Reaction of Acyl(hydrido)cobalt(III) Complexes with (2-Diphenylphosphanyl)phenol and Influence of Chelating Ligands Containing Hard/Soft Donor Atoms on the Stability of Cobalt Complexes

Hongjian Sun,*,[†] Xiaoyan Li,[†] Hans-Friedrich Klein,[‡] Ulrich Flörke,[§] and Hans-Jürgen Haupt[§]

School of Chemistry and Chemical Engineering, Shandong University, Shanda Nanlu 27, 250100 Jinan, People's Republic of China, Eduard-Zintl-Institut für Anorganische und Physikalische Chemie der Technischen Universität Darmstadt, Petersenstrasse 18, 64287 Darmstadt, Germany, and Anorganische und Analytische Chemie der Universität Paderborn, Warburger Strasse, 33098 Paderborn, Germany

(Acylphenolato)hydridocobalt(III) complexes by reaction with (2-diphenylphosphanyl) phenol deliver (2-diphenylphosphanyl)phenolatocobalt(III) complexes with a 2-acylphenolato chelating ligand as co-ligand (complexes **2**, **4−6**, and **10−12**). Depending on the substituents in the chelating ligands *trans/cis*-isomers were detected by NMR and IR spectroscopy. Complex **2** was shown by X-ray crystallography to attain an octahedral structure. Under specific conditions substituted (2-hydroxymethyl)phenol and a (2-diphenylphosphanyl)- phenolatocobalt(I) complex were obtained. A likely reaction route is presented. Influences of chelating ligands containing hard/soft donor atoms on the stability of the cobalt complexes will be discussed.

Introduction

(2-Diphenylphosphanyl)phenol and its derivatives are weakly [P,O]-chelating ligands containing an acidic OH function.[1,2] If there is no steric hindrance, the phosphorus atom can coordinate to the metal center. Deprotonated (2-diphenylphosphanyl)phenol is considered to be an anionic chelating ligand of increased strength. Ligand systems that are used as catalysts in the shell higher olefin process (SHOP)[3] for oligomerization of ethene or α-olefins usually contain a [P,O]-chelating part and nickel as central atom (Figure 1). The organic part serves to stabilize the catalyst, while the chelating part controls the catalytic activity and selectivity. The SHOP process, with over one million ton capacity, is one of the largest applications of homogeneous catalysis by a transition metal compound.

A recent account by Heinicke et al. summarizes the development concerning the syntheses and structural aspects of neutral and cationic organonickel and palladium (2-phosphanyl)phenol(ate) complexes and catalysts for ethylene-coupling reactions.[4] Klein and co-workers reported on the synthesis and characterization of cobalt complexes containing chelating (2-diphenylphosphanyl)phenolato ligands.[2] They obtained cobalt(I) complexes containing one chelating ligand and cobalt(II) complexes bearing two chelating ligands.
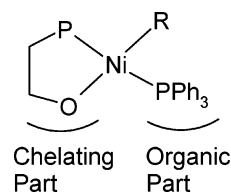

Figure 1.

Hydrido compounds play a central role among transition metal complexes. According to a widely accepted mechanism for the hydroformylation process given by Heck and Breslow, the hydridocobalt compound is a precatalyst.[5] Formation of a Co−H bond is achieved through oxidative addition. Thermodynamically it is unfavorable to cleave C−H bonds at a cobalt center because the sum of the Co−C and Co−H bond energies is not sufficient to account for breaking a C−H bond.[6] Reactions of this type have been observed for the heavier congeners of cobalt for which bond energies are larger. There are reports of several reactions that give products indicating oxidative addition of C−H bonds to cobalt.[7] However, hydridocobalt complexes in these reactions are postulated only as intermediates and were not experimentally isolated. So far few examples of hydridocobalt-(III) complexes are known.

Acyl(hydrido)cobalt species were postulated as carbonylcobalt intermediates in the catalytic cycle.[8] In 1998 Klein and co-workers reported on acyl(hydrido)cobalt-

[†] Shandong University.
[‡] Technischen Universität Darmstadt.
[§] Universität Paderborn.
(1) Brand, A. Doctoral thesis, Technische Universität Darmstadt, 1998.
(2) Klein, H.-F.; Brand, A.; Cordier, G. *Z. Naturforsch.* **1998**, *53b*, 307.
(3) Kaim, W. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 235.
(4) Heinicke, J.; Peulecke, N.; Koehler, M.; He, M.; Kaim, W. *J. Organomet. Chem.* **2004**, in press.

(5) Heck, R. F.; Breslow, D. S. *J. Am. Chem. Soc.* **1961**, 4023.
(6) Halper, J. *Inorg. Chim. Acta* **1985**, *100*, 41.
(7) Habadie, N.; Dartiguenave, M.; Dartiguenave, Y.; Britten, J. F.; Beauchamp, A. L. *Organometallics* **1989**, *81*, 2564.
(8) Parshall, G. W.; Ittel, S. D. *Homogeneous Catalysis*, 2nd ed.; Wiley: New York, 1992; p 109.

