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Complexes of Functional Phosphines. 22.[1] Cobalt(II) Complexes with β-Keto Phosphines and Corresponding Cobalt(III) Enolates. Crystal and Molecular Structures of the *fac* and *mer* Isomers of $[\overline{\mathrm{Co\{Ph_2PCH{\sqcup}C({\sqcup}O}})\mathrm{Ph\}_3}]$

Pierre Braunstein,*,† David G. Kelly,† Antonio Tiripicchio,‡ and Franco Ugozzoli‡

Laboratoire de Chimie de Coordination, UA 416 CNRS, Université Louis Pasteur, 4 rue Blaise Pascal, F-67070 Strasbourg Cédex, France, and Istituto di Chimica Generale ed Inorganica, Università di Parma, Centro di Studio per la Strutturistica Diffrattometrica del CNR, 78 Viale delle Scienze, I-43100 Parma, Italy

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Cobalt(II) complexes $[\mathrm{CoX_2\{Ph_2PCH_2C(O)R\}_2}]$ (**1a**, X = Cl, R = Ph; **1b**, X = Cl, R = $\{(\eta^5\text{-}\mathrm{C_5H_4})\mathrm{Fe}(\eta^5\text{-}\mathrm{C_5H_5})\}$; **2**, X = Br, R = Ph; **3**, X = I, R = Ph) containing keto phosphine ligands have been synthesized. The complexes react with base (NaH, NaOMe, K[OSiMe$_3$]) in toluene or THF at 0 °C to afford octahedral cobalt(III) enolates *fac*-$[\overline{\mathrm{Co\{Ph_2PCH{\sqcup}C({\sqcup}O}})\mathrm{R\}_3}]$ (**5a**, R = Ph; **5b**, R = $\{(\eta^5\text{-}\mathrm{C_5H_4})\mathrm{Fe}(\eta^5\text{-}\mathrm{C_5H_5})\}$) plus free ligand and inorganic products. Cobalt(II) intermediates are formed by the same reaction in methanol which precipitates the complexes formulated as $\{\overline{\mathrm{Co}(\mu\text{-}\mathrm{Cl})\mathrm{\{Ph_2PCH{\sqcup}C({\sqcup}O}})\mathrm{R\}\{Ph_2PCH_2C(O)R\}\}_2}$ (**4a**, R = Ph; **4b**, R = $\{(\eta^5\text{-}\mathrm{C_5H_4})\mathrm{Fe}(\eta^5\text{-}\mathrm{C_5H_5})\}$). The latter react in the presence of other solvents to give **5a**,**b**. Disproportionation is proposed as the route to cobalt(III) enolates. **5a** is formed as the kinetic product, and at higher reaction temperatures (ca. 100 °C) **5a** and the corresponding meridional isomer *mer*-$[\overline{\mathrm{Co\{Ph_2PCH{\sqcup}C({\sqcup}O}})\mathrm{Ph\}_3}]$ (**6a**) are produced in a 1:2 ratio. The solid-state structure of the *fac* and *mer* isomers **5a** and **6a** has been determined by single-crystal X-ray analysis. The toluene solvate of **5a** crystallizes in the monoclinic space group $P2_1/a$ with $Z = 4$ in a unit cell of dimensions $a = 23.820(8)$ Å, $b = 13.096(6)$ Å, $c = 17.532(6)$ Å, and $\beta = 97.98(2)°$. **6a** crystallizes in the monoclinic space group $P2_1/n$ with $Z = 4$ in a unit cell of dimensions $a = 13.592(8)$ Å, $b = 21.175(6)$ Å, $c = 16.930(6)$ Å, and $\beta = 94.23(2)°$. The structures have been solved and refined on the basis of 3110 (**5a**) and 3215 (**6a**) observed reflections to R and R_w values of 0.0575 and 0.0630 (**5a**) and 0.0323 and 0.0343 (**6a**), respectively.

Introduction

There is considerable current interest in the functionalization of phosphine ligands, and a range of phosphorus–oxygen donor systems incorporating ether, ester, carboxylate, ketone, or enolate groups have been developed.[2] The reactivity of complexes containing the 3-electron donor phosphino–enolate group $[\mathrm{Ph_2PCH{\sqcup}C({\sqcup}O)R}]^-$ is of special interest because of the ligand's role in the nickel-catalyzed ethene oligomerization reaction operated as the SHOP process.[3] Numerous group 8–10 complexes containing the enolate moiety have been synthesized, and reactivity with organic substrates such as alkynes and isocyanates as well as sulfur dioxide, carbon monoxide, and carbon dioxide has been observed.[4] However, despite these extensive studies little attention has been paid to comparable cobalt systems. Furthermore, the role of the ligands in the reactivity of Co(II)/Co(III) systems is exemplified by the recent report[5a] that the Co(II) acetonitrile complex $[\mathrm{Co(N{\equiv}CCH_3)_4}][\mathrm{PF_6}]_2$ (in acetonitrile) is capable of catalyzing the oxidation of alkanes by oxygen under milder conditions that the industrial catalyst used for the air oxidation of cyclohexane, $[\mathrm{Co(oct)_2}]$ (oct = 2-(ethylhexyl)octanoate).[5b]

