Steric Control of Cyclometallation Reactions in Schiff-Base Complexes of Cobalt(I) Containing an Anchoring Diphenylphosphanyl Group

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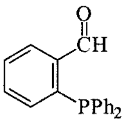
Keywords: Cyclometallation / Cobalt / P ligands / Schiff bases / Regioselectivity

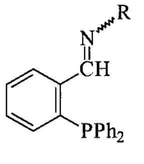
2-(Diphenylphosphanyl)alkyliminobenzaldehydes (2-$Ph_2PC_6H_4CHNR$) react with $[CoCH_3(PMe_3)_4]$ forming five-membered metallacycles in complexes $[(2\text{-}Ph_2PC_6H_4CNR\text{-}C,P)Co(PMe_3)_3]$ [**1**: R = C_2H_5, **2**: R = $CH(CH_3)_2$, **3**: R = *cyclo*-C_6H_{11}] while the *ortho*-metallation pathway is selectively followed in the formation of $[\{2\text{-}Ph_2PC_6H_3(CHNR)\text{-}C^1,P\}Co(PMe_3)_3]$ [**4**: R = $C(CH_3)_3$]. The presence of a four-membered cobaltocycle in the molecular structure of **4** was confirmed by X-ray analysis. Carbonylation of **2** and **3** gives the monocarbonyl derivatives $[(2\text{-}Ph_2PC_6H_4CNR\text{-}C,P)Co(CO)(PMe_3)_2]$ [**5**: R = $CH(CH_3)_2$, **6**: R = *cyclo*-C_6H_{11}] while **4** undergoes ring expansion by insertion forming $[\{2\text{-}Ph_2PC_6H_3(CHNR)CO\text{-}C,P\}Co(CO)(PMe_3)_2]$ [**7**: R = $C(CH_3)_3$]. Monosubstitution occurs under 1 bar of ethene giving the π-ethene complexes $[(2\text{-}Ph_2PC_6H_4CNR\text{-}C,P)Co(C_2H_4)(PMe_3)_2]$ [**8**: R = $CH(CH_3)_2$, **9**: R = *cyclo*-C_6H_{11}] and $[\{2\text{-}Ph_2PC_6H_3(CHNR)\text{-}C^1,P\}Co(C_2H_4)(PMe_3)_2]$ [**10**: R = $C(CH_3)_3$]. The molecular structure of **9** shows an equatorial π-ethene ligand. Iodomethane oxidizes **2** and **3** to afford the cobalt(II) complexes $[(2\text{-}Ph_2PC_6H_4CNR\text{-}C,P)CoI(PMe_3)_2]$ [**11**: R = $CH(CH_3)_2$, **12**: R = *cyclo*-C_6H_{11}] and oxidatively adds to **4** to give *mer-trans*-$[\{2\text{-}Ph_2PC_6H_3(CHNR)\text{-}C^1,P\}CoI(CH_3)(PMe_3)_2]$ [**13**: R = $C(CH_3)_3$].

Introduction

Methylnickel complexes have been shown to activate the CHO function of 2-diphenylphosphanylbenzaldehyde forming acylnickel compounds.[1]



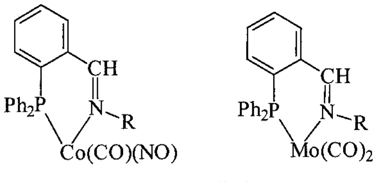
A



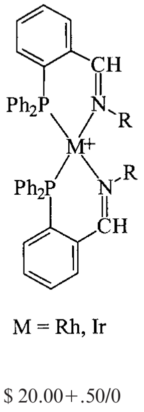
B

We have recently described cobalt(I) complexes containing soft/hard P,N-chelating ligands,[2] where the introduction of an imino ligand function increases the softness of the N-donor. The isoelectronic relationship between 2-diphenylphosphanyl benzaldehyde **A** and its Schiff base derivatives **B** raises the possibility of a cyclometallation route to iminoacyl metal complexes. The coordination modes of iminoacyl complexes, which depend on the number of metal valence electrons and steric limitations, show an active participation of the neighbouring N-donor whenever needed.

Therefore, in Schiff-base complexes of transition metal ions six-membered rings are the dominant structural features, and complexes of the chelating ligands **B** are no exception, as shown by the few reported examples of complexes of these ligands with cobalt,[3] molybdenum,[4] rhodium,[5] and iridium.[6] Preferred coordination of the N-donor would appear to prevent an attack of the metal at the C−H bond which would explain the scarcity of iminoacyl metal complexes arising from C−H activation.[7] However, in cyclometallation reactions with $[CoMe(PMe_3)_4]$ there is evidence for steric control being dominant.[8] Consequently we have studied the effect of a bulky N-substituent in our investigation of the prechelate species **B**.



R = alkyl



M = Rh, Ir

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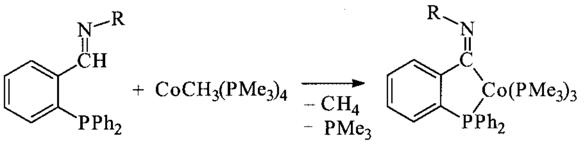
Results and Discussion

Metallation Reactions

An iminoacyl side-chain containing an N-donor function and an activated C−H bond was attached to one of the six *ortho*-positions of triphenylphosphane to give the Schiff-base compounds 2-(diphenylphosphanyl)alkyliminobenzaldehyde. Reaction with [CoMe(PMe$_3$)$_4$] proceeded at −70 °C in THF [Equation (1)] and afforded the C-metallated complexes **1**−**3**.



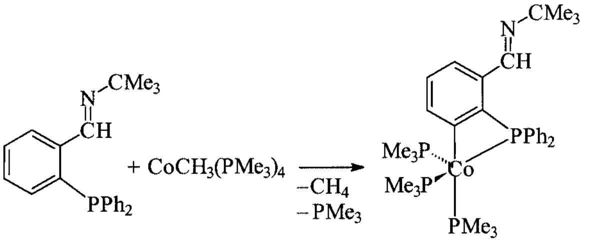
(1)

	1	**2**	**3**
R	C_2H_5	$CH(CH_3)_2$	*cyclo*-C_6H_{11}

Black quadrangular crystals of **1** and **2** were obtained from pentane solution while **3** formed dark brown scales. Decomposition was noticed above 109−113 °C under argon. The ν(C=N) absorptions in the IR spectra are shifted bathochromically (by about 100 cm^{-1}) with respect to those of the free ligands upon metallation. The ^{31}P NMR spectra of **1**−**3** show little variation in the dominant signals. A large low-field shift of the PPh$_2$ resonances is compatible only with five-membered cobaltocycles, and two doublets of doublets for one axial and two equatorial P-donor atoms with almost identical $J_{P,P}$ values indicate a tbp-coordinated cobalt in **1**−**3**. Only in the spectrum of **1** (Figure 1) are all the resonances accompanied by those of an isomer (12%) with quite different coupling constants.

Angular distortions of the tbp geometry can be expected in a configuration [(*E*)-alkyliminoacyl] where the ethyl substituent is sterically accommodated within the ligand sphere. Therefore the larger substituents in **2** and **3** are exclusively arranged in the opposite *Z*-configuration.

At first glance 2-diphenylphosphanyl-*tert*-butylbenzimide appeared to react similarly as evolution of a gas was observed at −70 °C. The reaction mixture became a slightly deeper red colour than **1**−**3**, and eventually dark red rhombic crystals of **4** were obtained from pentane. However, upon metallation there is almost no shift in the infrared absorption of the C=N band (1626 cm^{-1}), and in the ^{1}H NMR spectrum a singlet resonance (δ = 7.95 ppm) clearly represents an aldimine proton. The ^{31}P NMR spectrum shows a pattern of resonances well-known from *ortho*-metallated complexes,[8] strongly suggesting a regioselective cyclometallation reaction [Equation (2)].