(III) complexes, which are stabilized by a (2-acyl)-phenolato chelating ligand and supporting trimethylphosphine.[9] We know that in the molecule [CoH(CO)$_4$] electrons flow from the hydrogen atom to the cobalt center because of the strong back-bonding between the CO ligands and the cobalt atom. Therefore a most impressive aspect of the chemistry of [CoH(CO)$_4$] is its acidity.[10] By contrast, the hydrogen atoms in the thermally stable acyl(hydrido)cobalt(III) complexes bear a partial negative charge.[9] Studies on their properties and reactions confirmed this inference from spectroscopy. Reactions with perchloric, hydrochloric, acetic acid, alkyl halides, salicylaldehyde, or malondialdhyde proceed as with metal hydrides.[11] Acyl(phenolato)hydridocobalt(III) complexes upon reaction with 2-nitrophenol or 2-nitronaphthol eliminate dihydrogen and afford 2-nitrophenolato or 2-nitronaphtholato cobalt(III) compounds.[12] In addition, formal insertion of phenylethyne into the Co−H function was found to give vinylcobalt(III) complexes.[13]

Here we report on our recent progress in studying the chemistry of acyl(hydrido)cobalt(III) complexes. In this account reactions between acyl(hydrido)cobalt(III) complexes and several (2-diphenylphosphanyl)phenols are described. The products obtained contain two chelating ligands. With respect to the positions of two trimethylphosphine ligands *cis/trans*-isomers are found in the products of some of the reactions. A crystal structure analysis by X-ray diffraction confirmed their molecular geometry. As byproducts a cobalt(I) complex containing a monochelating ligand and substituted (2-hydroxymethyl)phenol was isolated. A likely formation route will be discussed.

Results and Discussion

The (2-acylphenolato)hydridocobalt(III) complex **1** by reaction with (2-diphenylphosphanyl)phenol afforded the six-coordinate cobalt(III) complex **2** (eq 1).

$$L = PMe_3 \tag{1}$$
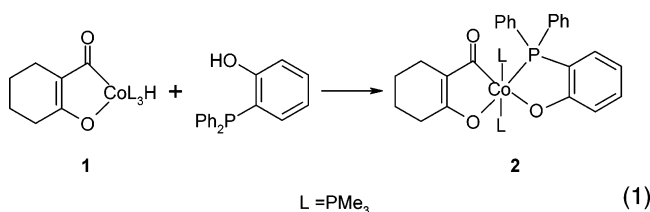
The (2-diphenylphosphanyl)phenolatocobalt(III) complex **2** forms orange cubic crystals (from pentane), which are air-stable and decompose above 160 °C. In the IR spectra the conspicuous ν(Co−H) absorption of the starting complex is absent. The ¹H NMR spectrum indicates the presence of **2** by the expected pattern of PCH$_3$ signals as a virtual triplet for two *trans*-trimethylphosphine groups. ³¹P data clearly show one signal

(9) Klein, H.-F.; Haller, S.; Sun, H.; Li, X.; Jung, T.; Röhr, C.; Flörke, U.; Haupt, H.-J. *Z. Naturforsch.* **1998**, *53b*, 587.
(10) Moore, E. J.; Sullivan, J. M.; Norton, J. R. *J. Am. Chem. Soc.* **1986**, *108*, 2257.
(11) Klein, H.-F.; Haller, S.; Sun, H.; Li, X.; Jung, T.; Röhr, C.; Flörke, U.; Haupt, H.-J. *Z. Naturforsch.* **1998**, *53b*, 856.
(12) Klein, H.-F.; Li, X.; Flörke, U.; Haupt, H.-J. *Inorg. Chim. Acta* **2003**, *342*, 179.
(13) Klein, H.-F.; Li, X.; Flörke, U.; Haupt, H.-J. *Z. Naturforsch.* **2000**, *55b*, 707.

as a doublet for two *trans*-trimethylphosphines, and a triplet for the diphenylphosphanyl group.
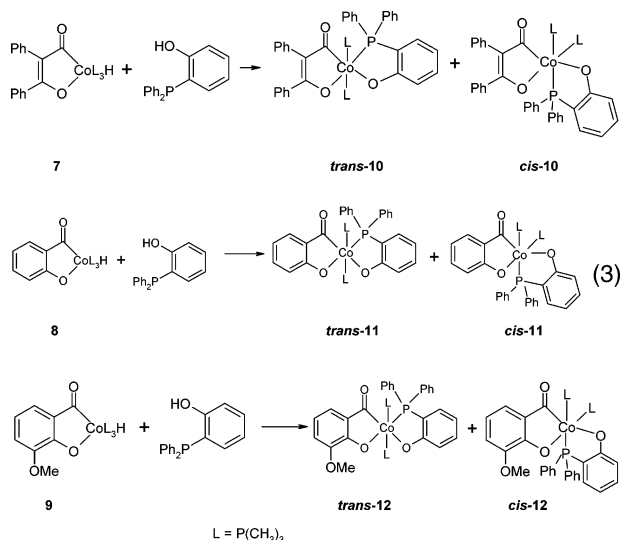
The molecular structure of **2** (Figure 2) shows a hexacoordinate cobalt atom and three P-donor atoms lying in a plane, while one phenolato-O donor and one enolato-O donor and an acyl group are arranged in a plane perpendicular to the first. In opposite position to the acyl group the Co−O distance (Co1−O3 = 2.0346(4) Å) is larger than that opposite to the diphenylphosphanyl group (Co1−O2 = 1.9414(13) Å), indicating a stronger *trans*-influence in the former.

