50 mL) and the red brown solution cooled to –27 °C to afford a black solid which was isolated by decanting and drying in vacuo to give a waxy solid of **2**. Yield 395 mg (35%). **Method b:** Chloro[2-(diphenylphosphanyl)-*N*-methylaniline]bis(trimethylphosphane)cobalt (**5**) (580 mg, 1.08 mmol) and trimethylphosphane (1100 mg, 14.4 mmol) in THF (70 mL) were combined at –70 °C with MeLi (1.6 M in diethyl ether (0.67 mL, 1.08 mmol) causing the dark green colour to turn red brown. The mixture was warmed to 20 °C and stirred for 30 min. The volatiles were removed in vacuo and the residue was extracted with three 50 mL portions of pentane. Crystallisation at 4 °C afforded black crystals of **2**. Yield 395 mg (29%); m.p. 130–135 °C (dec.). ^1H NMR (300 MHz, $[\text{D}_8]\text{THF}$, 233 K): δ = 0.90 (br. s, 9 H, PCH_3), 1.25 (br. s, 18 H, PCH_3), 2.66 (s, 3 H, NCH_3), 5.80–7.78 (m, 14 H, CH) ppm. ^{31}P NMR (81 MHz, $[\text{D}_8]\text{THF}$, 233 K): δ = –8 (dd, $^2J_{\text{P,P}} = 103$ and 59 Hz, 2 P, PCH_3), 29 (dt, $^2J_{\text{P,P}} = 60$ and 59 Hz, 1 P, PC_6H_5), 52 (dt, $^2J_{\text{P,P}} = 103$ and 59 Hz, 1 P, PCH_3) ppm. MS (70 eV): m/z (%) = 577 (20) $[\text{M}^+]$, 501 (30) $[\text{M}^+ - \text{PMe}_3]$.

[2-(Diphenylphosphanyl)-*N*-methylanilido-*N*,*P*]bis(trimethylphosphane)cobalt (3**):** 2-(Diphenylphosphanyl)aniline (685 mg, 2.35 mmol) in THF (50 mL) was combined with $[\text{CoMe}(\text{PMe}_3)_4]$ (890 mg, 2.35 mmol) in THF (50 mL), at –70 °C, and after heating to 20 °C, the mixture was stirred for 16 h. The volatiles were removed in vacuo and the residue was extracted with two portions of pentane (50 mL). Crystallisation at 4 °C afforded red brown rods of **3**. Yield 763 mg (69%); m.p. 135–136 °C (dec.). Magnetic moment (299 K): $\mu_{\text{eff}} = 2.97 \mu_{\text{B}}$. $\text{C}_{25}\text{H}_{35}\text{CoNP}_3$ (501.4): calcd. C 59.89, H 7.04, N 2.79, P 18.53; found C 59.78, H 7.00, N 2.83, P 18.75.

Chloro[2-(diphenylphosphanyl)aniline]bis(trimethylphosphane)cobalt (4**):** 2-(Diphenylphosphanyl)aniline (584 mg, 2.10 mmol) in THF (50 mL) was combined with $\text{CoCl}(\text{PMe}_3)_3$ (680 mg, 2.10 mmol) in THF (50 mL) and within 10 min a dark green solution formed. After 1 h, the volatiles were removed in vacuo and the residue was extracted with three portions of diethyl ether (80 mL). Crystallisation at 4 °C afforded dark green prisms of **4**. Yield 716 mg (65%); m.p. 126–127 °C (dec.). Magnetic moment (299 K): $\mu_{\text{eff}} = 3.25 \mu_{\text{B}}$. IR (Nujol): $\tilde{\nu} = 3404, 3211 \text{ cm}^{-1}$ (N–H). $\text{C}_{24}\text{H}_{34}\text{ClCoNP}_3$ (523.8): calcd. C 55.03, H 6.54, N 2.67, P 17.74; found C 55.09, H 6.40, N 2.66, P 17.89.

Chloro[2-(diphenylphosphanyl)-*N*-methylaniline]bis(trimethylphosphane)cobalt (5**):** 2-(Diphenylphosphanyl)-*N*-methylaniline (803 mg, 2.75 mmol) in THF (50 mL) and $[\text{CoCl}(\text{PMe}_3)_3]$ (890 mg, 2.75 mmol) in THF (50 mL) formed a dark green solution. After 1 h, the volatiles were removed in vacuo and the residue was extracted as above. Crystallisation at 4 °C afforded dark green platelets of **5**. Yield 1130 mg (77%); m.p. 130–131 °C (dec.). Magnetic moment (299 K): $\mu_{\text{eff}} = 3.29 \mu_{\text{B}}$. IR (Nujol): $\tilde{\nu} = 3332 \text{ cm}^{-1}$ (N–H). $\text{C}_{25}\text{H}_{36}\text{ClCoNP}_3$ (537.9): calcd. C 55.83, H 6.75, N 2.60, P 17.28; found C 55.78, H 6.52, N 2.58, P 17.33.