(2)

4

The presence of a four-membered cobaltocycle in **4** was confirmed by elucidation of the molecular structure (Figure 2).

The cobalt atom occupies the central position of a trigonal bipyramid with an axial C1 atom and a PMe$_3$ group

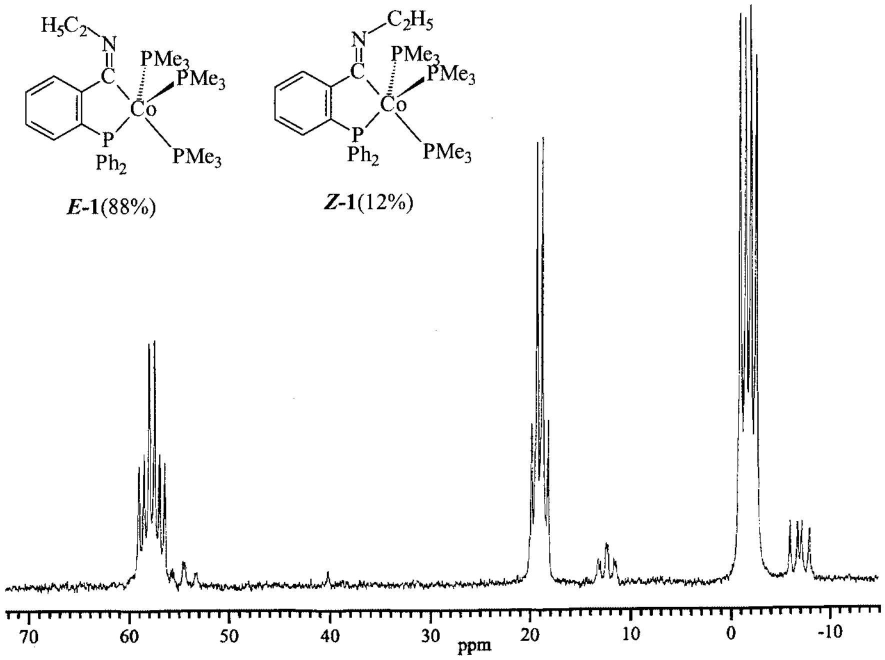

***E*-1**(88%) ***Z*-1**(12%)

Figure 1. ^{31}P NMR spectrum of **1** (81 MHz, [D$_8$]THF, 203 K)

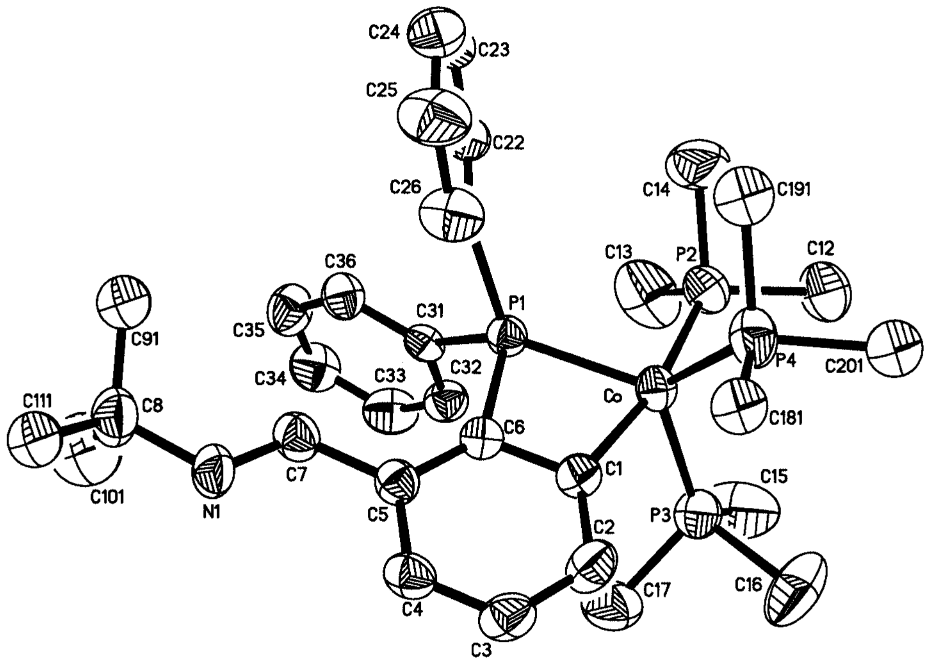


Figure 2. Molecular structure of 4, only one position of disordered *t*Bu and PMe_3 groups shown (ORTEP plot with hydrogen atoms omitted); selected bond lengths [Å] and angles [°]: Co−C1 1.977(4), Co−P1 2.2075(12), Co−P2 2.1997(15), Co−P3 2.1836(14), Co−P4 2.1821(15), P1−C6 1.802(4), C1−C6 1.403(5); C1−Co−P1 71.09(12), C1−Co−P2 167.82(12), C1−Co−P3 87.92(12), C1−Co−P4 90.78(12), P1−Co−P2 97.11(5), P1−Co−P3 124.02(5), P1−Co−P4 113.76(5), P2−Co−P3 96.66(6), P2−Co−P4 96.96(6), P3−Co−P4 117.93(6)

(P2). A planar [C,P] metallacycle (sum of internal angles = 360°) spans the axial and equatorial positions with a narrow bite-angle [C1−Co−P1 = 71.09(12)°]. Except for one of the equatorial PMe_3 groups (P4), which shows rotational disorder, the Co−C, Co−P, and P−C bond lengths are close to the average of reported values in arylcobalt compounds. The bond lengths and angles resemble those found in the unsubstituted parent compound.[8]

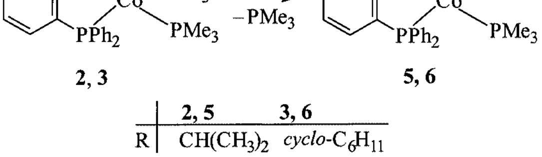
The bulky CMe_3 substituent appears to prevent a close approach of the CH=N group to the cobalt and causes complete switching of the metallation reaction onto the selective *ortho*-pathway where the four *ortho* positions of the PPh_2 group are not involved.[2]

Reactions with Carbon Monoxide

An experimental distinction between four- and five-membered cobaltocycles was achieved by placing solutions of **2**−**4** under a pressure of 1 bar CO at 20 °C. While the iminoacyl complexes **2** and **3** undergo monosubstitution [Equation (3)], compound **4** takes up two equivalents of CO and undergoes a ring expansion [Equation (4)].

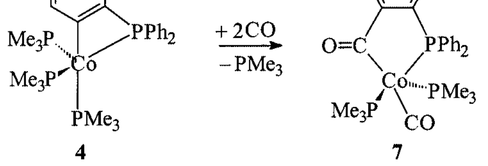
The iminoacyl(carbonyl)cobalt complexes **5** and **6** are yellow solids that can be handled in air for several hours and under argon are thermally stable up to 165 °C. They are insoluble in pentane or diethyl ether and show moderate solubility in THF. Their IR spectra display characteristic bands around 1876 cm^{-1} for terminal carbonyl ligands and around 1539 cm^{-1} for exocyclic C=N groups; these are hypsochromically shifted by about 18 cm^{-1} with respect to **2** and **3**. The ^{31}P NMR spectra show three resonances as doublets of doublets which are compatible with trimethylphosphane in axial and equatorial positions and an equatorial CO ligand.