Analogous reactions according to eq 2 have been carried out with *mer*-hydrido(3-*tert*-butyl-5-methyl-2-oxobenzoyl)tris(trimethylphosphine)cobalt(III) (**3**) and (2-diphenylphosphanyl)phenol, (4-methyl-2-diphenylphosphanyl)phenol, and (4-methoxy-2-diphenylphosphanyl)-phenol. The new cobalt(III) complexes **4**−**6** as main products (see below) containing two chelating ligands, one 2-acylphenolato ligand and one (2-diphenylphosphanyl)phenolato ligand, and two *trans*-trimethylphosphine ligands were shown by spectroscopy in solution to attain a configuration similar to complex **2**.
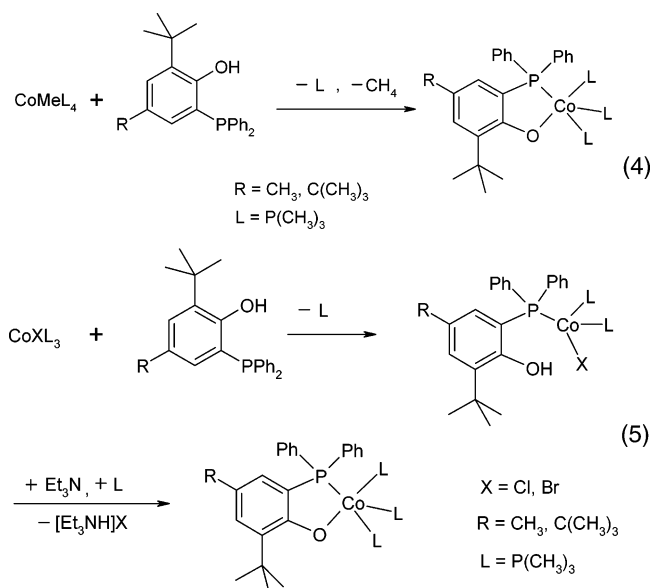

$$\tag{2}$$

R = H   **4**
Me   **5**
OMe   **6**

L = P(CH$_3$)$_3$
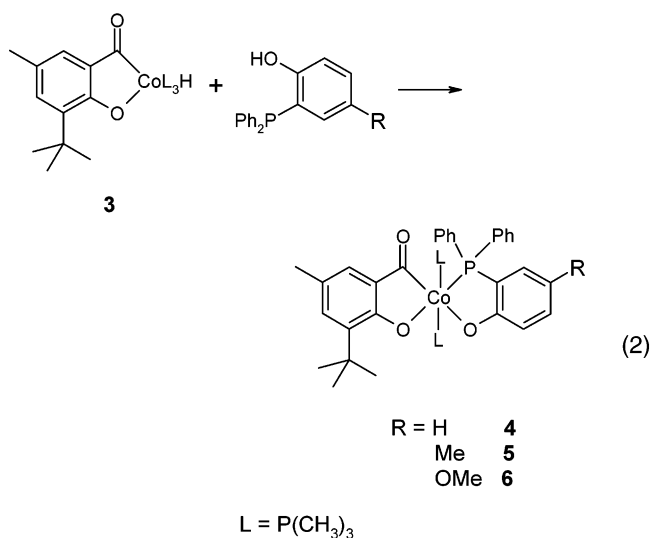
However, under the same conditions reactions of the (2-acylphenolato/enolato)hydrido cobalt(III) complexes **7**−**9** with (2-diphenylphosphanyl)phenol afforded *cis*-products ***cis*-10**−***cis*-12** (eq 3) besides ***trans*-10**−***trans*-12**, corresponding with product **2** in eq 1 and products **4**−**6** in eq 2. Well-resolved ¹H and ³¹P NMR spectra clearly show the presence of these two isomers in solutions.
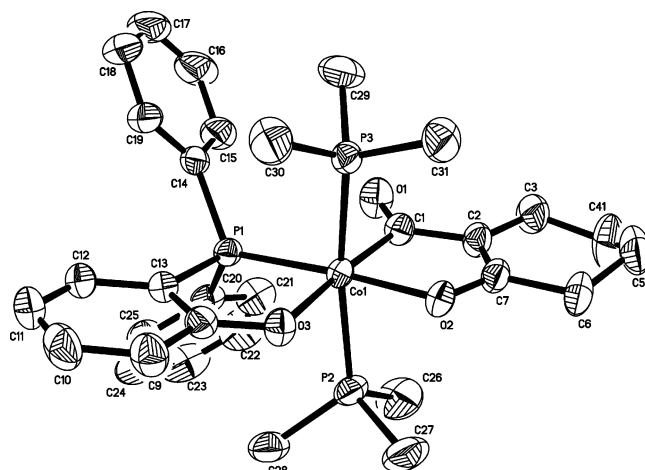
The reaction of complex **3** with (2-diphenylphosphanyl)phenol (eq 2) produced not only complex **4** but also complex **14** and (2-*tert*-butyl-6-hydroxymethyl-4-methyl)phenol as byproducts. The first step in the proposed mechanism (Figure 3) consists of a substitution of the coordinated phenoxy group of the 2-acylphenolato chelating ligand by that of a (2-diphenylphosphanyl)phenolato chelating ligand. Complex **13** is a likely intermediate. The (2-diphenyl phosphanyl)phenolato cobalt(I) complex **14** originates through reductive elimination from complex **13**. In a parallel reaction the hydridocobalt complex **3** reacts with (2-diphenylphosphanyl)phenol under participation of regenerated 3-*tert*-butyl-5-methylsalicylsaldehyde to afford the bis-chelate complex **4** together
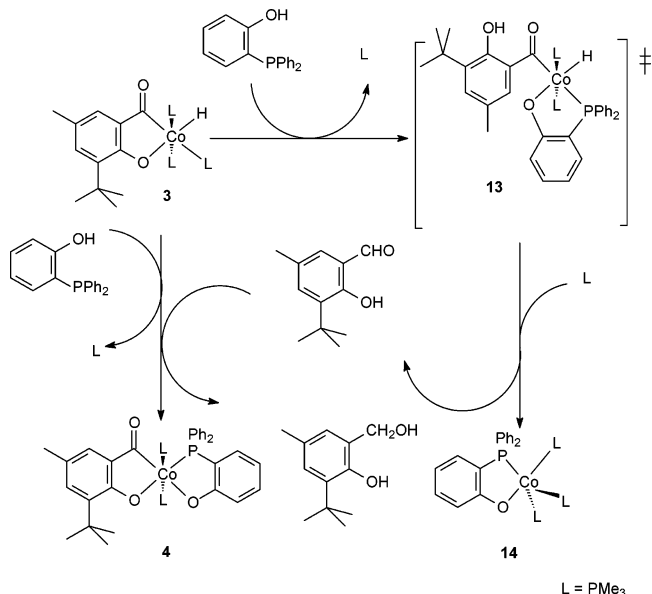
Figure 2. Molecular structure of **2**. Selected distances (Å) and angles (deg): Co1−C1 1.919(2), Co1−O2 1.9494(13), Co1−O3 2.0346(14), Co1−P1 2.2181(5), Co1−P2 2.2688-(6), Co1−P3 2.2496(6), O1−C1 1.226(2), O2−C7 1.312(2), C2−C7 1.357(3); C1−Co1−O3 175.00(7), C1−Co1−O2 85.32-(8), O2−Co1−O3 89.69(6), C1−Co1−P1 99.66(6), O2−Co1−P1 174.89(5), O3−Co1−P1 85.32(4), C1−Co1−P3 87.84(7), O2−Co1−P3 86.25(5), O3−Co1−P3 92.00(5), P1−Co1−P3 95.02(2), C1−Co1−P2 94.94(6), O2−Co1−P2 82.77(5), O3−Co1−P2 84.25, P1−Co1−P2 95.60(2), P2−Co1−P3 168.41-(2).