Carbonyl[2-(diphenylphosphanyl)anilido-*N*,*P*]bis(trimethylphosphane)cobalt (6**):** A sample of **1** (710 mg, 1.26 mmol) in THF (70 mL) was stirred under 1 bar of CO for 30 min and afforded a red solution. The volatiles were removed in vacuo and the residue was extracted with two portions of pentane (70 mL). At 4 °C short orange red rods of **6** were obtained. Yield 487 mg (75%); m.p. 153–157 °C (dec.). IR (Nujol): $\tilde{\nu} = 3375 \text{ cm}^{-1}$ (N–H), 1887 cm^{-1} (CO). ^1H NMR (300 MHz, $[\text{D}_8]\text{THF}$, 296 K): δ = 1.15 (s, 18 H,

PCH_3), 1.35 (br. s, 1 H, NH), 5.93 (dd, $^3J = 7.2$, $^4J = 1.1$ Hz, 1 H, CH), 6.34 (dd, $^3J = 5.1$, $^4J_{\text{P,H}} = 3.1$ Hz, 1 H, CH), 6.60 (dd, $^3J = 6.7$, $^4J = 1.4$ Hz, 1 H, CH), 7.06 (dt, $^3J = 7.8$, $^4J = 1.4$ Hz, 1 H, CH), 7.25–7.31 (m, 6 H, CH), 7.52–7.61 (m, 4 H, CH) ppm. ^{13}C NMR (75.4 MHz, $[\text{D}_8]\text{THF}$, 296 K): δ = 18.6 (s, PCH_3), 109.7 (d, $^3J_{\text{P,C}} = 4.5$ Hz, CH), 116.7 (d, $^1J_{\text{P,C}} = 13.2$ Hz, CH), 128.5 (d, $^2J_{\text{P,C}} = 9.4$ Hz, CH), 130.3 (s, CH), 132.7 (d, $^2J_{\text{P,C}} = 12.5$ Hz, CH), 133.8 (s, CH), 135.0, 142.0 (s, C) ppm. ^{31}P NMR (81 MHz, $[\text{D}_8]\text{THF}$, 233 K): δ = 5 (d, $^2J_{\text{P,P}} = 97$ Hz, 2 P, PCH_3), 63 (t, $^2J_{\text{P,P}} = 97$ Hz, 1 P, PC_6H_5) ppm. $\text{C}_{25}\text{H}_{33}\text{CoNOP}_3$ (515.4): calcd. C 58.26, H 6.45, N 2.72, P 18.03; found C 58.03, H 6.64, N 2.66, P 18.11.

Carbonyl[2-(diphenylphosphanyl)-*N*-methylanilido-*N*,*P*]bis(trimethylphosphane)cobalt (7**):** A sample of **2** (590 mg, 1.02 mmol) in THF (70 mL) was stirred under 1 bar of CO for 30 min to afford a light red solution. The volatiles were removed in vacuo and the residue was extracted with two portions of pentane (70 mL). At 4 °C short dark red rods of **7** were obtained. Yield 492 mg (91%); m.p. 165–170 °C (dec.). IR (Nujol): $\tilde{\nu} = 1906 \text{ cm}^{-1}$ (CO). ^1H NMR (300 MHz, $[\text{D}_8]\text{THF}$, 296 K): δ = 1.17 (s, 18 H, PCH_3), 2.74 (s, 3 H, NCH_3), 5.72 (dd, $^3J = 7.4$, $^4J = 1.3$ Hz, 1 H, CH), 6.22 (dd, $^3J = 6.2$, $^4J_{\text{P,H}} = 2.8$ Hz, 1 H, CH), 6.60 (dd, $^3J = 6.2$, $^4J = 1.4$ Hz, 1 H, CH), 7.15 (dd, $^3J = 7.4$, $^4J = 1.4$ Hz, 1 H, CH), 7.31–7.36 (m, 6 H, CH), 7.45–7.52 (m, 4 H, CH) ppm. ^{13}C NMR (75.4 MHz, $[\text{D}_8]\text{THF}$, 296 K): δ = 18.1 (s, PCH_3), 39.4 (s, NCH_3), 109.2 (s, CH), 112.5 (d, $^4J_{\text{P,C}} = 4.9$ Hz, CH), 117.2 (d, $^1J_{\text{P,C}} = 14.9$ Hz, CH), 127.4 (d, $^2J_{\text{P,C}} = 12.3$ Hz, CH), 130.3 (s, CH), 133.4 (d, $^2J_{\text{P,C}} = 12.5$ Hz, CH), 133.7, 135.0 (s, C), 169.1 (d, $^2J_{\text{P,C}} = 30.5$ Hz, NC) ppm. ^{31}P NMR (81 MHz, $[\text{D}_8]\text{THF}$, 233 K): δ = 6 (d, $^2J_{\text{P,P}} = 97$ Hz, 2 P, PCH_3), 65 (t, $^2J_{\text{P,P}} = 97$ Hz, 1 P, PC_6H_5) ppm. $\text{C}_{26}\text{H}_{35}\text{CoNOP}_3$ (529.4): calcd. C 58.99, H 6.66, N 2.65, P 17.55; found C 58.98, H 6.73, N 2.55, P 17.48.