The acyl(carbonyl)cobalt complex **7** is soluble in pentane or diethyl ether. In the IR spectrum the acyl and carbonyl groups are represented by new bands that fall precisely in the positions expected for a tbp molecular configuration with axial acyl and CO ligands.[2] The NMR spectroscopic data confirm this configuration in solution, and isomers with equatorial CO ligands are not detected.



(3)

	2, 5	**3, 6**
R	$CH(CH_3)_2$	*cyclo*-C_6H_{11}

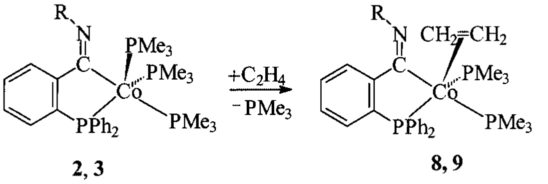


4 **7**

(4)

Reactions with Ethene

Red-brown solutions of **2** or **3** under 1 bar C_2H_4 turned orange red within 5 min indicating that a reaction had taken place [Equation (5)].



2, 3 **8, 9** (5)

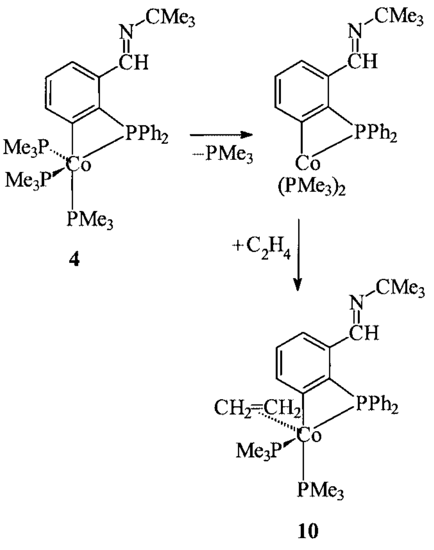
	2, 8	**3, 9**
R	CH(CH$_3$)$_2$	*cyclo*-C$_6$H$_{11}$

Short orange rods of **8** or orange rhombs of **9** were obtained from pentane that release ethene while decomposing above 93 °C under argon. The ^{31}P NMR spectra consist of three doublets of doublets with $J_{P,P}$ coupling constants of between 24 and 36 Hz, indicating P-nuclei of trimethylphosphanes in axial and equatorial positions leaving an equatorial position free for coordination of the ethene ligand.

In the crystal **9** has a molecular structure showing the expected configuration (Figure 3).

A cobalt atom in the centre of a trigonal bipyramid is coordinated to an equatorial ethene and two trimethylphosphanes in axial and equatorial positions. A five-membered metallacycle spans the C-axial and P-equatorial positions with a C7−Co−P1 bite angle of 79.11(9)° and considerable bending (sum of internal angles = 520.7° as compared with 540° for a planar arrangement). The side-on coordinated ethene shows the expected increase of 5 pm in the C8−C9 bond relative to free ethene. The Co−C1 and Co−P bond lengths fall in the typical range reported for arylcobalt complexes.

When compared with the isoelectronic (2-diphenylphosphanyl)benzoyl complex derived from the prechelate system **A**, in which cobalt fails to coordinate ethene, the iminoacyl group places enough electron density on the metal centre to support olefin binding. As was observed earlier a four-membered cobaltocycle induces weaker olefin coordination.[2] Compound **4** forms a π-ethene compound **10** [Equation (6)] only after thermal pretreatment.



(6)

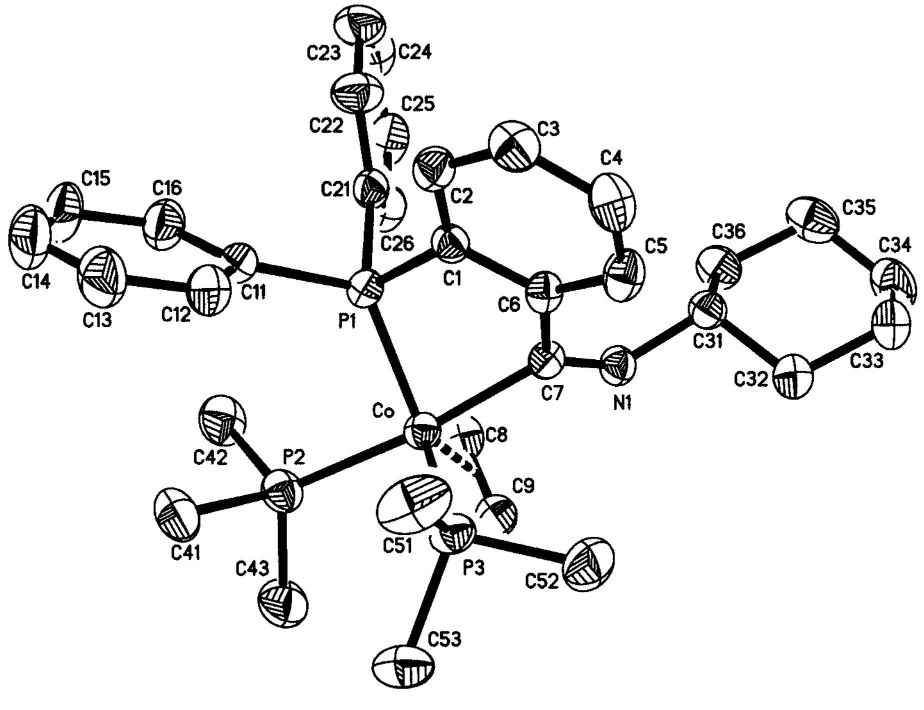
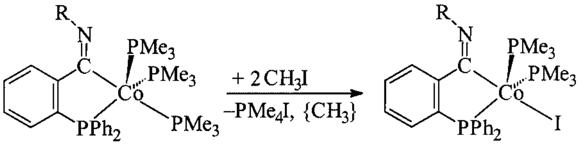


Figure 3. Molecular structure of **9** (ORTEP plot with hydrogen atoms omitted); selected bond lengths [Å] and angles [°]: Co−C7 2.014(3), Co−C8 2.055(3), Co−C9 2.046(3), Co−P1 2.1748(10), Co−P2 2.2232(12), Co−P3 2.1985(11), P1−C1 1.803(3), C1−C6 1.401(4), C6−C7 1.507(4), C8−C9 1.397(5); C7−Co−P1 79.11(9), C7−Co−P2 173.14(9), C7−Co−P3 87.17(9), P1−Co−P2 95.40(4), P1−Co−P3 113.32(4), P2−Co−P3 98.84(4), Co−C7−C6 114.3(2), C1−C6−C7 114.3(3), C6−C1−P1 110.4(2)

The orange crystals of **10** are readily soluble in diethyl ether or pentane. Before melting under argon at 105−107 °C with decomposition they turn red brown. This behaviour indicates a tetracoordinate intermediate which, however, could not be isolated as an analytically pure compound. The spectroscopic data of **10** are in agreement with an overall replacement reaction of one equatorial trimethylphosphane ligand by ethene.

Reactions with Iodomethane

Complexes **2** and **3** react with two molar equivalents of iodomethane in tetrahydrofuran [Equation (7)] to form the iodocobalt(II) complexes **11** and **12** with formal loss of a methyl group.



