

2-Diphenylphosphinobenzaldehyde as Chelating Ligand in Trimethylphosphine Complexes of Cobalt and Nickel

Hans-Friedrich Klein,* Ute Lemke, Mathias Lemke, and Alexandra Brand

Institute for Inorganic Chemistry, Darmstadt University of Technology, Petersenstrasse 18, 64287 Darmstadt, FRG

Received June 5, 1998

Methylnickel complexes activate the C(O)–H function of 2-diphenylphosphinobenzaldehyde to form five-membered chelate rings Ni(Ph₂P(=O)C=O) which occupy OC-axial and P-equatorial positions in the trigonal bipyramidal configuration of nickel(d⁸) compounds Ni(Ph₂P(=O)C=O)X(PMe₃)₂ (X = Cl (**1**), Br (**2**), I (**3**), Me (**4**)). Methylcobalt complexes react with 2-diphenylphosphinobenzaldehyde to afford an isoelectronic species Co(Ph₂P(=O)C=O)(PMe₃)₃ (**5**) of similar configuration, while cobalt halides CoX(PMe₃)₃ oxidatively add the aldehyde function to produce octahedral compounds *mer*-CoH(X)(Ph₂P(=O)C=O)(PMe₃)₂ (X = Cl (**6**), Br (**7**), I (**8**)). Carbon monoxide replaces an axial trimethylphosphine in **5**, while iodomethane gives rise to an oxidative substitution producing CoI(Ph₂P(=O)C=O)(PMe₃)₂ (**10**) (17 valence electrons). The molecular structures of compounds **3**, **5**, **6**, and **10** have been solved by X-ray crystallography.

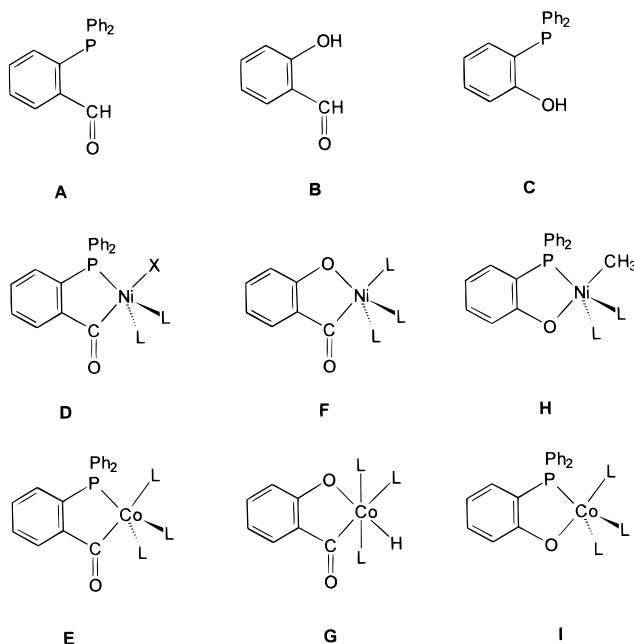
Introduction

Chelating ligands containing hard/soft donor atoms at a bite angle close to 90° can alter the reactivity of metal centers by setting up *trans* and *cis* influences of different strengths in perpendicular directions. For example acylphenolato dianions ⁻O(=C)O⁻ when assisted by trimethylphosphines (complex **F** in Scheme 1) can polarize a nickel d⁸ center in such a way as to effect an oxidative addition of iodoalkane,¹ which is otherwise not observed.

We set out to investigate the effect that a soft/soft chelating ligand would exert on metal centers if combined with trimethylphosphines.

An anionic chelating acyl ligand containing soft/soft donor atoms can be derived from 2-diphenylphosphinobenzaldehyde (**A**). Addition of the aldehyde C–H function across platinum group metals has been observed with Rh,² Ir,³ Pd,⁴ and Pt⁵ complex centers, and the expected five-membered metallocycles have been established by X-ray crystallography. As no complexes of 2-phosphinoacyl ligands with nickel or cobalt have been reported, we chose as target molecules the pertinent nickel halide compounds **D** and the isoelectronic cobalt(I) complex **E**, in order to compare their properties with those of the corresponding 2-acylphenolato compounds **F**⁶ and **G**⁷ of the hard/soft type as derived from

Scheme 1. 18-Electron Chelates of Nickel(II) and Cobalt(I,III)



X = Halide, L = PMe₃

salicylaldehyde (**B**) and with those of 2-phosphinophenolato chelates **H**⁸ and **I**⁹ of the soft/hard type as derived from phosphinophenols (**C**).

Results and Discussion

Methyl(trimethylphosphine)nickel halide complexes in a sluggish reaction according to eq 1, which is slowest

(7) Klein, H.-F.; Haller, S.; Sun, H.; Li, X.; Jung, T.; Röhr, C.; Floerke, U.; Haupt, H.-J. *Z. Naturforsch.*, in press.

(8) Dal, A. Thesis, Greifswald University, 1998.

(9) Klein, H.-F.; Brand, A.; Cordier, G. *Z. Naturforsch.* **1998**, *53b*, 307.

(1) Klein, H.-F.; Bickelhaupt, A.; Jung, T.; Cordier, G. *Organometallics* **1994**, *13*, 2557–2559.

(2) (a) Ko, J.; Joo, W. C.; Kong, Y. K. *Bull. Korean Chem. Soc.* **1986**, *7*, 338–341. (b) Ko, J.; Joo, W. C.; *Bull. Korean Chem. Soc.* **1987**, *8*, 372–376.

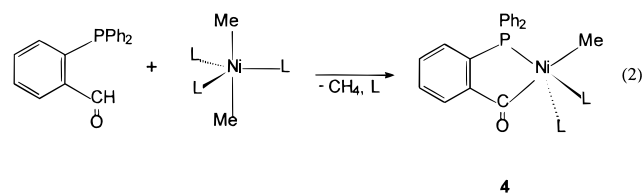
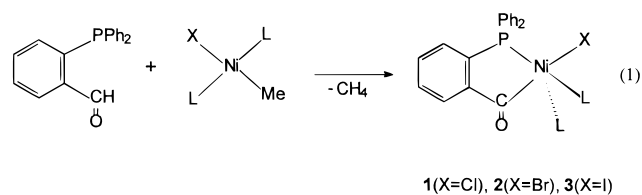
(3) Landvatter, E. B.; Rauchfuss, T. B. *Organometallics* **1982**, *1*, 506–513.