[2-(Diphenylphosphanyl)anilido-*N*,*P*](ethene)bis(trimethylphosphane)cobalt (8**):** A sample of **1** (580 mg, 1.02 mmol), suspended in pentane (70 mL), was stirred under 1 bar of C_2H_4 for 30 min to afford a red solution which was filtered and cooled to –27 °C. Short red rods of **8** were dried in a stream of ethene at 20 °C. Yield 281 mg (53%); m.p. 45–50 °C (dec.). IR (Nujol): $\tilde{\nu} = 3342 \text{ cm}^{-1}$ (N–H). ^1H NMR (300 MHz, $[\text{D}_8]\text{THF}$, 296 K): δ = 1.17 (d, $^2J_{\text{P,H}} = 7.3$ Hz, 9 H, PCH_3), 1.32 (d, $^2J_{\text{P,H}} = 4.5$ Hz, 9 H, PCH_3), 1.74 (m, 2 H, $\text{C}=\text{CH}_2$), 2.85 (m, 2 H, $\text{C}=\text{CH}_2$), 4.21 (br. s, 1 H, NH), 5.85 (m, 1 H, CH), 5.94 (m, 1 H, CH), 6.71 (m, 2 H, CH), 7.35–7.39 (m, 6 H, CH), 7.75–7.78 (m, 4 H, CH) ppm. ^{13}C NMR (75.4 MHz, $[\text{D}_8]\text{THF}$, 296 K): δ = 17.8 (d, $^1J_{\text{P,C}} = 19.4$ Hz, PCH_3), 20.4 (d, $^1J_{\text{P,C}} = 16.3$ Hz, PCH_3), 44.1 (m, CH_2), 108.1, 111.5, 123.2 (s, CH), 127.3 (m, C), 128.8, 130.7, 133.2 (s, CH), 134.4 (d, $^2J_{\text{P,C}} = 25.3$ Hz, C), 141.7 (s, CH) ppm. ^{31}P NMR (81 MHz, $[\text{D}_8]\text{THF}$, 193 K): δ = 3 (dd, $^2J_{\text{P,P}} = 34$ and 52 Hz, 1 P, PCH_3), 24 (dd, $^2J_{\text{P,P}} = 30$ and 52 Hz, 1 P, PCH_3), 61 (dd, $^2J_{\text{P,P}} = 34$ and 30 Hz, 1 P, PC_6H_5) ppm. $\text{C}_{26}\text{H}_{37}\text{CoNP}_3$ (515.4): calcd. C 60.59, H 7.24, N 2.72, P 18.03; found C 60.54, H 7.43, N 2.74, P 17.92.

[2-(Diphenylphosphanyl)-*N*-methylanilido-*N*,*P*](ethene)bis(trimethylphosphane)cobalt (9**):** A sample of **2** (720 mg, 1.24 mmol) in pentane (70 mL) was stirred under 1 bar of C_2H_4 for 30 min to afford a red solution which was filtered and cooled to 4 °C. Short red rods of **9** were dried in a stream of ethene at 20 °C. Yield 410 mg (62%); m.p. 45–50 °C (dec.). ^1H NMR (300 MHz, $[\text{D}_8]\text{THF}$, 296 K): δ = 0.72 (d, $^2J_{\text{P,H}} = 7.2$ Hz, 9 H, PCH_3), 1.30 (d, $^2J_{\text{P,H}} = 3.9$ Hz, 9 H, PCH_3), 1.73 (m, 2 H, $\text{C}=\text{CH}_2$), 2.16 (s, 3 H, NCH_3), 2.81 (m, 2 H, $\text{C}=\text{CH}_2$), 5.80 (m, 2 H, CH), 6.66–6.68 (m, 2 H, CH), 7.31–7.33 (m, 6 H, CH), 7.67–7.75 (m, 4 H, CH) ppm. ^{13}C NMR (75.4 MHz, $[\text{D}_8]\text{THF}$, 296 K): δ = 17.8 (d, $^1J_{\text{P,C}} = 22.6$ Hz, PCH_3), 20.4 (d, $^1J_{\text{P,C}} = 14.6$ Hz, PCH_3), 38.2 (s, NCH_3), 45.3 (d,