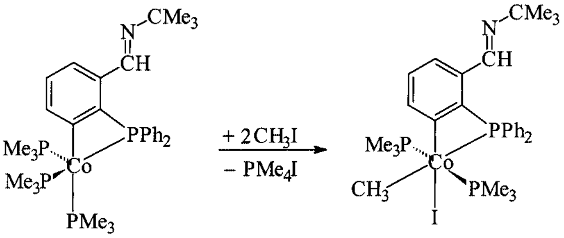
2, 3 **11, 12** (7)

	2, 11	**3, 12**
R	$CH(CH_3)_2$	*cyclo*-C_6H_{11}

Dark brown crystals with a magnetic moment of 1.98 were obtained. A diamagnetic cobalt(III) intermediate as described earlier[2] could not be isolated from reactions in less polar diethyl ether or pentane solvents.

This particular reactivity has been observed with type **A** systems where structural proof of a tbp molecular structure was obtained with acyl and iodo groups in axial positions.[1] On the basis of their mutual *trans*-influences a *trans*-arrangement of the iminoacyl and iodo ligands would suggest itself also for **11** and **12**.

Under otherwise similar conditions **4** oxidatively adds iodomethane with substitution and quaternization of a trimethylphosphane ligand [Equation (8)].The dark red crystals of **13** melt at 117−119 °C with decomposition and with no indication of the formation of a paramagnetic iodocobalt(II) complex as an intermediate. Solutions in THF slowly decompose at 273 K, but at 203 K the ^{31}P NMR spectroscopic data confirm a *mer-trans* arrangement of the six ligand functions.



4 **13** (8)

The steric influence of the alkylimino group in **13** does not affect the coordination sphere of cobalt, therefore the stereoselective oxidative *cis*-addition proceeds with retention of the metallacycle, as with other ring substituents.[1] As the iminoacyl group remains uncoordinated, it retains an *E*-configuration.

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, Germany. Melting points/decomposition temperatures: Sealed capillaries, uncorrected values. Chemicals (Merck/Schuchardt) were used as purchased. Literature methods were followed in the preparation of 2-(diphenylphosphanyl)-benzaldehyde,[9,10] 2-(diphenylphosphanyl)-*N*-alkyliminobenzaldehyde,[5,11] and $[CoMe(PMe_3)_4]$.[12] 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. Magnetic susceptibility data were obtained by the Faraday method using a Cahn D 200 torsion balance (Bruker) at 1.5 Tesla.

[(*E*,*Z*)-2-(Diphenylphosphanyl)-*N*-ethylbenzimino-*C*,*P*]tris(trimethylphosphane)cobalt(I) (1): 2-(Diphenylphosphanyl)-*N*-ethylbenzimide (377 mg, 1.18 mmol) in 30 mL of THF was combined at −70 °C with $[CoMe(PMe_3)_4]$ (450 mg, 1.18 mmol) in 80 mL of THF. During warm-up evolution of gas was noticed and the mixture became red brown. The mixture was kept at 20 °C for 18 h. The volatiles were then removed in vacuo, and the solid residue was extracted with two 70 mL portions of pentane. The solution was cooled to −27 °C to afford dark crystals of **1**. Yield 322 mg (45%); m.p. 109−111 °C (dec.). IR (Nujol): $\tilde{\nu} = 1542\ cm^{-1}$ (C=N). ^1H NMR (300 MHz, $[D_8]THF$, 296 K): $\delta = 0.89$ (br. s, 9 H, PCH_3), 1.18 (br. s, 18 H, PCH_3), 1.29 (t, $^3J = 6.9$ Hz, 3 H, CH_3), 3.65 (q, $^3J = 6.9$ Hz, 2 H, CH_2), 6.90 (t, $^3J = 7.2$ Hz, 1 H, CH), 7.01 (t, $^3J = 7.3$ Hz, 1 H, CH), 7.18−7.29 (m, 8 H, CH), 7.47−7.53 (m, 4 H, CH) ppm. ^{13}C NMR (75.4 MHz, $[D_8]THF$, 296 K): $\delta = 17.9$ (s, CH_3), 23.0 (m, PCH_3), 24.8 (m, PCH_3), 50.5 (s, CH_2), 123.4 (d, $^2J_{P,C} = 17.8$ Hz, CH), 125.8, 126.2 (s, CH), 128.1 (d, $^2J_{P,C} =$ 7.2 Hz, CH), (s, CH), 131.1 (s, CH), 133.8 (d, $^2J_{P,C} = 12.2$ Hz, CH), 142.2 (s, C) ppm. ^{31}P NMR (81 MHz, $[D_8]THF$, 203 K): *E*-**1** (88%) $\delta = -1$ (dd, $^2J_{P,P} = 84$ and 44 Hz, 2 P, PCH_3), 18 (dd, $^2J_{P,P} = 45$ and 44 Hz, 1 P, PCH_3), 57 (dt, $^2J_{P,P} = 84$ and 45 Hz, 1 P, PPh_2); *Z*-**1** (12%) $\delta = -6$ (dd, $^2J_{P,P} = 95$ and 63 Hz, 2 P, PCH_3), 12 (dt, $^2J_{P,P} = 63$ and 15 Hz, 1 P, PCH_3), 56 (dt, $^2J_{P,P} = 95$ and 15 Hz, 1 P, PPh_2) ppm. $C_{30}H_{46}CoNP_4$ (603.2): calcd. C 59.70, H 7.68, N 2.32, P 20.53; found C 59.85, H 7.60, N 2.35, P 20.52.

[(*Z*)-2-(Diphenylphosphanyl)-*N*-isopropylbenzimino-*C*,*P*]tris(trimethylphosphane)cobalt(I) (2): 2-(Diphenylphosphanyl)-*N*-isopropylbenzimide (622 mg, 1.87 mmol) was combined with $[CoMe(PMe_3)_4]$ (710 mg, 1.87 mmol) as described above to afford dark red crystals of **2**. Yield 683 mg (59%); m.p. 109−111 °C (dec.). IR (Nujol): $\tilde{\nu} = 1520\ cm^{-1}$ (C=N). ^1H NMR (300 MHz, $[D_8]THF$, 296 K): $\delta = 0.99$ (d, $^2J_{P,H} = 6.1$ Hz, 9 H, PCH_3), 1.29 (d, $^3J =$ 5.9 Hz, 6 H, CH_3), 1.12 (br. s, 18 H, PCH_3), 4.20 (septet, $^3J =$ 5.9 Hz, 1 H, CH), 3.65 (q, $^3J = 6.9$ Hz, 2 H, CH_2), 6.88 (dt, $^3J =$ 5.9, $^4J = 1.5$ Hz, 1 H, CH), 6.98 (dt, $^3J = 5.9$, $^4J = 1.5$ Hz, 1 H, CH), 7.08 (m, 2 H, CH), 7.20−7.22 (m, 6 H, CH), 7.77−7.84 (m, 4 H, CH) ppm. ^{13}C NMR (75.4 MHz, $[D_8]THF$, 296 K): $\delta = 21.4$ (m, PCH_3), 23.9 (s, CH_3), 53.5 (s, CMe_2), 120.4 (d, $^1J_{P,C} = 17.2$ Hz, CH), 123.6, 123.9 (s, CH), 126.2 (d, $^3J_{P,C} = 7.2$ Hz, CH), 128.6 (s, C), 132.1 (d, $^2J_{P,C} = 11.8$ Hz, CH) ppm. ^{31}P NMR (81 MHz, [D$_8$]THF, 203 K): δ = −4 (dd, $^2J_{P,P}$ = 79 and 45 Hz, 2 P, PCH$_3$), 17 (dd, $^2J_{P,P}$ = 45 and 44 Hz, 1 P, PCH$_3$), 55 (dt, $^2J_{P,P}$ = 79 and 44 Hz, 1 P, PPh$_2$) ppm. $C_{31}H_{48}CoNP_4$ (617.2): calcd. C 60.29, H 7.83, N 2.27, P 20.06; found C 59.95, H 7.40, N 2.26, P 20.43.