(4) Gao, J.; Wang, Y.; Lin, Z.; Wan, H. *Tianranqi Huagong* **1994**, *19*, 6–10. (b) Gao, J.-X.; Wang, J.-Z.; Hu, S.-Z.; Wan, H.-L. *Gaodeng Xuexiao Huaxue Xuebao* **1995**, *16*, 666–669.

(5) Ghilardi, C. A.; Midollini, S.; Moneti, S.; Orlandini, A. *J. Chem. Soc., Dalton Trans.* **1988**, 1833–1836.

(6) Klein, H.-F.; Bickelhaupt, A.; Hammerschmitt, B.; Floerke, U.; Haupt, H.-J. *Organometallics* **1994**, *13*, 2944–2950.

for chloride, are converted by 2-diphenylphosphino-benzaldehyde to afford the new nickel chelates **1–3** in good to excellent yields. Added trimethylphosphine effectively blocks the reaction (eq 1) but does not interfere in the formation of the methylnickel compound **4** according to eq 2.



L = PMe₃

Only the generation of **1** is accompanied by P–C bond cleavage and formation of *trans*-NiCl(Ph)(PMe₃)₂.¹⁰ The remainders of the 2-phosphinoacyl ligand have not been detected among the products.

Complexes **1–4** form dark-red/violet or bright red (**4**) crystals which are soluble in ether or pentane, as expected for coordinatively saturated molecular species. ³¹P NMR resonances show a pattern of couplings that are in accord with angles PNiP close to 120° and a D-type configuration. A marked low-field shift of the carbonyl ¹³C signal is caused by the strong trans influence of the NiX group, which decreases in the order X = Me > I > Br > Cl.

In an attempted decarbonylation reaction, which is typical for nonchelating acylnickel compounds,¹¹ **1** was found to be unreactive toward Ni(PMe₃)₄. There was no indication of ligand dissociation, and the air stability is good.

The molecular structure of **3** is shown in Figure 1. The nickel atom is centered in a trigonal bipyramid of donor atoms attaining an unusual pentacoordination. The 18-valence electron count is at variance with the usual square planar geometry of acylnickel halides.¹² The most likely explanation for the stable pentacoordination is based on a steric argument. In a supposed square planar arrangement of ligand functions the acyl group would be forced into the plane of the chelate ring, thereby causing repulsion with an in-plane trimethylphosphine group at an angle C(O)–Ni–P of about 90°. A freely rotating acyl group would be oriented in a direction perpendicular to the plane of coordination.¹² The three equatorial phosphine-donor groups are oriented for optimum p interactions. To arrive at the

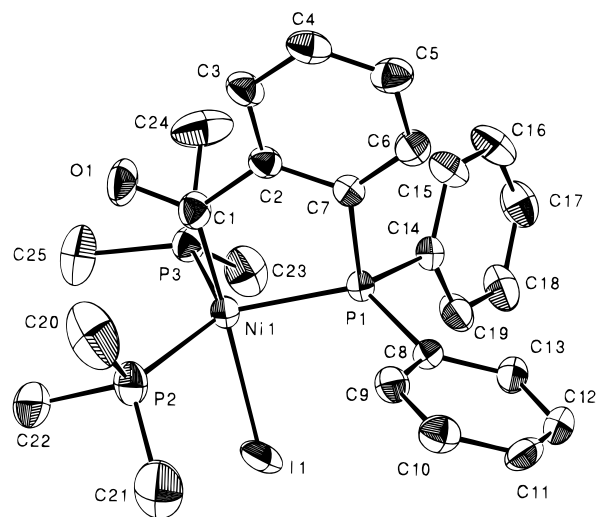


Figure 1. Molecular structure of **3**; selected distances (Å) and angles (deg): Ni1–I1 2.6633(6), Ni1–C1 1.892(4), Ni1–P1 2.2282(11), Ni1–P2 2.2400(13), Ni1–P3 2.2517(12), O1–C1 1.212(5), C1–C2 1.510(6), P1–C7 1.823(4), P1–C8 1.830(4), P1–C14 1.829(4); C1–Ni1–P2 89.70(14), C1–Ni1–P3 86.93(14), C1–Ni1–P1 88.15(13), C2–C1–Ni1 118.1(3), C7–C2–C1 119.9(4), C8–C7–P1 112.9(3), C7–P1–Ni1 100.79(13), C1–Ni1–I1 177.98(13), P1–Ni1–P2 126.54(5), P2–Ni1–P3 123.39(5), P1–Ni1–P3 109.81(4), P1–Ni1–I1 93.87(3), P2–Ni1–I1 89.00(4), P3–Ni1–I1 92.50(3), O1–C1–C2 118.5(4), O1–C1–Ni1 123.4(3).

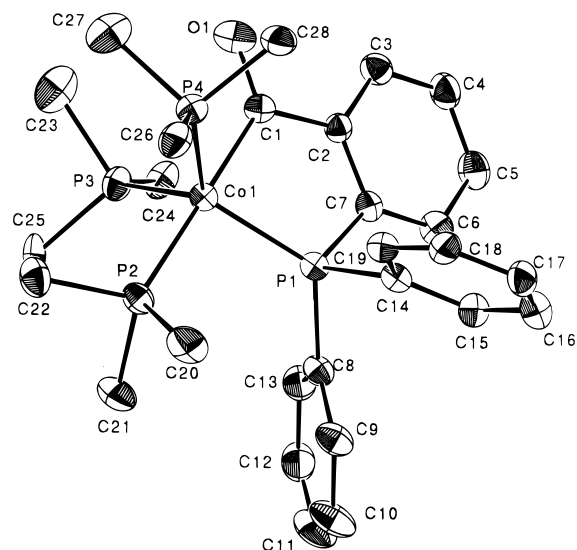


Figure 2. Molecular structure of **5**; selected distances (Å) and angles (deg): Co1–C1 1.950(3), Co1–P1 2.1588(7), Co1–P2 2.2215(8), Co1–P3 2.1898(9), Co1–P4 2.2238(8), O1–C1 1.230(3), C1–C2 1.523(4), C7–P1 1.828(3), P1–C14 1.862(3); C1–Co1–P2 179.01(9), C1–Co1–P1 85.56(8), C1–Co1–P3 82.39(8), C1–Co1–P4 84.88(8), P1–Co1–P2 94.61(3), P1–Co1–P3 117.54(3), P1–Co1–P4 122.14(3), Co1–C1–C2 118.4(2), C1–C2–C7 118.2(2), C2–C7–P1 111.1(2), C7–P1–Co1 103.85(9), O1–C1–C2 115.5(2), O1–C1–Co1 126.0(2).