$^2J_{\text{PC}} = 18.3$ Hz, CH_2), 45.9 (m, CH_2), 108.4, 111.0, 123.3 (s, CH), 128.4 (d, $^1J_{\text{PC}} = 19.1$ Hz, C), 128.8, 130.7, 133.2 (s, CH), 133.8 (d, $^2J_{\text{PC}} = 24.3$ Hz, C), 141.7 (s, CH), 166.0 (s, NC) ppm. ^{31}P NMR (81 MHz, $[\text{D}_8]\text{THF}$, 193 K): $\delta = 3$ (dd, $^2J_{\text{P,P}} = 36$ and 56 Hz, 1 P, PCH_3), 23 (dd, $^2J_{\text{P,P}} = 32$ and 56 Hz, 1 P, PCH_3), 61 (dd, $^2J_{\text{P,P}} = 36$ and 32 Hz, 1 P, PC_6H_5) ppm. $\text{C}_{27}\text{H}_{39}\text{CoNP}_3$ (529.2): calcd. C 61.25, H 7.42, N 2.65, P 17.55; found C 61.18, H 7.52, N 2.51, P 17.62.

[2-(Diphenylphosphanyl)-*N*-methylanilido-*N*,*P*](propene)bis(trimethylphosphane)cobalt (10): A sample of **2** (830 mg, 1.43 mmol) in pentane (70 mL) was stirred under 1 bar of C_3H_6 for 30 min to afford a red solution which was filtered and cooled to -27°C . Red triangular platelets of **10** together with those of **2** were dried in a stream of propene at 20°C and separated mechanically. Yield 179 mg (23%); m.p. $85\text{--}87^\circ\text{C}$ (dec.). ^1H NMR (300 MHz, $[\text{D}_8]\text{THF}$, 296 K): $\delta = 0.74$ (d, $^2J_{\text{P,H}} = 8.0$ Hz, 9 H, PCH_3), 1.30 (d, $^2J_{\text{P,H}} = 6.1$ Hz, 9 H, PCH_3), 1.36 (m, 3 H, CCH_3), 2.42 (s, 3 H, NCH_3), 2.79 (m, 1 H, $\text{C}=\text{CH}$), 2.81 (m, 2 H, $\text{C}=\text{CH}_2$), 6.55 (m, 1 H, CH), 6.61 (m, 1 H, CH), 6.55 (m, 2 H, CH), 7.21–7.35 (m, 6 H, CH), 7.65–7.80 (m, 4 H, CH) ppm. ^{31}P NMR (81 MHz, $[\text{D}_8]\text{THF}$, 193 K): $\delta = 3$ (dd, $^2J_{\text{P,P}} = 38$ and 52 Hz, 1 P, PCH_3), 22 (dd, $^2J_{\text{P,P}} = 30$ and 52 Hz, 1 P, PCH_3), 61 (dd, $^2J_{\text{P,P}} = 38$ and 30 Hz, 1 P, PC_6H_5) ppm. $\text{C}_{28}\text{H}_{41}\text{CoNP}_3$ (543.2): calcd. C 61.88, H 7.60, N 2.58, P 17.10; found C 61.08, H 7.65, N 2.56, P 17.41.

[2-(Diphenylphosphanyl)-*N*-methylanilido-*N*,*P*](iodo)bis(trimethylphosphane)cobalt(diethyl ether) (11): A sample of **2** (780 mg, 1.35 mmol) in THF (50 mL) was combined with iodomethane (441 mg, 3.10 mmol), at -70°C , and the solution heated to 20°C to form a heterogeneous mixture. After 3 h, an off-white solid of tetramethylphosphonium iodide (IR) was removed by filtration and the dark brown solution concentrated to dryness in vacuo. Extraction with three portions of diethyl ether (80 mL) and crystallisation at 4°C afforded black cubic crystals of **11**. Yield 426 mg (45%); m.p. $85\text{--}86^\circ\text{C}$ (dec.). Magnetic moment (299 K): $\mu_{\text{eff}} = 2.09 \mu_{\text{B}}$. $\text{C}_{29}\text{H}_{45}\text{CoINOP}_3$ (702.4): calcd. C 49.59, H 6.46, N 1.99, P 13.23; found C 50.20, H 6.12, N 2.10, P 14.03.