with (2-*tert*-butyl-6-hydroxymethyl-4-methyl)phenol, by hydrogen transfer to 3-*tert*-butyl-5-methylsalicylaldehyde. In the reaction mixture complex **14** and 2-*tert*-butyl-6-hydroxymethyl-4-methylphenol were identified by NMR. Analoguous complexes of **14** can also be prepared either by reaction of CoMe(PMe₃)₄ with (2-diphenylphosphanyl)phenol (eq 4) or by a two-step-method (eq 5).[1] From the reactions according to eq 3 complex **14** could also be isolated.

In earlier work[12] we had been able to obtain only *cis/ trans*-cobalt(III) complexes with two chelating ligands; that is, one 2-acylphenolato ligand and one 2-nitrophenolato ligand were coordinated in the reaction of an acyl-(hydrido)cobalt(III) complex with 2-nitrophenol. No (2-nitrophenolato)cobalt(I) complex was detected. Correspondingly 2-hydroxymethylphenol was also absent. According to the HSAB rule[14] a (phosphanylphenolato)-cobalt(I) complex is more stable than a nitrophenolato-cobalt(I) complex because a nitro-[O]-donor is much harder than a P-donor. In fact a (2-nitrophenolato)-cobalt(I) complex could not be verified by experiment.[15] Instead, the reaction of CoMe(PMe₃)₄ with 2-nitrophenol

afforded a (2-nitrosophenolato)cobalt(I) complex. Recent research by Li revealed that the acyl(hydrido)cobalt(III) complex **3** reacts with (2-diphenylphosphanyl)thiophenol to afford a (2-diphenylphosphanyl)thiophenolatocobalt-(I) complex exclusively.[16] In this reaction no formation of an analoguous cobalt(III) product with two chelating ligands was indicated. This formal substitution reaction is very fast, and the soft/soft chelating [P,S] ligand appears to stabilize the corresponding cobalt(I) complex much better than any type of [P,O] ligand in the other cobalt(I) complexes in Figure 4. Therefore for the formation of (2-*tert*-butyl-6-hydroxymethyl-4-methyl)-

Figure 3.

(14) Pearson, R. G. *J. Am. Chem. Soc.* **1963**, *85*, 3533.

(15) Klein, H.-F.; Schmidt, A.; Flörke, U.; Haupt, H.-J. *Inorg. Chim. Acta* **2003**, *342*, 171.

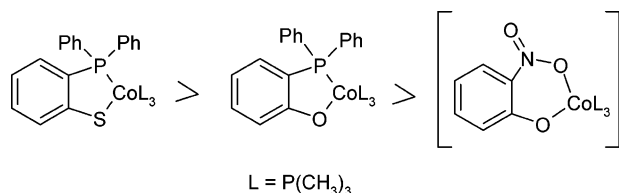(16) Li, X. Unpublished results.

L = P(CH$_3$)$_3$

Figure 4.

phenol the soft/hard (2-diphenyl phosphanyl)phenolato ligand plays an important role in the hydrogen transfer reaction.

Conclusion

Combination of cobalt with anionic phenolate as hard oxygen donor and anionic acyl or neutral diarylphosphino groups as soft carbon or phosphor donor function in ortho-positions of an aromatic ring generates two five-membered chelate rings with closely related geometry. Under the same experimental conditions different substituents at the aromatic ring of chelating ligands, e.g., 2-acylphenolato and (2-diphenylphosphanyl)phenolato ligands, give rise to products with different ratios of *trans/cis*-isomers. In the generation of complexes **4** and **10**−**12** the five-coordinate cobalt(I) complex **14** was identified (Figure 3). This fact implies the liberation of (3-*tert*-butyl-5-methyl)salicylaldehyde, which is hydrogenated in situ by complex **3** to give 2-*tert*-butyl-6-hydroxymethyl-4-methylphenol. This hydrogen transfer reaction proceeds in the presence of (2-diphenylphosphanyl)phenol, which eventually winds up in complex **4**. This multistep process appears to be controlled by the chelating ligands at the cobalt center and is favored by the strongly donating trimethylphosphine ligands.