molecular structure of the cobalt(II) analogue **10** (17 valence electrons, Figure 4), considerable distortion of ligand positions is required.

The corresponding 18-electron cobalt(I) complex **5** is smoothly formed by an aldehyde reaction with a suitable methylcobalt(I) or trimethylcobalt(III) complex according to eq 3.

(10) (a) Klein, H.-F.; Reitzel, L. *Chem. Ber.* **1988**, *121*, 1115–1118. (b) Carmona, E.; Paneque, M.; Poveda, M. L. *Polyhedron* **1989**, *8*, 285–291.

(11) Klein, H.-F.; Karsch, H. H. *Chem. Ber.* **1976**, *109*, 2524–2532.

(12) (a) Huttner, G.; Orama, O.; Bejenke, V. *Chem. Ber.* **1976**, *109*, 2533–2536. (b) Cámpora, J.; Gutiérrez, E.; Monge, A.; Poveda, M. L.; Carmona, E. *Organometallics* **1992**, *11*, 2644–2649.

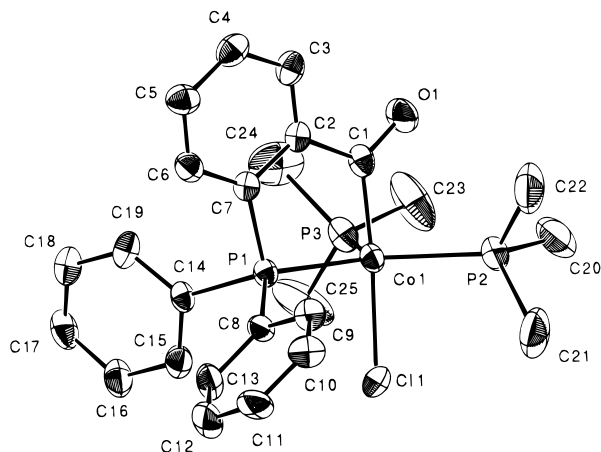
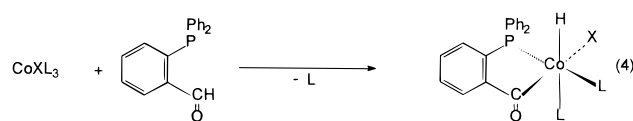
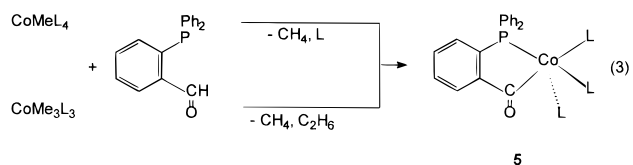


Figure 3. Molecular structure of **6**; selected distances (Å) and angles (deg): Co1–C11 2.4061(11), Co1–P1 2.1750(10), Co1–P2 2.2230(11), Co1–P3 2.2549(12), Co1–C1 1.891(4), P1–C7 1.818(3), P1–C8 1.826(4), P1–C14 1.833(3), C2–C7 1.392(5), C1–C2 1.521(5); C1–Co1–P2 92.42(12), C1–Co1–P1 88.01(11), C1–Co1–P3 87.30(12), C1–Co1–C11 176.08(12), P1–Co1–P2 147.29(5), P1–Co1–P3 103.96(4), P1–Co1–C11 88.23(4), Co1–C1–C2 118.3(2), C1–C2–C7 118.2(3), C2–C7–P1 112.7(3), C7–P1–Co1 101.91(11), C7–P1–C14 105.5(2), C8–P1–C14 104.1(2), C7–P1–C8 102.8(2).



L = PMe₃

6(X=Cl), **7**(X=Br), **8**(X=I)

Using cobalt(I) halides in a synthesis according to eq 4, the aldehyde reaction proceeds to air-stable cobalt(III) species **6–8**, which do not spontaneously eliminate HX to form **5** and are inert toward triethylamine at 20 °C. Complex **5** forms dark brown crystals, **6** forms dark olive crystals, while **7** and **8** are obtained as yellow and orange microcrystals, respectively. Infrared spectra of compounds **6–8** contain medium-intensity bands at 1923–1929 cm⁻¹ which are assigned to CoH stretching vibrations, and each correspond with a high-field CoH proton multiplet resonance. Other NMR data are compatible with a low-spin state and octahedral coordination of cobalt(d⁶).

The molecular structure of **5** is shown in Figure 2. The cobalt atom resides in the center of a trigonal bipyramidal arrangement of one carbon and four phosphorus donor atoms with an axial acyl group (type **E** in Scheme 1). The bite-angle φ of the chelating 2-phospha-1-phenylphenolato ligand C1–Co–P1 = 85.56(8)° is equal within experimental error to those of the phosphinophenolato monoanionic ($\varphi = 85.65(4)^\circ$)⁹ or the acylphenolato dianionic ($\varphi = 85.5(2)^\circ$) ligands.⁷

In Figure 3 the molecular structure of **6** is consistent with a *mer*-octahedral coordination of a cobalt(d⁶) center