[2-(Diphenylphosphanyl)anilido-*N*,*P*](methyl)bis(trimethylphosphane)cobalt (12): 2-(Diphenylphosphanyl)aniline (615 mg, 2.11 mmol) in diethyl ether (50 mL) and $\text{CoMe}_2(\text{PMe}_3)_3$ (670 mg, 2.11 mmol) in diethyl ether (50 mL) were combined at -70°C and heated to 20°C . After 16 h, the volatiles were removed in vacuo, and the solid residue was extracted with two portions of pentane (50 mL). Crystallisation at 4°C afforded black crystals of **12**. Yield 752 mg (71%); m.p. $117\text{--}119^\circ\text{C}$ (dec.). IR (Nujol): $\tilde{\nu} = 3341 \text{ cm}^{-1}$ (N–H). Magnetic moment (299 K): $\mu_{\text{eff}} = 1.65 \mu_{\text{B}}$. MS (70 eV): m/z (%) = 502 (14) $[\text{M}^+]$, 350 (30) $[\text{M}^+ - 2 \text{PMe}_3]$. $\text{C}_{25}\text{H}_{36}\text{CoNP}_3$ (502.4): calcd. C 59.77, H 7.22, N 2.79, P 18.49; found C 59.78, H 7.12, N 2.78, P 18.31.

Bis[2-(diphenylphosphanyl)anilido-*N*,*P*]cobalt (13). **Method a:** 2-(Diphenylphosphanyl)aniline (1060 mg, 3.84 mmol) in diethyl ether (50 mL) and $\text{CoMe}_2(\text{PMe}_3)_3$ (610 mg, 1.92 mmol) in diethyl ether (50 mL) were combined at -70°C and heated to 20°C . After 16 h, the volatiles were removed in vacuo, the solid residue was washed with cold pentane (5 mL) and extracted with two portions of diethyl ether (50 mL). Crystallisation at 4°C afforded dark red crystals of **13**. Yield 458 mg (39%). **Method b:** 2-(Diphenylphosphanyl)aniline (2050 mg, 7.39 mmol) in THF (30 mL) and CoCl_2 (480 mg, 3.69 mmol) in THF (50 mL) were combined at -70°C and MeLi (1.6 M) in diethyl ether (4.6 mL, 7.39 mmol) was added causing the colour to turn dark red. The mixture was warmed to 20°C and the volatiles were removed in vacuo. The residue was extracted with

two portions of diethyl ether (50 mL) and kept at 4°C to afford crystals of **13**. Yield 1150 mg (51%); decomp. $> 250^\circ\text{C}$. IR (Nujol): $\tilde{\nu} = 3337 \text{ cm}^{-1}$ (N–H). Magnetic moment (299 K): $\mu_{\text{eff}} = 2.05 \mu_{\text{B}}$. $\text{C}_{36}\text{H}_{30}\text{CoN}_2\text{P}_2$ (611.5): calcd. C 70.71, H 4.95, N 4.58, P 10.13; found C 71.09, H 5.33, N 4.39, P 10.46.

Bis[2-(diphenylphosphanyl)-*N*-methylanilido-*N*,*P*]cobalt (14).

Method a: 2-(Diphenylphosphanyl)-*N*-methylaniline (1040 mg, 3.59 mmol) in diethyl ether (40 mL) and $\text{CoMe}_2(\text{PMe}_3)_3$ (570 mg, 1.79 mmol) in diethyl ether (70 mL) were combined at -70°C and heated to 20°C . After 5 h, the volatiles were removed in vacuo, the solid residue was extracted with two portions of diethyl ether (70 mL). Crystallisation at 4°C afforded dark red crystals of **14**. Yield 551 mg (48%). **Method b:** 2-(Diphenylphosphanyl)aniline (1130 mg, 3.86 mmol) in THF (30 mL) and CoCl_2 (250 mg, 1.93 mmol) in THF (70 mL) were combined at -70°C and MeLi (1.6 M) in diethyl ether (2.42 mL, 3.86 mmol) was added causing the colour to turn dark red. The mixture was heated to 20°C and the volatiles were removed in vacuo. The residue was extracted with two portions of diethyl ether (50 mL) and kept at 4°C to afford crystals of **14**. Yield 390 mg (32%); decomp. $> 202^\circ\text{C}$. Magnetic moment (299 K): $\mu_{\text{eff}} = 2.33 \mu_{\text{B}}$. $\text{C}_{38}\text{H}_{34}\text{CoN}_2\text{P}_2$ (639.6): calcd. C 71.36, H 5.36, N 4.38, P 9.69; found C 70.78, H 5.46, N 4.39, P 9.88.