[(*E*)-2-(Diphenylphosphanyl)-*N*-cyclohexylbenzimino-*C,P*]tris(trimethylphosphane)cobalt(I) (3): 2-(Diphenylphosphanyl)-*N*-cyclohexylbenzimide (790 mg, 2.08 mmol) was combined with [CoMe(PMe$_3$)$_4$] (775 mg, 2.08 mmol) as described above to afford dark red crystals of **3**. Yield 1070 mg (78%); m.p. 113−115 °C (dec.). IR (Nujol): ṽ = 1527 cm^{-1} (C=N). ^{1}H NMR (300 MHz, [D$_8$]THF, 296 K): δ = 0.98 (br. s, 9 H, PCH$_3$), 1.18 (br. s, 18 H, PCH$_3$), 1.34−1.84 (m, 10 H, CH$_2$), 3.90 (m, 1 H, CH), 6.90 (t, ^3J = 7.1 Hz, 1 H, CH), 7.00 (t, ^3J = 7.0 Hz, 1 H, CH), 7.05 (m, 2 H, CH), 7.21−7.31 (m, 6 H, CH), 7.61−7.95 (m, 4 H, CH) ppm. ^{13}C NMR (75.4 MHz, [D$_8$]THF, 296 K): δ = 21.4 (m, PCH$_3$), 23.2, 25.2, 30.9, 34.3 (s, CH$_2$), 60.2 (s, NCH), 120.6 (d, $^1J_{P,C}$ = 17.3 Hz, CH), 123.6, 124.0 (s, CH), 126.3 (d, $^3J_{P,C}$ = 7.1 Hz, CH), 127.3 (d, $^2J_{P,C}$ = 12.2 Hz, CH), 128.8, 130.9 (s, C), 131.1 (d, $^2J_{P,C}$ = 9.5 Hz, CH), 132.1 (d, $^2J_{P,C}$ = 11.9 Hz, CH) ppm. ^{31}P NMR (81 MHz, [D$_8$]THF, 203 K): δ = −4 (dd, $^2J_{P,P}$ = 80 and 44 Hz, 2 P, PCH$_3$), 16 (dd, $^2J_{P,P}$ = 45 and 44 Hz, 1 P, PCH$_3$), 56 (dt, $^2J_{P,P}$ = 80 and 45 Hz, 1 P, PPh$_2$) ppm. $C_{34}H_{52}CoNP_4$ (657.2): calcd. C 62.10, H 7.97, N 2.13, P 18.84; found C 62.22, H 7.41, N 2.10, P 19.09.

[(*E*)-2-(Diphenylphosphanyl)-*N*-*tert*-butylbenzimide-*C^1*,*P*]tris(trimethylphosphane)cobalt(I) (4): 2-(Diphenylphosphanyl)-*tert*-butylbenzimide (530 mg, 1.50 mmol) in 50 mL of THF was combined at −70 °C with [CoMe(PMe$_3$)$_4$] (570 mg, 1.50 mmol) in 50 mL of THF and a gas evolved. After 16 h at 20 °C all volatiles were removed from the mixture in vacuo, and the solid residue was extracted with 80 mL of pentane. From the solution 250 mg of dark red rhombic crystals were obtained which proved suitable for X-ray diffraction. Upon cooling to −27 °C a second fraction of **4** was collected and combined with the first. Yield 790 mg (83%); m.p. 114−116 °C (dec.). IR (Nujol): ṽ = 1625 cm^{-1} (C=N). ^{1}H NMR (300 MHz, [D$_8$]THF, 296 K): δ = 0.91 (s, 9 H, CH$_3$), 1.11 (d, $^2J_{P,H}$ = 6.4 Hz, 9 H, PCH$_3$), 1.28 (t′, |$^2J_{P,H}$ + $^4J_{P,H}$| = 4.7 Hz, 18 H, PCH$_3$), 6.70 (t, ^3J = 7.4 Hz, 1 H, CH), 6.90 (m, 1 H, CH), 7.13 (d, ^3J = 7.0 Hz, 1 H, CH), 7.25−7.30 (m, 6 H, CH), 7.74−7.82 (m, 4 H, CH), 7.95 (s, 1 H, NCH) ppm. ^{13}C NMR (75.4 MHz, [D$_8$]THF, 296 K): δ = 21.7−22.9 (m, PCH$_3$), 27.3 (s, CH$_3$), 55.6 (s, CMe$_3$), 115.4 (s, CH), 126.5 (d, $^3J_{P,C}$ = 7.8 Hz, CH), 126.8, 127.5 (s, CH), 131.7 (d, $^2J_{P,C}$ = 12.9 Hz, CH), 138.0, 138.6 (s, C), 152.2 (d, $^2J_{P,C}$ = 6.9 Hz, NCH) ppm. ^{31}P NMR (81 MHz, [D$_8$]THF, 233 K): δ = −28 (dt, $^2J_{P,P}$ = 90 and 71 Hz, 1 P, PPh$_2$), −3 (dd, $^2J_{P,P}$ = 90 and 48 Hz, 2 P, PCH$_3$), 21 (dt, $^2J_{P,P}$ = 71 and 48 Hz, 1 P, PCH$_3$) ppm. $C_{32}H_{50}CoNP_4$ (631.2): calcd. C 60.86, H 7.98, N 2.22, P 19.62; found C 60.55, H 7.98, N 2.21, P 19.98.

[(*E*)-2-(Diphenylphosphanyl)-*N*-isopropylbenzimino-*C,P*]carbonylbis(trimethylphosphane)cobalt(I) (5): A sample of **2** (430 mg, 0.69 mmol) in 70 mL of diethyl ether was kept stirring under 1 bar of CO for 30 min to form a light yellow precipitate. The volatiles were then removed in vacuo, and the solid residue of **5** was washed with 20 mL of cold diethyl ether and dried in vacuo. Yield 368 mg (93%); m.p. 185−187 °C (dec.). IR (Nujol): ṽ = 1874 cm^{-1} (C≡O), 1538 cm^{-1} (C=N). ^{1}H NMR (300 MHz, [D$_8$]THF, 296 K): δ = 1.05 (br. s, 18 H, PCH$_3$), 1.30 (m, 6 H, CH$_3$), 4.30 (m, 1 H, NCH), 7.09 (m, 2 H, CH), 7.29−7.31 (m, 8 H, CH), 7.43−7.58 (m, 2 H, CH), 8.22−8.28 (m, 2 H, CH) ppm. ^{13}C NMR (75.4 MHz, [D$_8$]THF, 296 K): δ = 19.9 (m, PCH$_3$), 23.1 (s, CH$_3$), 8.5 (s, NCH), 127.5 (d, $^2J_{P,C}$ = 16.5 Hz, CH), 128.2 (d, $^2J_{P,C}$ = 15.9 Hz, CH), 129.1 (d, $^2J_{P,C}$ = 7.0 Hz, CH), 143.1 (m, C) ppm. ^{31}P NMR (81 MHz, [D$_8$]THF, 203 K): δ = −4 (dd, $^2J_{P,P}$ = 63 and 53 Hz, 1 P, PCH$_3$), 21 (dd, $^2J_{P,P}$ = 53 and 36 Hz, 1 P, PCH$_3$), 68 (dd, $^2J_{P,P}$ = 63 and 36 Hz, 1 P, PPh$_2$) ppm. $C_{29}H_{39}CoNOP_3$ (569.2): calcd. C 61.16, H 6.90, N 2.46, P 16.32; found C 60.97, H 6.87, N 2.45, P 16.20.