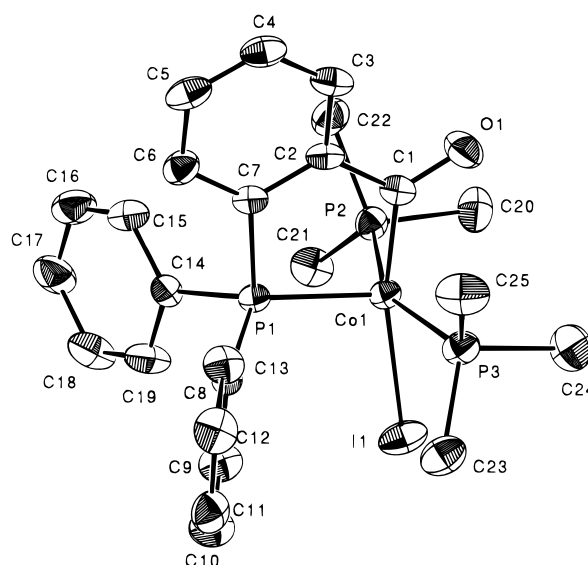


Figure 4. Molecular structure of **10**; selected distances (Å) and angles (deg): Co1–I1 2.6629(12), Co1–P1 2.2149(12), Co1–P2 2.2402(14), Co1–P3 2.2409(14), Co1–C1 1.878(4), P1–C7 1.828(4), P1–C14 1.839(4), C2–C7 1.381(6), C1–C2 1.508(6); C1–Co1–P2 87.26(13), C1–Co1–P1 88.58(14), C1–Co1–P3 86.20(13), C1–Co1–I1 167.32(14), P1–Co1–P2 102.33(5), P1–Co1–P3 103.81(5), P1–Co1–I1 104.09(4), Co1–C1–C2 118.5(3), C1–C2–C7 119.1(3), C2–C7–P1 113.5(3), C7–P1–Co1 100.16(14), C7–P1–C14 105.0(2), C8–P1–C14 107.2(2), C7–P1–C8 105.3(2).

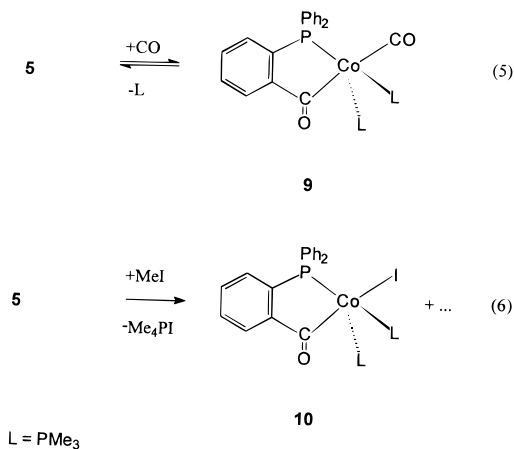
if the large angle P1–Co–P2 = 147.29(5)° is taken to indicate where the hydride ligand resides. The CoH function has not been fully located in the molecular structure but is strongly supported by spectroscopy. The Co–C bond in **6** is 6 pm shorter and the chelate bite angle ($\varphi = 88.01(11)^\circ$) is 3° larger than in **5**, while other values remain in the expected range.

As an electron-rich compound of cobalt(I), **5** is expected to react with p-acceptor ligands. We have not succeeded in reacting ethene with **5** under conditions that proved suitable for 2-phospha-1-phenylphenolato complexes (**I** in Scheme 1).⁹ However, carbon monoxide according to eq 5 substitutes one of the trimethylphosphines, selectively occupying the ligand position opposite the acyl group as shown by ³¹P doublet (2P) and doublet of doublets (1P) resonances. The $\nu(\text{CO})$ value observed in this case, 1920 cm⁻¹, approaches that in a corresponding 2-phospha-1-phenylphenolato carbonyl complex⁹ (type **I** in Scheme 1), where $\nu(\text{CO}) = 1900$ cm⁻¹. Both values indicate tight Co–CO bonding in an apical position, which is unusual for pentacoordinate d⁸ complexes.¹³

While **5** does not react with bromomethane or dibromomethane, oxidative addition of iodomethane according to eq 6 yields an odd-electron oxidation product (d⁷) instead of transforming **5** into an octahedral cobalt (d⁶) complex. Complex **10** is obtained as black crystals with an elemental composition that makes it a 17-electron homologue of **3**.

It was therefore of interest to compare the two molecular structures. No attempt has been made at drawing a molecule **10** (Figure 4) in a way that would

(13) Mcgregor, S. A.; Lu, Z.; Eisenstein, O.; Crabtree, R. H. *Inorg. Chem.* **1994**, *33*, 3616–3618.



match the picture of **3** (Figure 1), as both structures have little in common. The molecules **10** and **3** adopt the same configuration, while bond lengths around the two metals are of the expected order and show a pairwise correspondence. However, angles and coordination geometries of **10** and **3** and the packings are more different than accounted for by substituting a d⁷ for a d⁸ metal center. The observed structural diversity merits further investigation.

Conclusion

Combining nickel and cobalt with anionic phenolate as hard oxygen donor and anionic acyl or neutral diarylphosphino groups as soft C or P donor functions in 1,2 positions of an aromatic ring (as derived from **A**, **B**, and **C** in Scheme 1) gives five-membered chelate rings of closely related geometries. Bidentate bite angles range from 85° to 88°. Ring-opening reactions and tetrahedral coordination of metals are not observed. In trigonal bipyramidal or octahedral complexes regioselective dissociation of monodentate co-ligands and substitution reactions are controlled by the whole set of donor functions and modified by the anisotropy of metal centers which is imposed by the different trans influences. Starting from CoBr(PMe₃)₃ and **C**, the chelate ring is incorporated in a pentacoordinate cobalt-(I) complex by amine-assisted elimination of HBr.⁹ CoCl(PMe₃)₃ oxidatively adds **A** to give exclusively *mer*-**6**, which does not eliminate HCl toward triethylamine. Only the soft/soft chelate ligand derived from **A** appears to favor oxidation of cobalt (d⁸ → d⁶) but is not observed to form an isoelectronic hydridonickel(d⁶) intermediate in the generation of **1–4**. Trimethylphosphine ligands in **4** are tightly coordinated, as shown by extensive coupling of ³¹P nuclei. Formally replacing the soft acyl function by a hard phenolate ligand preserves the configuration (of **D** and **H** in Scheme 1) but induces fast dissociation of trimethylphosphines in solution and loss of 1 equiv in vacuo at 20 °C to reversibly form a square planar methylnickel complex.⁸

Experimental Section

General Procedures and Materials. Standard vacuum techniques were used in manipulations of volatile and air-sensitive material. Details of characterization and spectroscopic instrumentation have been given elsewhere.⁶

2-Diphenylphosphinobenzaldehyde,¹⁴ methylcobalt,¹⁵ CoX(PMe₃)₃,¹⁶ and methylnickel complexes¹⁷ were prepared by

published procedures. Other chemicals (Aldrich) were used as purchased.