Bis[2-(diphenylphosphanyl)anilido-*N*,*P*](trimethylphosphane)cobalt (15):

A sample of **13** (660 mg, 1.07 mmol) was recrystallised from diethyl ether (40 mL) containing excess trimethylphosphane (280 mg, 3.67 mmol) at 4°C to afford bunches of red brown crystals. Yield 248 mg **15** (47%); m.p. $148\text{--}150^\circ\text{C}$ (dec.). IR (Nujol): $\tilde{\nu} = 3337 \text{ cm}^{-1}$ (N–H). Magnetic moment (299 K): $\mu_{\text{eff}} = 2.10 \mu_{\text{B}}$. $\text{C}_{39}\text{H}_{39}\text{CoN}_2\text{P}_3$ (687.6): calcd. C 68.12, H 5.72, N 4.07, P 13.51; found C 68.10, H 5.85, N 4.02, P 13.61.

Bis[2-(diphenylphosphanyl)-*N*-methylanilido-*N*,*P*](trimethylphosphane)cobalt (16):

A sample of **14** (450 mg, 0.70 mmol) was recrystallised from diethyl ether (50 mL) containing excess trimethylphosphane (730 mg, 9.59 mmol) at -27°C to afford bunches of short red brown rods of **16**. Yield 206 mg (41%); m.p. $165\text{--}167^\circ\text{C}$ (dec.). Magnetic moment (299 K): $\mu_{\text{eff}} = 2.04 \mu_{\text{B}}$. $\text{C}_{41}\text{H}_{43}\text{CoN}_2\text{P}_3$ (715.7): calcd. C 68.81, H 6.06, N 3.91, P 12.98; found C 68.79, H 5.45, N 4.06, P 13.25.

mer-trans-Dimethyl[2-(diphenylphosphanyl)anilido-*N*,*P*]bis(trimethylphosphane)cobalt (17):

2-(Diphenylphosphanyl)aniline (850 mg, 3.06 mmol) in diethyl ether (70 mL) were treated with MeLi (1.6 M) in diethyl ether (1.9 mL, 3.06 mmol). At -70°C , $\text{CoClMe}_2(\text{PMe}_3)_3$ (1080 mg, 3.06 mmol) in diethyl ether (50 mL) was added to the mixture which was heated to 20°C and stirred for 16 h. The volatiles were removed in vacuo, and the solid residue was extracted with two portions of pentane (70 mL). Crystallisation at -27°C afforded short orange rods of **17**. Yield 1030 mg (65%); m.p. $85\text{--}87^\circ\text{C}$ (dec.). IR (Nujol): $\tilde{\nu} = 3338 \text{ cm}^{-1}$ (N–H). ^1H NMR (200 MHz, $[\text{D}_8]\text{THF}$, 233 K): $\delta = -0.65$ (q, $^3J_{\text{P,H}} = 6.6$ Hz, 3 H, CoCH_3), 0.50 (t, $^3J_{\text{P,H}} = 9.9$ Hz, 3 H, CoCH_3), 0.67 (br. s, 18 H, PCH_3), 1.47 (br. s, 1 H, NH), 6.02 (t, $^3J = 6.9$ Hz, 1 H, CH), 6.37 (t, $^3J = 5.9$ Hz, 1 H, CH), 6.67 (t, $^3J = 7.5$ Hz, 1 H, CH), 7.19–7.26 (m, 6 H, CH), 7.49 (m, 1 H, CH), 7.78–7.82 (m, 4 H, CH) ppm. ^{31}P NMR (81 MHz, $[\text{D}_8]\text{THF}$, 193 K): $\delta = 12$ (br. s, 2 P, PCH_3), 41 (br. s, 1 P, PC_6H_5) ppm. $\text{C}_{26}\text{H}_{39}\text{CoNP}_3$ (517.5): calcd. C 60.35, H 7.60, N 2.71, P 17.96; found C 60.09, H 7.60, N 2.65, P 17.99.

mer-trans-[2-(Diphenylphosphanyl)-*N*-methylanilido-*N*,*P*]dimethylbis(trimethylphosphane)cobalt (18):