Experimental Section

General Procedures and Materials. Standard vacuum techniques were used in manipulations of volatile and air-sensitive material. Solvents were dried by known procedures and used freshly distilled. Melting points/decomposition temperatures: sealed capillaries, uncorrected values. Literature methods were applied in the preparation of (2-acylphenolato-hydrido)cobalt compounds,[9] (2-diphenylphosphanyl)phenol, (4-methyl-2-diphenylphosphanyl)phenol, and (4-methoxy-2-diphenylphosphanyl)phenol.[17] IR: Nujol mulls between KBr disks, Bruker spectrophotometer type FRA 106. ^{1}H and ^{13}C NMR spectra (300 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. C, H analyses were carried out in a German ELEMNTAR Vario ELIII analyzer.

Synthesis of *mer*-(1-Carbonyl-2-oxo-cyclohexenediyl)-(2-diphenylphosphanylphenolato)bis(trimethylphosphine)cobalt(III) (2). *mer*-Hydrido(1-carbonyl-2-oxo-cyclohexenediyl)tris(trimethylphosphine)cobalt(III) (**1**) (0.71 g, 1.70 mmol) was dissolved in 30 mL of THF. To this solution was added 0.48 g (1.73 mmol) of (2-diphenylphosphanyl)phenol in 20 mL of THF at −80 °C. The mixture was warmed to 20 °C and stirred for 18 h. During this period the reaction solution turned red. Evaporation of the filtrate under vacuum followed by washing with pentane resulted in an orange solid, which was extracted with diethyl ether. Crystallization at −27 °C

(17) Dal, A. Doctoral thesis, Universität Greifswald, 1998.

afforded orange crystals, which were found suitable for X-ray diffraction: yield 0.18 g of **2** (17%), mp (dec) > 160 °C. Anal. Calcd for C$_{31}$H$_{40}$CoO$_3$P$_3$ (mol wt 612.5): C, 60.79; H, 6.58. Found: C, 60.56; H, 6.75. IR (Nujol mull, 2600−1500 cm^{-1}): 1583 s, ν(C=O); 1560 s, 1537 s, ν(C=C). ^{1}H NMR (300 MHz, THF-d_8, 300 K): δ(PC*H*$_3$) 0.68 (t′, |^2J(PH) + ^4J(PH)| = 8.7 Hz, 18 H); δ(C*H*$_2$) 1.51 (m, 2 H); δ(C*H*$_2$) 1.62 (m, 2 H), 2.24 (m, 4 H); δ(C*H*) 6.50 (m, 1 H), 6.84 (m, 1 H), 7.20 (m, 1 H), 7.28 (m, 6 H), 7.49 (m, 1 H), 8.27 (m, 4 H). ^{13}C NMR (75.4 MHz, THF-d_8, 300 K): δ(PC*H*$_3$) 10.0 (t′, |^1J(PC) + ^3J(PC)| = 26.4 Hz); δ(*C*H$_2$) 21.4, 21.8, 22.1, 22.4; δ(*C*H) 109.2, 120.2, 125.8, 125.9, 127.2, 130.5, 130.6, 130.7, 132.7; δ(*C*O) 170.1; δ(*C*CO) 218.3. ^{31}P NMR (81.0 MHz, THF-d_8, 213 K): δ(P*C*H$_3$) 17.2 (d, ^2J(PP) = 70.6 Hz, 2 P); δ(P*C*$_6$H$_5$) 25.1 (t, ^2J(PP) = 70.6 Hz, 1 P).