Preparation of *trans*-(2-Diphenylphosphino)benzoylchlorobis(trimethylphosphine)nickel (1**).** *trans*-NiCl(Me)(PMe₃)₂ (0.56 g, 2.14 mmol) and 2-diphenylphosphinobenzaldehyde (0.62 g, 2.14 mmol) in 70 mL of THF were allowed to react at 20 °C. After 18 h the volatiles were removed from a dark red mixture in vacuo, and the red solid was extracted with ether over a glass-sinter disk (G3). From a volume of 60 mL at -25 °C dark red microcrystals (0.66 g, 57%) and large orange needles of *trans*-NiCl(Ph)(PMe₃)₂¹⁰ (0.39 g, 1.21 mmol) as a byproduct were isolated and mechanically separated (identified by NMR), mp 95–102 °C (dec). Anal. Calcd for C₂₅H₃₂ClNiOP₃ (535.6): C, 56.06; H, 6.02; P, 17.35. Found: C, 56.01; H, 6.01; P, 16.72. IR (Nujol solution, 4000–1600 cm⁻¹): 3043 (w) ν(CC-H), 1614 (vs) ν(CO). ¹H NMR (300 MHz, THF-d₈, 25 °C): δ(PCH₃) 1.08 (s, 18 H), δ(CH) 7.5 (m, 14 H). ¹³C NMR (75.4 MHz, THF-d₈, 25 °C): δ(PCH₃) 13.7, δ(CC) 120–151, δ(OC) 230.0. ³¹P NMR (81 MHz, THF-d₈, 25 °C): δ(PCH₃) -13.5 (d, 2 P, ²J(PP) = 176 Hz), δ(PCC) 38.1 (dd, 1 P, ²J(PP) = 176 and 180 Hz).

Preparation of *trans*-(2-Diphenylphosphino)benzoylbromobis(trimethylphosphine)nickel (2**).** *trans*-NiBr(Me)(PMe₃)₂ (0.80 g, 2.62 mmol) and 2-diphenylphosphinobenzaldehyde (0.76 g, 2.66 mmol) in 60 mL of THF were kept at 20 °C for 6 h. The dark red solution was evaporated to dryness and the residue crystallized from ether to afford as the only product dark red crystals (0.62 g, 40%), mp 144–147 °C (dec). Anal. Calcd for C₂₅H₃₂BrNiOP₃ (580.0): C, 51.77; H, 5.56; P, 16.02. Found: C, 51.80; H, 5.56; P, 16.12. IR (Nujol solution, 4000–1600 cm⁻¹): 3042 (w) ν(CC-H), 1614 (vs) ν(CO). ¹H NMR (300 MHz, THF-d₈, 25 °C): δ(PCH₃) 1.17 (t', 18 H, ²J(PH) + ⁴J(PH) = 6.9 Hz), δ(CH) 7.5 (m, 14 H). ¹³C NMR (75.4 MHz, THF-d₈, 25 °C): δ(PCH₃) 14.5, δ(CC) 120–151, δ(OC) 233.7. ³¹P NMR (81 MHz, THF-d₈, 25 °C): δ(PCH₃) -16.6 (d, 2 P, ²J(PP) = 172 Hz), δ(PCC) 39.8 (dd, 1 P, ²J(PP) = 172 and 170 Hz).

Preparation of *trans*-(2-Diphenylphosphino)benzoyliodobis(trimethylphosphine)nickel (3**).** From *trans*-NiI(Me)(PMe₃)₂ (0.50 g, 1.42 mmol) and 2-diphenylphosphinobenzaldehyde (0.42 g, 1.45 mmol) in 70 mL of THF in a similar procedure dark violet crystals (0.77 g, 86%) were obtained, mp 197–198 °C (dec). Anal. Calcd for C₂₅H₃₂I NiOP₃ (627.1): C, 47.89; H, 5.14. Found: C, 47.71; H, 5.14. IR (Nujol solution, 4000–1600 cm⁻¹): 3043 (w) ν(CC-H), 1613 (vs) ν(CO). ¹H NMR (300 MHz, THF-d₈, 25 °C): δ(PCH₃) 1.24 (s, 18 H), δ(CH) 7.5 (m, 14 H). ¹³C NMR (75.4 MHz, THF-d₈, 25 °C): δ(PCH₃) 16.1, δ(CC) 121–151, δ(OC) 237.0. ³¹P NMR (81 MHz, THF-d₈, 25 °C): δ(PCH₃) -18.9 (d, 2 P, ²J(PP) = 171 Hz), δ(PCC) 43.7 (dd, 1 P, ²J(PP) = 171 and 169 Hz).

Preparation of *trans*-(2-Diphenylphosphino)benzoylmethylbis(trimethylphosphine)nickel (4**).** *trans*-NiMe₂(PMe₃)₃ (0.92 g, 2.90 mmol) and 2-diphenylphosphinobenzaldehyde (0.84 g, 2.66 mmol) were combined in 70 mL of THF at -70 °C. During warmup the orange mixture slowly turned dark red, and after 5 h at 20 °C the volatiles were removed in vacuo. Crystallization from pentane at -25 °C gave bunches of red needles (0.24 g, 16%), mp 48–52 °C (dec). Anal. Calcd for C₂₆H₃₂NiOP₃ (515.2): C, 60.62; H, 6.85; P, 18.04. Found: C, 59.68; H, 6.83; P, 18.44. IR (Nujol solution, 4000–1580 cm⁻¹): 3049 (w) ν(CC-H), 1588 (vs) ν(CO). ¹H NMR (300 MHz, THF-d₈, 25 °C): δ(NiCH₃) -0.79 (q, 3 H, ³J(PH) = 11.8 Hz), δ(PCH₃) 0.97 (s, 18 H), δ(CH) 7.4 (m, 14 H). ¹³C NMR (75.4 MHz, THF-d₈, 25 °C): δ(NiCH₃) -14.9 (q, ²J(PC) = 18.3 Hz), δ(PCH₃) 16.6, δ(CC) 120–158, δ(OC) 266.6. ³¹P NMR (81 MHz, THF-d₈): δ(PCH₃) -8.4 (d, 2 P, ²J(PP) = 175 Hz), δ(PCC) 52.6 (dd, 1 P, ²J(PP) = 169 and 175 Hz).