2-(Diphenylphosphanyl)-*N*-methylaniline (345 mg, 1.18 mmol) in diethyl ether (70 mL) was

treated with MeLi (1.6 m^l in diethyl ether (0.74 mL, 1.18 mmol). At -70°C , $\text{CoClMe}_2(\text{PMe}_3)_3$ (417 mg, 1.18 mmol) in diethyl ether (50 mL) was added to the mixture which was heated to 20°C and stirred for 16 h. The volatiles were removed in vacuo, and the solid residue was extracted with two portions of pentane (70 mL). Crystallisation at -27°C afforded short orange rods of **18**. Yield 630 mg (59%); m.p. $89-91^{\circ}\text{C}$ (dec.). ^1H NMR (300 MHz, $[\text{D}_8]\text{THF}$, 233 K): $\delta = -0.60$ (q, $^3J_{\text{P,H}} = 6.7$ Hz, 3 H, CoCH_3), 0.53 (t, $^3J_{\text{P,H}} = 9.2$ Hz, 3 H, CoCH_3), 0.64 (br. s, 18 H, PCH_3), 2.48 (s, 3 H, NCH_3), 6.20 (t, $^3J = 6.8$ Hz, 1 H, CH), 6.35 (t, $^3J = 7.0$ Hz, 1 H, CH), 6.67 (t, $^3J = 7.9$ Hz, 1 H, CH), 6.96–7.01 (m, 6 H, CH), 7.55 (t, $^3J = 6.8$ Hz, 1 H, CH), 7.69–7.75 (m, 4 H, CH) ppm. ^{31}P NMR (81 MHz, $[\text{D}_8]\text{THF}$, 193 K): $\delta = 15$ [d(br), $^2J_{\text{P,P}} = 35$ Hz, 2 P, PCH_3], 40 (t, $^2J_{\text{P,P}} = 35$ Hz, 1 P, PC_6H_5) ppm. $\text{C}_{27}\text{H}_{41}\text{CoNP}_3$ (531.5): calcd. C 61.02, H 7.78, N 2.64, P 17.48; found C 61.08, H 7.43, N 2.64, P 17.43.

[3-(Dimethylamino)-2-(diphenylphosphanyl)phenyl- C' ,P]tris(trimethylphosphane)cobalt (19): 2-(Diphenylphosphanyl)-*N,N*-dimethylaniline (1100 mg, 3.60 mmol) in diethyl ether (50 mL) was combined at -70°C with $\text{CoMe}(\text{PMe}_3)_4$ (1360 mg, 3.60 mmol) in diethyl ether (80 mL), with the evolution of a gas. The mixture was heated to 20°C and turned red brown. The volatiles were removed in vacuo, the residue was extracted with two portions of pentane (80 mL), and from the red solution dark red crystals of **19** were obtained. Yield 1550 mg (85%); m.p. $112-113^{\circ}\text{C}$ (dec.). ^1H NMR (300 MHz, $[\text{D}_8]\text{THF}$, 296 K): $\delta = 1.02$ (d, $^2J_{\text{P,H}} = 5.6$ Hz, 9 H, PCH_3), 1.23 (br. s, 18 H, PCH_3), 2.13 (s, 6 H, NCH_3), 5.90 (m, 1 H, CH), 6.19–6.28 (m, 2 H, CH), 7.22–7.24 (m, 6 H, CH), 7.75–7.79 (m, 4 H, CH) ppm. ^{13}C NMR (75.4 MHz, $[\text{D}_8]\text{THF}$, 296 K): $\delta = 22.2-22.7$ (m, PCH_3), 23.3 (m, PCH_3), 43.3 (s, NCH_3), 109.3 (s, CH), 125.9 (d, $^3J_{\text{P,C}} = 3.1$ Hz, CH), 126.0 (s, CH), 126.3 (d, $^3J_{\text{P,C}} = 5.6$ Hz, CH), 126.9 (s, CH), 133.2 (d, $^3J_{\text{P,C}} = 7.6$ Hz, CH), 133.3 (d, $^3J_{\text{P,C}} = 7.6$ Hz, CH), 139.1 (d, $^1J_{\text{P,C}} = 9.6$ Hz, C), 171.3 (m, CoC) ppm. ^{31}P NMR (81 MHz, $[\text{D}_8]\text{THF}$, 233 K): $\delta = -24$ (dt, $^2J_{\text{P,P}} = 89$ and 68 Hz, 1 P, PC_6H_5), -4 (dt, $^2J_{\text{P,P}} = 89$ and 47 Hz, 2 P, PCH_3), 22 (dt, $^2J_{\text{P,P}} = 68$ and 47 Hz, 1 P, PCH_3) ppm. $\text{C}_{29}\text{H}_{46}\text{CoNP}_4$ (591.5): calcd. C 58.89, H 7.84, N 2.37, P 20.95; found C 58.92, H 7.82, N 2.27, P 20.83.