Synthesis of (3-*tert*-Butyl-5-methyl-2-oxobenzoyl)(2-diphenylphosphanylphenolato)bis(trimethylphosphine)cobalt(III) (4). A sample of 0.61 g (1.28 mmol) of *mer*-hydrido(3-*tert*-butyl-5-methyl-2-oxobenzoyl)tris(trimethylphosphine) cobalt(III) (**3**) and 0.37 g (1.33 mmol) of (2-diphenylphosphanyl)phenol in 20 mL of THF after 18 h at room temperature formed a dark red solution. The volatiles were removed in vacuo, and the resulting solid was extracted with pentane and diethyl ether, respectively. Crystallization at −27 °C afforded orange microcrystals of **4**: yield 0.094 g (11%), mp (dec) > 190 °C. A second crystallization afforded orange crystals of complex **14**: yield 0.20 g (28%), mp (dec) > 110 °C. **4**: Anal. Calcd for C$_{36}$H$_{46}$CoO$_3$P$_3$ (mol wt 678.6): C, 63.72; H, 6.83. Found: C, 63.66; H, 7.01. IR (Nujol mull, 2600−l570 cm^{-1}): 1609 s, 1582 s, ν(C=O); 1537m, ν(C=C). ^{1}H NMR (300 MHz, THF-d_8, 300 K): δ(PC*H*$_3$) 0.67 (t′, |^2J(PH) + ^4J(PH)| = 8.9 Hz, 18H); δ[C(C*H*$_3$)$_3$] 1.46 (s, 9 H); δ(CC*H*$_3$) 2.19 (s, 3 H); δ(C*H*) 6.54−8.26 (m, 16 H). ^{13}C NMR (75.4 MHz, THF-d_8, 300 K): δ(PC*H*$_3$) 13.1 (t′, |^1J(PC) + ^3J(PC)| = 27.7 Hz); δ(*C*H$_3$)-20.0; δ[C(*C*H$_3$)$_3$] 31.0; δ[*C*(CH$_3$)$_3$] 34.9; δ(*C*H) 112.0, 112.1, 118.2, 122.2, 122.3, 128.2, 128.3, 129.8, 131.4, 133.0, 133.2, 133.3, 134.3; δ(*C*)110.7, 121.4, 135.9, 136.8, 137.2, 138.0, 176.0, 179.6. ^{31}P NMR (81.0 MHz, THF-d_8, 300 K): δ(P*C*H$_3$) 3.2 (d, $_2J$(PP) = 62.8 Hz, 2P); δ(P*C*$_6$H$_5$)19.2 (s(br), 1 P). **14**: Anal. Calcd for C$_{27}$H$_{41}$CoOP$_4$ (mol wt 564.4): C, 57.46; H, 7.32. Found: C, 57.66; H, 7.11. IR (Nujol mull, 2600−l570 cm^{-1}): 1580 m ν(C=C). ^{1}H NMR (300 MHz, THF-d_8, 300 K): δ(PC*H*$_3$)-1.19 (s, 27 H); δ(C*H*) 6.07 (t, ^3J(HH) = 8.0 Hz, 1 H), 6.33 (d, ^3J(HH) = 8.0 Hz, 1 H), 6.63 (t, ^3J(HH) = 8.0 Hz, 1 H), 6.67 (d, ^3J(HH) = 8.0 Hz, 1 H), 7.16−7.75 (m, 10 H). ^{13}C NMR (75.4 MHz, THF-d_8, 300 K): δ(PC*H*$_3$) 19.7; δ(*C*H) 110.8, 116.4, 126.2, 126.3, 127.5, 130.6, 132.3; δ(*C*H) 141.8. ^{31}P NMR (81.0 MHz, THF-d_8, 213 K): δ(P*C*H$_3$) −6.1 (dd, $_{trans}$$^2J$(PP) = 111 Hz, $_{cis}$$^2J$(PP) = 57 Hz, 2P), 31.1 (dd, $_{cis}$$^2J$(PP) = 57 Hz, 1P); δ(P*C*$_6$H$_5$) 42.5 (dt, $_{trans}$$^2J$(PP) = 111 Hz, $_{cis}$$^2J$(PP) = 57 Hz, 1P).

Synthesis of (3-*tert*-Butyl-5-methyl-2-oxobenzoyl)(4-methyl-2-diphenylphosphanylphenolato)bis(trimethylphosphine)cobalt(III) (5). A sample containing 0.70 g (1.46 mmol) of *mer*-hydrido(3-*tert*-butyl-5-methyl-2-oxobenzoyl)tris(trimethylphosphine)cobalt(III) (**3**) and 0.43 g (1.48 mmol) of (4-methyl-2-diphenylphosphanyl)phenol in 50 mL of THF after 18 h at room temperature formed a dark brown solution. The volatiles were removed in vacuo, and the resulting solid was extracted with pentane. Crystallization at −27 °C afforded orange microcrystals: yield 0.080 g of **5** (8%), mp (dec) > 170 °C. Anal. Calcd for C$_{37}$H$_{48}$CoO$_3$P$_3$ (mol wt 692.6): C, 64.16; H, 6.98. Found: C, 63.86; H, 7.09. IR (Nujol mull, 2600−l570 cm^{-1}): 1605 s, 1586 s, ν(C=O); 1546 m, ν(C=C). ^{1}H NMR (300 MHz, THF-d_8, 300 K): δ(PC*H*$_3$) 0.66 (t′, |^2J(PH) + ^4J(PH)| = 8.9 Hz, 18 H); δ[C(C*H*$_3$)$_3$] 1.45 (s, 9 H); δ(C*H*$_3$) 2.19 (s, 3 H), 2.28 (s, 3 H); δ(C*H*) 6.75−8.26 (m, 15 H). ^{13}C NMR (75.4 MHz, THF-d_8, 300 K): δ(PC*H*$_3$) 12.4 (t′, |^1J(PC) + ^3J(PC)| = 27.7 Hz); δ(*C*H$_3$) 19.3, 19.4; δ[C(*C*H$_3$)$_3$ 30.3; δ[*C*(CH$_3$)$_3$] 33.7; δ(*C*H) 117.4, 127.3, 128.2, 129.0, 130.6, 132.5, 132.7, 133.8; δ(*C*) 117.9, 133.8, 134.4, 136.4; δ(*C*O) 176.4; δ(*C*CO) 202.7. ^{31}P NMR (81.0 MHz, THF-d_8, 300 K): δ(P*C*H$_3$) 5.3 (s(br), 2 P); δ(P*C*$_6$H$_5$) 21.4 (s(br), 1 P).