(14) Rauchfuss, T. B.; Hoots, J. E. *Inorg. Synth.* **1982**, *21*, 175–179.

(15) Klein, H.-F.; Karsch, H. H. *Chem. Ber.* **1975**, *108*, 944–955.

(16) Klein, H.-F.; Karsch, H. H. *Inorg. Chem.* **1974**, *14*, 473–478.

(17) Klein, H.-F.; Karsch, H. H. *Chem. Ber.* **1973**, *106*, 1433–1452.

Preparation of (2-Diphenylphosphino)benzoyltris(trimethylphosphine)cobalt (5). CoMe(PMe₃)₄ (0.92 g, 2.43 mmol) and 2-diphenylphosphinobenzaldehyde (0.68 g, 2.34 mmol) in 60 mL of ether were allowed to react at 20 °C until evolution of gas ceased. After 2 h the orange-brown solution was filtered, reduced to a volume of 20 mL in vacuo, and kept at -25 °C. Black crystals (0.36 g) were isolated by decantation and drying in vacuo. From the mother liquor (10 mL) a second crop was obtained (combined yields 0.58 g, 43%), mp 129–131 °C. Anal. Calcd for C₂₈H₄₁CoOP₄ (576.4): C, 58.34; H, 7.12; P, 21.49. Found: C, 58.19; H, 7.04; P, 20.78. IR (Nujol solution, 4000–1500 cm⁻¹): 1583 (m), 1533 (vs) ν(CO). ¹H NMR (300 MHz, THF-*d*₆, 25 °C): δ(PC₂H₅) 0.95 (d, 9 H, ²J(PH) = 5.4 Hz), δ(PC₃H₇) 1.23 (t', 18 H, |²J(PH) + ⁴J(PH)| = 9.0 Hz), δ(CH) 7.4 (m, 14 H). ¹³C NMR (75.4 MHz, THF-*d*₆, 25 °C): δ(PC₂H₅) 21.3 (m), δ(CC) 117.7 (d, J(PC) = 18.3 Hz), 126.3 (d, J(PC) = 7.6 Hz), 127.0 (m), 127.3 (d, J(PC) = 2.7 Hz), 127.6 (d, J(PC) = 9.2 Hz), 132.4 (d, J(PC) = 13.7 Hz), 140.8 (m), δ(OC) 254.7. ³¹P NMR (81 MHz, THF-*d*₆, 233 K): δ(PC₂H₅) 1.1 (dd, 2 P, ²J(PP) = 82 and 45 Hz), δ(PC₃H₇) 16.2 (q, 1 P, ²J(PP) = 45 Hz), δ(PCC) 70.0 (dt, 1 P, ²J(PP) = 82 and 45 Hz).

Preparation of mer-Chloro(hydrido)(2-diphenylphosphino)benzoylbis(trimethylphosphine)cobalt (6). CoCl(PMe₃)₃ (0.90 g, 2.79 mmol) and 2-diphenylphosphinobenzaldehyde (0.72 g, 2.48 mmol) in 60 mL of THF were allowed to react at 20 °C. After 2 h the mixture was filtered, and an olive green solid was obtained, which was washed with ether. The raw product (1.30 g) was recrystallized from THF to afford dark green crystals (0.420 g, 32%), mp 109–111 °C (dec). Anal. Calcd for C₂₅H₃₃ClCoOP₃ (536.9): C, 55.93; H, 6.20; P, 17.31. Found: C, 55.68; H, 6.13; P, 17.05. IR (Nujol mull, 4000–1500 cm⁻¹): 1923 (m) ν(CoH), 1603 (s) ν(CO). ¹H NMR (300 MHz, THF-*d*₆, 25 °C): δ(CoH) -10.5 (m, 1 H), δ(PC₂H₅) 0.87 (s, 9 H), δ(PC₃H₇) 1.56 (s, 9 H), δ(CH) 7.2 (m, 14 H). ¹³C NMR (75.4 MHz, THF-*d*₆, 25 °C): δ(PC₂H₅) 15.9 (d, ¹J(PC) = 22.6 Hz), δ(PC₃H₇) 19.3 (d, ¹J(PC) = 26.6 Hz), δ(CC) 121.1 (d, J(PC) = 15.7 Hz), 129.0 (d, J(PC) = 10.3 Hz), 130.6 (d, J(PC) = 8.5 Hz), 131.2 (m), 133.4 (d, J(PC) = 8.6 Hz), 136.0 (d, J(PC) = 10.2 Hz), 139.6 (m), 152.6 (m), δ(OC) 248.6. ³¹P NMR (81 MHz, THF-*d*₆, 233 K): δ(PC₂H₅) 5.9 (m, 1 P), δ(PC₃H₇) 15.8 (d, 1 P, ²J(PP) = 232 Hz), δ(PCC) 75.7 (d, 1 P, ²J(PP) = 227 Hz). MS (FD, 0–5 mA; *m/e* (³⁵Cl) (%)): 536(100), M; 460(13), M - PMe₃.