Crystal Structure Analyses: Crystal data are presented in Tables 2 and 3. Data collection: Complex **3**: A crystal was sealed under argon in a glass capillary and mounted on a Bruker AXS P4 diffractometer. Reflections were measured (ω -scans) using graphite-monochromated Mo- K_{α} radiation; Lp correction and absorption correction 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 idealised positions. Complex **6**: A crystal was sealed under argon in a glass capillary and mounted on a Stoe Stadi-4 diffractometer. Intensities were collected (ω -scans) using graphite-monochromated Mo- K_{α} radiation. No absorption correction was applied. The structure was solved as for **3**. Complex **12**: Crystal mounting, data collection, structure solution and refinement as for **3**. Complex **13**: 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 as for **3**. 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-184429 for **3**, -186376 for **6**, -184430 for **12**, -186377 for **13**) 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 **3** and **6**

	3	6
Empirical formula	$\text{C}_{25}\text{H}_{35}\text{CoNP}_3$	$\text{C}_{25}\text{H}_{33}\text{CoNOP}_3$
Formula mass	501.4	515.4
Crystal size [mm]	$0.44 \times 0.40 \times 0.36$	$0.44 \times 0.30 \times 0.26$
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1$
a [Å]	9.385(3)	9.8330(5)
b [Å]	12.502(2)	15.1030(7)
c [Å]	23.190(4)	18.1480(8)
β [°]	92.66(2)	89.940(4)
V [Å ³]	2718.0(11)	2695.1(2)
Z	4	2
$D_{\text{calcd.}}$ [g/cm ³]	1.225	1.270
$\mu(\text{Mo-}K_{\alpha})$ [mm ⁻¹]	0.820	0.386
Temperature [K]	293(2)	293(2)
Data coll. range [°]	$4.8 \leq 2\theta \leq 55$	$4.8 \leq 2\theta \leq 48$
h	$-1 \leq h \leq 12$	$-11 \leq h \leq 11$
k	$-1 \leq k \leq 16$	$0 \leq k \leq 17$
l	$-30 \leq l \leq 30$	$0 \leq l \leq 20$
No. reflect. measured	8023	8138
No. unique data	6232 ($R_{\text{int}} = 0.020$)	4209 ($R_{\text{int}} = 0.0494$)
Parameters	278	544
GoF on F^2	1.008	1.117
$R1$ [$I \geq 2\sigma(I)$]	0.0515	0.0607
$wR2$ (all data)	0.1171	0.1639

Table 3. Crystal data for compounds **12** and **13**

	12	13
Empirical formula	$\text{C}_{36}\text{H}_{30}\text{CoN}_2\text{P}_2$	$\text{C}_{28}\text{H}_{42}\text{CoIO}_{0.5}\text{P}_3$
Formula mass	502.4	611.6
Crystal size [mm]	$0.46 \times 0.40 \times 0.37$	$0.49 \times 0.38 \times 0.31$
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/a$
a [Å]	9.908(2)	11.5617(10)
b [Å]	20.075(4)	14.9016(17)
c [Å]	13.311(2)	17.8507(18)
β [°]	94.36(1)	101.384(9)
V [Å ³]	2639.9(8)	3015.0(5)
Z	4	4
$D_{\text{calcd.}}$ [g/cm ³]	1.264	1.347
$\mu(\text{Mo-}K_{\alpha})$ [mm ⁻¹]	0.844	0.649
Temperature [K]	293(2)	293(2)
Data coll. range [°]	$4.0 \leq 2\theta \leq 55$	$5.4 \leq 2\theta \leq 50$
h	$-12 \leq h \leq 1$	$-13 \leq h \leq 13$
k	$-26 \leq k \leq 1$	$0 \leq k \leq 17$
l	$-17 \leq l \leq 17$	$0 \leq l \leq 21$
No. reflect. measured	7476	5689
No. unique data	6052 ($R_{\text{int}} = 0.0200$)	5267 ($R_{\text{int}} = 0.0593$)
Parameters	278	373
GoF on F^2	1.046	1.131
$R1$ [$I \geq 2\sigma(I)$]	0.0403	0.0657
$wR2$ (all data)	0.0985	0.2085

Acknowledgments

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

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Received May 31, 2002

[I02281]