Synthesis of (3-*tert*-Butyl-5-methyl-2-oxobenzoyl)(4-methoxy-2-diphenylphosphanylphenolato)bis(trimethylphosphine)cobalt(III) (6). A sample containing 0.66 g (1.38 mmol) of *mer*-hydrido(3-*tert*-butyl-5-methyl-2-oxobenzoyl)tris-(trimethylphosphine)cobalt(III) (**3**) and 0.40 g (1.30 mmol) of (4-methoxy-2-diphenylphosphanyl)phenol in 40 mL of THF after 18 h at room temperature formed a dark red solution. The volatiles were removed in vacuo, and the resulting solid was extracted with diethyl ether. Crystallization at −27 °C afforded orange microcrystals: yield 0.12 g of **6** (13%), mp (dec) >205 °C. Anal. Calcd for $C_{37}H_{48}CoO_4P_3$ (mol wt 708.6): C, 62.72; H, 6.83. Found: C, 62.69; H 7.01. IR (Nujol mull, 2600−l570 cm^{-1}): 1606 s, 1588 s, ν(C=O); 1553 m ν(C=C). ^{1}H NMR (300 MHz, THF-d_8, 300 K): δ(PCH_3) 0.67 (t′, |^2J(PH) + ^4J(PH)| = 8.9 Hz, 18 H); δ [C(CH_3)$_3$] 1.45 (s, 9 H); δ(CH_3) 2.19 (s, 3 H); δ(OCH_3) 3.72 (s, 3 H); δ(CH) 6.86−8.29 (m, 15 H). ^{13}C NMR (75.4 MHz, THF-d_8, 300 K): δ(PCH_3) 11.2 (t′, |^1J(PC) + ^3J(PC)| = 26.4 Hz,); δ(CH$_3$) 18.1; δ(CCH_3) 29.2, δ(CCH_3) 33.0; δ(OCH_3) 51.7; δ(CH) 114.0, 116.3, 120.5, 120.6, 120.7, 126.3, 126.4, 127.9, 131.4, 131.5 (CH); δ(C) 104.1, 118.4, 132.1, 133.2, 134.0, 144.1, 144.2, 172.9, 175.0. ^{31}P NMR (81.0 MHz, THF-d_8, 300 K): δ(PCH_3) 5.3 (d, ^2J(PP) = 75.3 Hz, 2 P); δ(PC$_6$H$_5$) 22.2 (s(br), 1 P).

Synthesis of (1-Carbonyl-2-oxo-1,2-diphenylethene-diyl)(2-diphenylphosphanylphenolato)bis(trimethyl-phosphine)cobalt(III) (10). A sample containing 2.14 g (4.19 mmol) of *mer*-hydrido(1-carbonyl-2-oxo-1,2-diphenylethene-diyl)tris(trimethylphosphine)cobalt(III) (**7**) and 1.18 g (4.26 mmol) of (2-diphenylphosphanyl)phenol in 80 mL of THF after 18 h at 20 °C formed a brown solution. The volatiles were removed in vacuo, and the resulting solid was extracted with pentane and diethyl ether. Crystallization from pentane at −27 °C afforded orange-red microcrystals: yield 0.43 g of **10** (14%); mp (dec) > 135 °C. Crystallization from diethyl ether gave dark brown cubes: yield 0.50 g of **14** (21%). **10**: Anal. Calcd for $C_{39}H_{42}CoO_3P_3$ (mol wt 710.6): C, 65.92; H, 5.96. Found: C, 65.78; H 6.11. IR (Nujol mull, 2600−1500 cm^{-1}): 1597 s, ν(C=O); 1578 s, 1526 s, ν(C=C). ^{1}H NMR (300 MHz, THF-d_8, 297 K): *cis/trans*-**10** = 64/36. *cis*-**10**: δ(PCH_3) 1.38 (d, ^2J(PH) = 10.0 Hz, 9 H), 0.94 (d, ^2J(PH) = 10.0 Hz, 9 H). *trans*-**10**: δ(PCH_3) 0.80 (t′, |^2J(PH) + ^4J(PH)| = 8.4 Hz, 18 H). Without assignment: δ(CH) 6.39−8.28 (m). ^{31}P NMR (81.0 MHz, THF-d_8, 296 K): *cis*-**10**: δ(PCH_3) 20.5 (s(br), 2 P); δ(PC$_6$H$_5$) 47.0 (s(br), 1 P); *trans*-**10**: δ(PCH_3) 14.9 (s(br), 2 P); δ(PC$_6$H$_5$) 24.3 (s(br), 1 P).

Synthesis of (2-Oxobenzoly)(2-diphenylphosphanylphe-nolato)bis(trimethylphosphine)cobalt(III) (11). A sample containing 1.09 g (2.67 mmol) of *mer*-hydrido(2-oxobenzoyl)-tris(trimethylphosphine)cobalt(III) (**8**) and 0.74 g (2.67 mmol) of (2-diphenylphosphanyl)phenol in 80 mL of THF after 18 h at room temperature formed a red-brown solution from which a red solid was deposited. The volatiles were removed in vacuo, and the resulting solid was washed with pentane and extracted with diethyl ether. Crystallization at −27 °C afforded orange microcrystals: yield 0.25 g of **11** (15%); mp (dec) > 250 °C. Anal. Calcd for $C_{31}H_{36}CoO_3P_3$ (mol wt 608.5): C, 61.19; H, 5.96. Found: C, 61.09; H 6.04. IR (Nujol mull, 2600−1570 cm^{-1}): 1605 s, ν(C=O); 1565 s, ν(C=C). ^{1}H NMR (300 MHz, THF-d_8, 300 K): *cis/trans*-**11** = 54/46. *cis*-**11**: δ(PCH_3) 0.84 (d, ^2J(PH) = 10.0 Hz, 9 H), 1.10 (dd, ^2J(PH) = 10.0 Hz, ^4J(PH) = 1.3 Hz, 9 H). *trans*-**11**: δ(PCH_3) 0.52 (t′, |^2J(PH) + ^4J(PH)| = 8.9 Hz, 18 H); without assignment: δ(CH) 5.60−8.17 (m). ^{13}C NMR (75.4 MHz, THF-d_8, 300 K): δ(PCH_3) 12.0 (t′, |^1J(PC) + ^3J(PC)| = 26.4 Hz), 13.0 (d, ^1J(PC) = 25.2 Hz), 15.0 (d, ^1J(PC) = 27.7 Hz), δ(CH) 112.1, 112.4, 113.1, 118.5, 119.4, 126.4, 126.5, 128.3, 128.4, 128.6, 128.7, 129.9, 132.4, 132.7, 132.9, 133.3, 133.4, 133.5, 134.6, 136.0; δ(CO) 173.2, 178.2; δ(CCO) 203.4. ^{31}P NMR (81.0 MHz, THF-d_8, 213 K): *cis*-**11**: δ(PCH_3) 22.0 (m, 2 P); δ(PC$_6$H$_5$) 47.5 (dd, ^2J(PP) = 220.0 Hz, ^2J(PP) = 57.8 Hz, 1 P), *trans*-**11**: δ(PCH_3) 16.2 (d, ^2J(PP) = 68.6 Hz, 2 P); δ(PC$_6$H$_5$) 26.3 (s(br), 1 P).