[(*E*)-2-(Diphenylphosphanyl)-*N*-cyclohexylbenzimino-*C,P*]-carbonylbis(trimethylphosphane)cobalt(I) (6): Carbonylation of **3** (510 mg, 0.77 mmol) in 50 mL of diethyl ether was carried out as in the preparation of **5** to afford **6** as a yellow solid. Yield 449 mg (95%); m.p. 165−167 °C (dec.). IR (Nujol): ṽ = 1880 cm^{-1} (C≡O), 1540 cm^{-1} (C=N). ^{1}H NMR (300 MHz, [D$_8$]THF, 296 K): δ = 1.04 (br. s, 18 H, PCH$_3$), 1.26−1.86 (m, 10 H, CH$_2$), 3.99 (m, 1 H, NCH), 7.04 (m, 2 H, CH), 7.29−7.31 (m, 8 H, CH), 7.41−7.43 (m, 2 H, CH), 8.00−8.03 (m, 2 H, CH) ppm. ^{13}C NMR (75.4 MHz, [D$_8$]THF, 296 K): δ = 21.9 (m, PCH$_3$), 24.7, 25.2, 26.8, 34.5 (s, CH$_2$), 68.8 (s, NCH), 125.5 (d, $^2J_{P,C}$ = 16.5 Hz, CH), 128.2 (d, $^3J_{P,C}$ = 3.9 Hz, CH), 128.7 (s, CH), 129.1 (d, $^2J_{P,C}$ = 7.1 Hz, CH), 133.8 (m, C) ppm. ^{31}P NMR (81 MHz, [D$_8$]THF, 203 K): δ = −4 (dd, $^2J_{P,P}$ = 61 and 54 Hz, 1 P, PCH$_3$), 21 (dd, $^2J_{P,P}$ = 54 and 39 Hz, 1 P, PCH$_3$), 69 (dd, $^2J_{P,P}$ = 61 and 39 Hz, 1 P, PPh$_2$) ppm. $C_{32}H_{43}CoNOP_3$ (609.2): calcd. C 63.05, H 7.11, N 2.30, P 15.24; found C 61.62, H 6.35, N 2.06, P 16.49. (Crystals of the analytical sample contained ca. 3% of trimethylphosphane oxide.)

[(*E*)-2-(Diphenylphosphanyl)benzoyl-3-*N*-*tert*-butylimidomethyl-*C,P*]carbonylbis(trimethylphosphane)cobalt(I) (7): A sample of **4** (520 mg, 0.82 mmol) in 70 mL of diethyl ether was kept stirring under 1 bar of CO for 1 h during which time the colour of the mixture turned from red brown to orange. The volatiles were removed in vacuo, and the solid residue was extracted with two 50 mL portions of pentane. Crystallization at −27 °C afforded dark red rhombs of **7**. Yield 380 mg (75%); m.p. 123−125 °C (dec.). IR (Nujol): ṽ = 1906 cm^{-1} (C≡O), 1630 cm^{-1} (C=N), 1540 cm^{-1} (C=O). ^{1}H NMR (300 MHz, [D$_8$]THF, 296 K): δ = 0.76 (s, 9 H, CH$_3$), 1.04 (t′, |$^2J_{P,H}$ + $^4J_{P,H}$| = 7.3 Hz, 18 H, PCH$_3$], 7.28−7.34 (m, 6 H, CH), 7.46 (dt, ^3J = 7.6, ^4J = 2.6 Hz, 1 H, CH), 7.54 (dd, ^3J = 6.4, ^4J = 1.6 Hz, 1 H, CH) ppm. ^{13}C NMR (75.4 MHz, [D$_8$]THF, 296 K): δ = 17.9 (m, PCH$_3$), 27.8 (s, CH$_3$), 56.1 (s, CMe$_3$), 68.8 (s, NCH), 125.5 (d, $^2J_{P,C}$ = 20.5 Hz, CH), 126.8 (s, CH), 127.3 (d, $^3J_{P,C}$ = 8.8 Hz, CH), 129.8 (d, $^2J_{P,C}$ = 11.4 Hz, CH), 137.1 (s, C), 138.5 (d, $^1J_{P,C}$ = 30.7 Hz, CH), 139.7 (d, $^2J_{P,C}$ = 23.9 Hz, CH), 153.3 (s, C), 159.1 (s, NCH) ppm. ^{31}P NMR (81 MHz, [D$_8$]THF, 233 K): δ = 9 (d, $^2J_{P,P}$ = 79 Hz, 1 P, PCH$_3$), 79 (t, $^2J_{P,P}$ = 79 Hz, 1 P, PPh$_2$) ppm. $C_{31}H_{41}CoNO_2P_3$ (611.2): calcd. C 60.89, H 6.76, N 2.29, P 15.20; found C 61.03, H 7.52, N 2.28, P 14.85.

[(*E*)-2-(Diphenylphosphanyl)-*N*-isopropylbenzimino-*C,P*]ethenebis(trimethylphosphane)cobalt(I) (8): A sample of **2** (650 mg, 1.05 mmol) in 50 mL of diethyl ether was kept stirring under 1 bar of C$_2$H$_4$ for 30 min to form an orange solution. The volatiles were removed in vacuo, and the solid residue was extracted with two 50 mL portions of pentane. Crystallization at −27 °C afforded orange crystals of **8**. Yield 365 mg (61%); m.p. 105−107 °C (dec.). IR (Nujol): ṽ = 1541 cm^{-1} (C=N). ^{1}H NMR (300 MHz, [D$_8$]THF, 296 K): δ = 0.69 (d, $^2J_{P,H}$ = 6.2 Hz, 9 H, PCH$_3$), 1.02 (d, ^3J = 5.9 Hz, 6 H, CH$_3$), 1.10 (d, $^2J_{P,H}$ = 6.1 Hz, 9 H, PCH$_3$), 1.67 (m, 2 H, CCH$_2$), 2.25 (m, 2 H, CCH$_2$), 3.98 (septet, $^2J_{P,H}$ = 6.2 Hz, 1 H, NCH), 6.79 (dd, ^3J = 5.7, ^4J = 1.4 Hz, 1 H, CH), 6.93 (dd, ^3J = 7.5, ^4J = 1.4 Hz, 1 H, CH), 7.03 (m, 1 H, CH), 7.26−7.30 (m, 6 H, CH), 7.74−7.83 (m, 4 H, CH) ppm. ^{13}C NMR (75.4 MHz, [D$_8$]THF, 296 K): δ = 17.5 (d, $^1J_{P,C}$ = 13.3 Hz, PCH$_3$), 21.1 (d, $^1J_{P,C}$ = 23.0 Hz, PCH$_3$), 23.9 (s, CH$_3$), 48.2 (d, $^2J_{P,C}$ = 20.4 Hz, CCH$_2$), 52.1 (d, $^2J_{P,C}$ = 13.9 Hz, CCH$_2$), 54.1 (s, NCH), 122.5 (d, $^2J_{P,C}$ = 15.2 Hz, CH), 126.8 (s, CH), 127.9−134.0 (s, CH), 134.9

(d, $^{2}J_{\mathrm{P,C}}$ = 12.1 Hz, CH), 138.3 (m, CH), 139.2 (d, $^{2}J_{\mathrm{P,C}}$ = 9.6 Hz, CH), 140.2 (d, $^{1}J_{\mathrm{P,C}}$ = 22.4 Hz, CH) ppm. ^{31}P NMR (81 MHz, [D$_8$]THF, 203 K): δ = 8 (dd, $^{2}J_{\mathrm{P,P}}$ = 30 and 26 Hz, 1 P, PCH$_3$), 16 (dd, $^{2}J_{\mathrm{P,P}}$ = 30 and 36 Hz, 1 P, PCH$_3$), 67 (dd, $^{2}J_{\mathrm{P,P}}$ = 36 and 26 Hz, 1 P, PPh$_2$) ppm. $C_{30}H_{43}CoNP_3$ (569.2): calcd. C 63.27, H 7.61, N 2.46, P 16.32; found C 63.40, H 7.80, N 2.41, P 15.80.