Preparation of mer-Bromo(hydrido)(2-diphenylphosphino)benzoylbis(trimethylphosphine)cobalt (7). CoBr(PMe₃)₃ (0.52 g, 1.42 mmol) and 2-diphenylphosphinobenzaldehyde (0.52 g, 1.42 mmol) in 60 mL of THF were allowed to react at 20 °C. After 4 h an orange-brown solution was obtained, from which a slight turbidity was removed by filtering over a glass-sinter disk (G3). The volatiles were removed in vacuo to yield 0.77 g of a yellow powder (93% raw yield). Crystallization from THF afforded yellow microcrystals (0.32 g, 39%), mp 143–145 °C (dec). Anal. Calcd for C₂₅H₃₃BrCoOP₃ (536.9): C, 51.66; H, 5.72; P, 15.98. Found: C, 51.78; H, 5.68; P, 15.84. IR (Nujol mull, 4000–1500 cm⁻¹): 1923 (m) ν(CoH), 1605 (s) ν(CO). ¹H NMR (300 MHz, THF-*d*₆, 25 °C): δ(CoH) -10.8 (m, 1 H), δ(PC₂H₅) 0.91 (d, 9 H, ²J(PH) = 5.7 Hz), δ(PC₃H₇) 1.90 (d, 9 H, ²J(PH) = 7.5 Hz), δ(CH) 7.7 (m, 14 H). ¹³C NMR (75.4 MHz, THF-*d*₆, 25 °C): δ(PC₂H₅) 14.8 (d, ¹J(PC) = 22.9 Hz), δ(PC₃H₇) 18.4 (d, ¹J(PC) = 27.5 Hz), δ(CC) 119.4 (d, J(PC) = 15.3 Hz), 126.5 (d, J(PC) = 10.7 Hz), 127.1 (d, J(PC) = 9.2 Hz), 129.0 (m), 129.5 (d, J(PC) = 4.6 Hz), 129.7, 131.7 (d, J(PC) = 9.2 Hz), 134.1 (d, J(PC) = 10.7 Hz). ³¹P NMR (81 MHz, THF-*d*₆, 233 K): δ(PC₂H₅) 3.1 (m, 1 P), δ(PC₃H₇) 13.4 (dd, 1 P, ²J(PP) = 225 and 36 Hz), δ(PCC) 76.5 (m, 1 P). MS (FD, 0–15 mA; *m/e* (⁸¹Br) (%)): 583(100), M.

Preparation of mer-Iodo(hydrido)(2-diphenylphosphino)benzoylbis(trimethylphosphine)cobalt (8). CoI(PMe₃)₃ (0.61 g, 1.47 mmol) and 2-diphenylphosphinobenzaldehyde (0.44 g, 1.52 mmol) in 70 mL of THF were allowed to react at 20 °C. After 1 h a yellow solution was obtained, from which a slight turbidity was removed by filtering over a glass-sinter

Table 1. Crystal Data and Refinement Details for 3 and 6

	3	5
formula	C ₂₅ H ₃₂ NiOP ₃	C ₂₈ H ₄₁ CoOP ₄
fw	627.1	576.4
cryst size, mm	0.64 × 0.21 × 0.36	0.19 × 0.34 × 0.31
cryst syst	monoclinic	triclinic
space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 1
<i>a</i> , Å	8.6929(12)	9.3472(6)
<i>b</i> , Å	20.050(2)	10.7934(7)
<i>c</i> , Å	15.7078(11)	15.3066(14)
α, deg	90	104.127(8)
β, deg	92.704(13)	91.399(7)
γ, deg	90	102.123(11)
<i>V</i> , Å ³	2734.7(5)	1459.5(2)
<i>Z</i>	4	2
<i>D</i> _{calc} , g/cm ³	1.523	1.312
μ(Mo Kα), mm ⁻¹	2.029	0.826
temp, K	293(2)	293(2)
data coll range, deg	2.03 ≤ θ ≤ 24.99	2 ≤ θ ≤ 30
limiting indices	-10 < <i>h</i> < 1, -23 < <i>k</i> < 1, -18 < <i>l</i> < 18	-13 < <i>h</i> < 1, -14 < <i>k</i> < 14, -21 < <i>l</i> < 21
no. of reflns measured	6198	9866
no. of unique data	4812 (<i>R</i> _{int} = 0.0353)	8469 (<i>R</i> _{int} = 0.0258)
parameters	282	309
goodness of fit on <i>F</i> ²	1.053	1.036
<i>R</i> 1 (<i>I</i> > 2σ(<i>I</i>))	0.0412	0.0479
<i>R</i> 1 (all data)	0.0506	0.0729
w <i>R</i> 2 (all data) ^a	0.1113	0.1467

$$^a w = 1/\sigma^2(F) + 0.0001F^2.$$

Table 2. Crystal Data and Refinement Details for 6 and 10

	6	10
formula	C ₂₅ H ₃₃ ClCoOP ₃	C ₂₅ H ₃₂ CoIOP ₃
fw	536.8	627.3
cryst size, mm	0.45 × 0.30 × 0.14	0.50 × 0.60 × 0.53
cryst syst	monoclinic	monoclinic
space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> , Å	8.5689(14)	9.045(3)
<i>b</i> , Å	20.057(3)	33.347(7)
<i>c</i> , Å	15.312(2)	9.150(3)
α, deg	90	90
β, deg	94.714(14)	98.83(4)
γ, deg	90	90
<i>V</i> , Å ³	2622.6(7)	2726.9(14)
<i>Z</i>	4	4
<i>D</i> _{calc} , g/cm ³	1.360	1.528
μ(Mo Kα), mm ⁻¹	0.955	1.952
temp, K	293(2)	293(2)
data coll range, deg	2.03 ≤ θ ≤ 25.00	2.28 ≤ θ ≤ 30.96
limiting indices	-10 < <i>h</i> < 1, -23 < <i>k</i> < 23, -18 < <i>l</i> < 18	-10 < <i>h</i> < 1, -1 < <i>k</i> < 39, -10 < <i>l</i> < 10
no. of reflns measured	11 020	6916
no. of unique data	4620 (<i>R</i> _{int} = 0.0376)	4788 (<i>R</i> _{int} = 0.0330)
parameters	280	280
goodness of fit on <i>F</i> ²	1.036	1.066
<i>R</i> 1 (<i>I</i> > 2σ(<i>I</i>))	0.0481	0.0359
<i>R</i> 1 (all data)	0.0667	0.0483
w <i>R</i> 2 (all data) ^a	0.1340	0.0969