Synthesis of (3-Methoxy-2-oxobenzoyl)(2-diphenylphos-phanylphenolato)bis(trimethylphosphine)cobalt(III) (12). A sample containing 2.25 g (5.13 mmol) of *mer*-hydrido(3-methoxy-2-oxobenzoyl)tris(trimethylphosphine)cobalt(III) (**9**) and 1.42 g (5.12 mmol) of (2-diphenylphosphanyl)phenol in 80 mL of THF after 18 h at room temperature formed a dark red-brown solution. The volatiles were removed in vacuo, and the resulting solid was extracted first with pentane and second with diethyl ether. Crystallization from pentane at −27 °C afforded orange microcrystals: yield 0.50 g of **12** (15%); mp (dec) > 230 °C. Crystallization from diethyl ether gave complex **14** (1.50 g, 51.9%). **12**: Anal. Calcd for $C_{32}H_{38}CoO_4P_3$ (mol wt 638.5): C, 60.19; H, 6.00. Found: C, 60.32; H 6.01. IR (Nujol, 2600−l570): 1615 s, 1578 s, ν(C=O); 1537 m ν(C=C). ^{1}H NMR (300 MHz, THF-d_8, 297 K): *cis/trans*-**12** = 96/4. *cis*-**12**: δ(PCH_3) 1.22 (dd, ^2J(PH) = 10.3 Hz, ^4J(PH) = 1.4 Hz, 9 H), 0.92 (d, ^2J(PH) = 9.9 Hz, 9 H); δ(OCH_3) 3.21 (s, 3 H); *trans*-**12**: δ(PCH_3) 0.63 (t′, |^2J(PH) + ^4J(PH)| = 8.9 Hz, 18 H), δ(OCH_3) 3.78 (s, 3H); without assignment: δ(CH) 5.96−8.28 (m). ^{13}C NMR (75.4 MHz, THF-d_8, 300 K): δ(PCH_3) 10.0 (t′, |^1J(PC) + ^3J(PC)| = 26.4 Hz), 11.6 (d, ^1J(PC) = 25.7 Hz), 13.8 (d, ^1J(PC) = 26.4 Hz), δ(OCH_3) 53.1; δ(CH) 110.2, 110.7, 110.8, 111.0, 113.2, 120.3, 124.7, 124.8, 126.6, 127.3, 127.4, 128.5, 131.1, 132.1, 132.3, 134.8, 150.3; δ(CO) 166.6, 178.4. ^{31}P NMR (81.0 MHz, THF-d_8, 213 K): *cis*-**12**: δ(PCH_3) 17.7 (t′, ^2J(PP) = 62 Hz, 1 P), 22.8 (dd, ^2J(PP) = 62 Hz, ^2J(PP) = 220 Hz, 1 P); δ(PC$_6$H$_5$) 46.8 (dd, ^2J(PP) = 62 Hz, ^2J(PP) = 220 Hz, 1 P). *trans*-**12**: δ(PCH_3) 16.2 (d, ^2J(PP) = 74 Hz, 2 P); δ(PC$_6$H$_5$) 26.4 (t, ^2J(PP) = 74 Hz, 1 P).

Crystallographic data for 2: $C_{31}H_{40}CoO_3P_3$, M_r = 612.5, crystal dimensions 0.50 × 0.25 × 0.20 mm, monoclinic, space group $P2_1/c$, a = 16.976(1) Å, b = 8.8627(5) Å, c = 21.5392 (12) Å, β = 107.154(1)°, V = 3096.5(3) Å^3, Z = 4, d_{calcd} = 1.314 g/cm^3, μ = 0.739 mm^{-1}. Data collection and refinement details: Bruker AXS SMART APEX, Mo Kα (λ = 0.71073 Å) radiation, graphite monochromator, T = 298(2) K. A total of 23 318 unique reflections with 4.0° ≤ 2θ ≤ 56.7° were collected, from which 7666 were independend (R_{int} = 0.07). Semiempiri-cal absorption correction (from equivalents) was applied. The structure was solved by direct methods[18] and refined with full-matrix least-squares[18] on F^2, 367 parameters. All non-hydrogen atoms were refined anisotropically, and H atoms were derived from ΔF maps and allowed to ride on their attached carbon atoms with U_{iso} = 1.2U_{iso}(C) and 1.5U_{iso}-(methyl-C). Disordered C atoms C4 and C5 were treated with a split model (C41/C51, C42/C52) with half-occupation each. Refinement converged at R1 = 0.048 (I > 2σ(I)), wR2 = 0.134 (all data), max. (Δ/σ) = 0.001, S = 1.01, min./max. height in final ΔF map −0.39/0.91 e/Å^3.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC 252875. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Supporting Information Available: Tables containing full X-ray crystallographic data for **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

(18) *SMART* (version 5.62), *SAINT* (version 6.02), *SADABS*, *SHELXTL* (version 6.10); Bruker AXS Inc.: Madison, WI, 2002.