[(*E*)-2-(Diphenylphosphanyl)-*N*-cyclohexylbenzimino-*C,P*]ethenebis(trimethylphosphane)cobalt(I) (9): A sample of **3** (680 mg, 1.03 mmol) in 50 mL of pentane was kept stirring under 1 bar of C_2H_4 for 20 min to form a yellow solid. The supernatant solution was decanted and kept at −4 °C to afford yellow crystals of **9**. The solid was recrystallised from pentane. Combined yields 460 mg (73%); m.p. 93−95 °C (dec.). IR (Nujol): ṽ = 1557 cm^{-1} (C=N). ^{1}H NMR (300 MHz, [D$_8$]THF, 296 K): δ = 0.66 (d, $^{2}J_{\mathrm{P,H}}$ = 6.3 Hz, 9 H, PCH$_3$), 1.07 (d, ^{3}J = 6.1 Hz, 9 H, PCH$_3$), 1.24−1.99 (m, 10 H, CH$_2$), 1.80 (m, 2 H, CCH$_2$), 2.19 (m, 2 H, CCH$_2$), 3.41 (septet, $^{3}J_{\mathrm{P,H}}$ = 3.8 Hz, 1 H, NCH), 6.83 (dd, ^{3}J = 5.5, ^{4}J = 1.5 Hz, 1 H, CH), 7.00 (dt, ^{3}J = 7.3, ^{4}J = 1.5 Hz, 1 H, CH), 7.26−7.30 (m, 6 H, CH), 7.34 (dt, ^{3}J = 5.2, ^{4}J = 0.9 Hz, 1 H, CH), 7.44 (ddd, ^{3}J = 5.7, 5.0, ^{4}J = 1.1 Hz, 2 H, CH), 7.98 (ddd, ^{3}J = 9.5, ^{4}J = 1.9, 1.5 Hz, 2 H, CH) ppm. ^{13}C NMR (75.4 MHz, [D$_8$]THF, 296 K): δ = 18.0 (d, $^{1}J_{\mathrm{P,C}}$ = 13.2 Hz, PCH$_3$), 20.6 (d, $^{1}J_{\mathrm{P,C}}$ = 22.8 Hz, PCH$_3$), 24.9, 25.2, 27.2, 35.2, 36.0 (s, CH$_2$), 48.3 (d, $^{2}J_{\mathrm{P,C}}$ = 18.4 Hz, CCH$_2$), 51.5 (d, $^{2}J_{\mathrm{P,C}}$ = 11.3 Hz, CCH$_2$), 60.3 (s, NCH), 122.5 (d, $^{3}J_{\mathrm{P,C}}$ = 16.0 Hz, CH), 125.1 (d, $^{4}J_{\mathrm{P,C}}$ = 4.4 Hz, CH), 126.8 (s, CH), 128.0 (d, $^{3}J_{\mathrm{P,C}}$ = 8.7 Hz, CH), 128.5 (d, $^{3}J_{\mathrm{P,C}}$ = 7.6 Hz, CH), 129.1 (d, $^{3}J_{\mathrm{P,C}}$ = 8.6 Hz, CH), 134.5 (d, $^{2}J_{\mathrm{P,C}}$ = 10.1 Hz, CH), 134.9 (d, $^{2}J_{\mathrm{P,C}}$ = 12.1 Hz, CH), 138.8 (d, $^{2}J_{\mathrm{P,C}}$ = 9.8 Hz, CH), 139.2 (d, $^{2}J_{\mathrm{P,C}}$ = 9.6 Hz, CH), 141.1 (d, $^{1}J_{\mathrm{P,C}}$ = 22.8 Hz, C], 146.7 (d, $^{1}J_{\mathrm{P,C}}$ = 44.9 Hz, C), 156.4 (dd, $^{1}J_{\mathrm{P,C}}$ = 43.5, $^{2}J_{\mathrm{P,C}}$ = 10.4 Hz, NC) ppm. ^{31}P NMR (81 MHz, [D$_8$]THF, 203 K): δ = 7 (dd, $^{2}J_{\mathrm{P,P}}$ = 30 and 24 Hz, 1 P, PCH$_3$), 16 (dd, $^{2}J_{\mathrm{P,P}}$ = 30 and 36 Hz, 1 P, PCH$_3$), 66 (dd, $^{2}J_{\mathrm{P,P}}$ = 36 and 24 Hz, 1 P, PPh$_2$) ppm. $C_{33}H_{47}CoNP_3$ (609.2): calcd. C 65.02, H 7.77, N 2.30, P 15.24; found C 64.79, H 7.39, N 2.22, P 15.30.

[(*E*)-2-(Diphenylphosphanyl)-*N*-*tert*-butylbenzimide-*C^{1}*,*P*]ethenebis(trimethylphosphane)cobalt(I) (10): A sample of **4** (640 mg, 1.01 mmol) was kept at 100 °C in vacuo for 5 h. After cooling 30 mL of diethyl ether was condensed upon the red brown solid, and at 20 °C the solution was kept stirring under 1 bar of ethene for 1 h. The volatiles were removed in vacuo, and the solid residue was extracted with two 30 mL portions of pentane. Crystallization at −4 °C afforded orange crystals of **10**. Yield 236 mg (40%); m.p. 105−107 °C (dec.). IR (Nujol): ṽ = 1633 cm^{-1} (C=N). ^{1}H NMR (300 MHz, [D$_8$]THF, 296 K): δ = 0.82 (s, 9 H, CH$_3$), 0.90 (d, $^{2}J_{\mathrm{P,H}}$ = 6.3 Hz, 9 H, PCH$_3$), 1.05 (d, ^{3}J = 6.2 Hz, 9 H, PCH$_3$), 1.61 (m, 2 H, CCH$_2$), 1.80 (m, 2 H, CCH$_2$), 5.99 (m, 1 H, CH), 6.44 (m, 1 H, CH), 6.75 (dt, ^{3}J = 7.5, ^{4}J = 2.0 Hz, 1 H, CH), 7.17−7.19 (m, 3 H, CH), 7.29 (s, 1 H, NCH), 7.34−7.36 (m, 3 H, CH), 7.71−7.77 (m, 2 H, CH), 7.92−7.98 (m, 2 H, CH) ppm. ^{13}C NMR (75.4 MHz, [D$_8$]THF, 296 K): δ = 16.8 (d, $^{1}J_{\mathrm{P,C}}$ = 17.9 Hz, PCH$_3$), 19.1 (d, $^{1}J_{\mathrm{P,C}}$ = 17.9 Hz, PCH$_3$), 24.9 (s, CH$_3$), 25.2 (s, CMe$_3$), 33.2 (m, CCH$_2$), 35.3 (m, CCH$_2$), 109.5 (s, CH), 125.8 (d, $^{2}J_{\mathrm{P,C}}$ = 15.6 Hz, C), 126.6 (d, $^{3}J_{\mathrm{P,C}}$ = 7.9 Hz, CH), 126.8 (d, $^{2}J_{\mathrm{P,C}}$ = 8.4 Hz, CH), 127.2, 128.8 (s, CH), 132.1 (d, $^{2}J_{\mathrm{P,C}}$ = 12.3 Hz, CH), 132.9 (d, $^{2}J_{\mathrm{P,C}}$ = 12.6 Hz, CH), 169.1 (s, NCH) ppm. ^{31}P NMR (81 MHz, [D$_8$]THF, 203 K): δ = −21 (dd, $^{2}J_{\mathrm{P,P}}$ = 51 and 47 Hz, 1 P, PPh$_2$), 9 (dd, $^{2}J_{\mathrm{P,P}}$ = 47 and 32 Hz, 1 P, PCH$_3$), 17 (dd, $^{2}J_{\mathrm{P,P}}$ = 32 and 51 Hz, 1 P, PCH$_3$) ppm. $C_{31}H_{45}CoNP_3$ (583.2): calcd. C 63.81, H 7.77, N 2.40, P 15.92; found C 63.46, H 7.30, N 2.36, P 16.48.