$$^a w = 1/\sigma^2(F) + 0.0001F^2.$$

disk (G3). The volatiles were removed in vacuo to yield 0.81 g of an orange solid (88% raw yield). Crystallization from THF afforded orange-red crystals (0.39 g, 42%), mp 146–148 °C. Anal. Calcd for C₂₅H₃₃CoIOP₃ (628.3): C, 47.79; H, 5.29; P, 14.79. Found: C, 47.66; H, 5.16; P, 14.77. IR (Nujol mull, 4000–1500 cm⁻¹): 1929 (m) ν(CoH), 1604 (s) ν(CO). ¹H NMR (300 MHz, THF-*d*₆, 25 °C): δ(CoH) -11.7 (m, 1 H), δ(PC₂H₅) 0.94 (s, 9 H), δ(PC₃H₇) 0.98 (s, 9 H), δ(CH) 7.7 (m, 14 H). ¹³C NMR (75.4 MHz, THF-*d*₆, 25 °C): δ(PC₂H₅) 16.2 (d, ¹J(PC) = 24.1 Hz), δ(PC₃H₇) 20.4 (d, ¹J(PC) = 28.2 Hz), δ(CC) 119.2 (d, J(PC) = 15.6 Hz), 127.1 (m), 129.0 (d, J(PC) = 22.9 Hz), 129.8,

132.1 (d, $J(\text{PC}) = 8.2$ Hz), 133.9 (d, $J(\text{PC}) = 10.0$ Hz). ^{31}P NMR (81 MHz, THF- d_6 , 223 K): $\delta(\text{PCH}_3) -1.6$ (m, 1 P), $\delta(\text{PCH}_3) 8.4$ (d, 1 P, $^2J(\text{PP}) = 182$ Hz), $\delta(\text{PCC}) 78.1$ (d, 1 P, $^2J(\text{PP}) = 216$ Hz). MS (FD, 0–5 mA; m/e (%)): 629(50), M; 553(19), M – PMe_3 .

Reaction of 5 with Carbon Monoxide. A 0.31 g (0.53 mmol) sample of **5** in 50 mL of ether was kept stirring under 1 bar CO for 15 h at 20 °C. The volatiles were removed in vacuo, and the dark residue was recrystallized from pentane to afford black cubes (0.12 g, 41%), mp 143–145 °C (dec). Anal. Calcd for $\text{C}_{26}\text{H}_{32}\text{CoO}_2\text{P}_3$ (528.4): C, 59.10; H, 6.10; P, 17.58. Found: C, 58.99; H, 6.10; P, 19.06. IR (Nujol mull, 4000–1560 cm^{-1}): 1920 (vs) $\nu(\text{C}=\text{O})$, 1583 (s) $\nu(\text{C}=\text{O})$. ^1H NMR (300 MHz, THF- d_6 , 25 °C): $\delta(\text{PCH}_3) 1.12$ (t', 18 H, $|^2J(\text{PH}) + ^4J(\text{PH})| = 7.3$ Hz), $\delta(\text{CH}) 7.4$ (m, 14 H). ^{13}C NMR (75.4 MHz, THF- d_6 , 25 °C): $\delta(\text{PCH}_3) 18.3$ (t', $|^1J(\text{PC}) + ^3J(\text{PC})| = 13.7$ Hz), $\delta(\text{CC}) 119.4$ (d, $J(\text{PC}) = 19.8$ Hz), 127.0 (d, $J(\text{PC}) = 9.2$ Hz), 127.6, 128.5 (m), 128.9, 129.1, 130.0 (d, $J(\text{PC}) = 12.2$ Hz), 138.7 (m), 139.2 (m), 141.3 (d, $J(\text{PC}) = 30.5$ Hz), 150.5 (d, $J(\text{PC}) = 62.6$ Hz), $\delta(\text{C}=\text{O}) 220.6$ (m), $\delta(\text{C}=\text{O}) 260.9$ (m). ^{31}P NMR (81 MHz, THF- d_6 , 223 K): $\delta(\text{PCH}_3) 9.0$ (d, 2 P, $^2J(\text{PP}) = 80$ Hz), $\delta(\text{PCC}) 83.0$ (t, 1 P, $^2J(\text{PP}) = 80$ Hz).

Reaction of 5 with Iodomethane. An ether solution (70 mL) containing iodomethane (0.40 g, 2.78 mmol) was condensed onto **5** (0.82 g, 11.42 mmol) at –70 °C. The brown mixture was kept at 20 °C for 15 h. An amber solid of tetramethylphosphonium chloride (IR) was removed by filtration, and the red-violet solution was kept at –25 °C to yield

black cubes (0.37 g, 41%), mp 181–183 (dec). Anal. Calcd for $\text{C}_{25}\text{H}_{33}\text{CoIOP}_3$ (627.3): C, 47.87; H, 5.14; P, 14.81. Found: C, 47.63; H, 5.12; P, 15.11. IR (Nujol mull, 4000–1500 cm^{-1}): 1592 (s), 1565 (s), 1559 (s) $\nu(\text{CO})$.

Crystal Structure Determinations. Crystal data for **3**, **5**, **6**, and **10** are given in Tables 1 and 2. Data collection and refinement details: Siemens P4 diffractometer, Mo $K\alpha$ ($\lambda = 0.71073$ Å) radiation, graphite monochromator. An empirical absorption correction via ψ -scans was applied in each case. The structures were solved by direct methods¹⁷ and refined by Fourier methods.¹⁸ All non-hydrogen atoms were refined anisotropically; hydrogen atoms were held in idealized positions.

Acknowledgment. Support of this work by Deutsche Forschungsgemeinschaft and Fonds der Chemischen Industrie is gratefully acknowledged.

Supporting Information Available: Tables of atomic coordinates, bond lengths and angles, and thermal parameters (20 pages). Ordering information is given on any current masthead page.

OM980462+

(18) Sheldrick, G. M. *Acta Crystallogr.* **1990**, A46, 467.

(19) For **3** and **5**: Sheldrick, G. M. SHELXL-86, University of Goettingen, 1993. For **6** and **10**: *ibid.*, 1997.