[(*E*)-2-(Diphenylphosphanyl)-*N*-isopropylbenzimino-*C,P*]iodobis(trimethylphosphane)cobalt(II) (11): A sample of **2** (850 mg, 1.37 mmol) in 50 mL of THF at −70 °C was combined with iodomethane (488 mg, 3.44 mmol). After 3 h at 20 °C an off-white solid of tetramethylphosphonium iodide (IR) was filtered off, and the filtrate was evaporated to dryness. Extraction with three 80 mL portions of diethyl ether and cooling to 4 °C afforded dark brown platelets of **11**. Yield 440 mg (48%); m.p. 130−132 °C (dec.). IR (Nujol): ṽ = 1554 cm^{-1} (C=N). Magnetic moment: μ_{eff} = 1.98 μ_{B}. $C_{28}H_{39}CoINP_3$ (668.1): calcd. C 50.32, H 5.88, N 2.10, P 13.90; found C 50.56, H 6.58, N 2.02, P 13.88.

[(*E*)-2-(Diphenylphosphanyl)-*N*-cyclohexylbenzimino-*C,P*]iodobis(trimethylphosphane)cobalt(II) (12): A sample of **3** (790 mg, 1.20 mmol) in 80 mL of THF at −70 °C was combined with iodomethane (375 mg, 2.64 mmol). After 3 h at 20 °C workup proceeded as in the preparation of **11** to afford dark brown platelets of **12**. Yield 505 mg (63%); m.p. 128−134 °C (dec.). IR (Nujol): ṽ = 1547 cm^{-1} (C=N). Magnetic moment: μ_{eff} = 1.98 μ_{B}. $C_{31}H_{43}CoINP_3$ (708.1): calcd. C 52.56, H 6.12, N 1.98, P 13.12; found C 52.60, H 5.74, N 1.98, P 12.58.

***mer-trans*-[(*E*)-2-(Diphenylphosphanyl)-*N*-*tert*-butylbenzimide-*C^{1}*,*P*]iodo(methyl)bis(trimethylphosphane)cobalt(III) (13):** A sample of **4** (920 mg, 1.45 mmol) in 50 mL of diethyl ether at −70 °C was combined with excess iodomethane (455 mg, 3.20 mmol). After 1 h at 20 °C the solution became red. An off-white solid of tetramethylphosphonium iodide was filtered off, and the solution at 4 °C afforded red crystals of **13**. Yield 518 mg (51%); m.p. 117−119 °C (dec.). IR (Nujol): ṽ = 1633 cm^{-1} (C=N). ^{1}H NMR (300 MHz, [D$_8$]THF, 296 K): δ = 0.54 (m, 3 H, CoCH$_3$), 0.80 (s, 9 H, CCH$_3$), 1.04 (br. s, 18 H, PCH$_3$), 7.51−7.56 (m, 6 H, CH), 7.74−7.79 (m, 4 H, CH), 8.20 (s, 1 H, NCH) ppm. ^{13}C NMR (75.4 MHz, [D$_8$]THF,

Table 1. Crystal data for compounds **4** and **9**

	4	**9**
Empirical formula	$C_{32}H_{50}CoNP_4$	$C_{33}H_{47}CoNP_3$
Molecular mass	631.5	609.6
Crystal size [mm]	0.48 × 0.42 × 0.30	0.52 × 0.30 × 0.26
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/c$
a [Å]	13.950(2)	14.930(4)
b [Å]	18.288(6)	12.674(3)
c [Å]	14.056(3)	18.584(4)
β [°]	102.18(1)	112.04(2)
V [Å^3]	3505.2(15)	3259.5(14)
Z	4	4
$D_{\mathrm{calcd.}}$ [g/cm^3]	1.197	1.242
μ(Mo-K_α) [mm^{-1}]	0.693	0.696
Temperature [K]	293(2)	293(2)
Data coll. range [°]	$4.4 \le 2\Theta \le 50$	$5.5 \le 2\Theta \le 55$
h	$-16 \le h \le 0$	$-1 \le h \le 14$
k	$0 \le k \le 21$	$-16 \le k \le 1$
l	$-16 \le l \le 16$	$-24 \le l \le 22$
No. reflect. measured	6439	8014
No. unique data	6171 [R_{int} = 0.0310]	6551 [R_{int} = 0.0205]
Parameters	394	356
GoF on F^2	0.982	1.045
$R1$ [$I \ge 2\sigma(I)$]	0.0536	0.0419
$wR2$ (all data)	0.1215	0.1094

296 K): δ = 16.9 (m, PCH_3), 28.2 (s, CH_3), 56.6 (s, CMe_3), 121.5 (d, $^2J_{P,C}$ = 11.5 Hz, C), 126.5 (s, CH), 128.4 (s, CH), 129.6 (d, $^2J_{P,C}$ = 11.4 Hz, CH), 137.1 (s, C), 138.2 (s, C), 139.5 (m, C), 160.1 (s, NCH) ppm. ^{31}P NMR (81 MHz, [D$_8$]THF, 203 K): δ = −34 (t, $^2J_{P,P}$ = 25 Hz, 1 P, PPh_2), 11 (d, $^2J_{P,P}$ = 25 Hz, 2 P, PCH_3) ppm. $C_{30}H_{44}CoINP_3$ (697.1): calcd. C 51.66, H 6.36, N 2.10, P 13.32; found C 51.65, H 6.52, N 1.98, P 13.26.

Crystal Structure Analyses: Crystal data are presented in Table 1. Data collection: Complex **4**: A crystal was sealed under argon in a glass capillary and mounted on a Bruker AXS P4 diffractometer. Reflections were collected (ω-scans) using graphite monochromated Mo-K_α radiation; a Lorentz polarisation and an absorption correction based on psi-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. The *t*Bu group as well as the P(4)Me_3 group are disordered over four positions along the N(1)−C(8) axis and the Co(1)−P(4) axis, respectively. These positions were refined with split models. Resulting site occupation factors for the 4 *t*Bu positions are 0.24(2), 0.24(2), 0.34(3), and 0.18(2); site occupation factors for the 4 PMe_3 positions are 0.26(2), 0.13(1), 0.36(2), and 0.25(2). Complex **9**: Crystal mounting, data collection, structure solution, and refinement as for **4**.

CCDC-184403 (**4**) and CCDC-184404 (**9**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44−1223/336−033; E-mail: deposit@ccdc.cam.ac.uk].

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