Cobalt(II) complexes containing neutral phosphino–ether ligands are known.[6] They, like their phosphine analogues,[7] are readily reduced to cobalt(I) complexes, which are themselves effective carbonylation catalysts.[6,8] Examples of chelating anionic carboxylate and alcoholate compounds have also been reported.[9,10] The former are represented by $[\mathrm{Co_6(Ph_2PCH_2CH_2CO_2)_{12}}]$, which contains a novel $\mathrm{Co_6O_6}$ ring maintained by the coordination of one phosphorus and five oxygen atoms to each metal center. In contrast, the alcoholate complex $[\overline{\mathrm{Co\{Ph_2PCH_2C(CF_3)_2O}}\mathrm{\}_2}]$ is mononuclear and adopts a square planar configuration rather than the more common tetrahedral geometry. In this paper we report the synthesis of cobalt(III) phosphino enolate complexes from cobalt(II) phosphine precursors.

Results

Synthesis and Characterization of the Complexes. The cobalt(II) functional phosphine complexes $[\mathrm{CoCl_2\{Ph_2PCH_2C(O)R\}_2}]$ (**1a**, R = Ph; **1b**, R = $\{(\eta^5\text{-}\mathrm{C_5H_4})\mathrm{Fe}(\eta^5\text{-}\mathrm{C_5H_5})\}$) were readily obtained from anhydrous cobalt(II) chloride and 2 equiv of

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† Université Louis Pasteur.

‡ Università di Parma.

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(1) Part 21: Balegroune, F.; Braunstein, P.; Douce, L.; Dusausoy, Y.; Grandjean, D.; Knorr, M.; Strampfer, M. *J. Cluster Sci.* **1992,** *3,* 275.

(2) Bader, A.; Lindner, E. *Coord. Chem. Rev.* **1991,** *108,* 27 and references cited therein.

(3) (a) Keim, W. *Chem.-Ing.-Tech.* **1984,** *56,* 850. (b) Keim, W.; Behr, A.; Gruber, B.; Hoffmann, B.; Kowaldt, F. H.; Kürschner, U.; Limbäcker, B.; Sistig, F. P. *Organometallics* **1986,** *5,* 2356. (c) Keim, W. *New J. Chem.* **1987,** *11,* 531. (d) Keim, W. *J. Mol. Catal.* **1989,** *52,* 19.

(4) (a) Bouaoud, S.-E.; Braunstein, P.; Grandjean, D.; Matt, D.; Nobel, D. *Inorg. Chem.* **1988,** *27,* 2279. (b) Alcock, N. W.; Platt, A. W. G.; Powell, H. H.; Pringle, P. G. *J. Organomet. Chem.* **1989,** *361,* 409. (c) Braunstein, P.; Gomes Carneiro, T. M.; Matt, D.; Balegroune, F.; Grandjean, D. *Organometallics* **1989,** *8,* 1737 and references therein.

(5) (a) Goldstein, A. S.; Drago, R. S. *Inorg. Chem.* **1991,** *30,* 4506. (b) Mimoun, H. Metal Complexes in Oxidations. In *Comprehensive Coordination Chemistry;* Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon Press: Oxford, England, 1987; Vol. 6.

(6) Lindner, E.; Schober, U.; Glaser, E.; Norz, H.; Wegner, P. Z. *Naturforsch., B* **1987,** *42,* 1527.

(7) Klein, H.-F.; Karsch, H. H. *Inorg. Chem.* **1975,** *14,* 473.

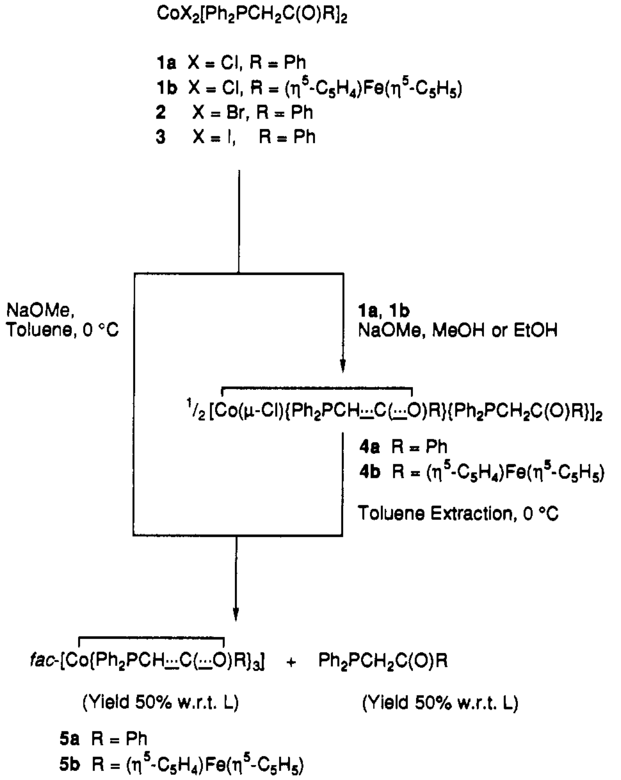
(8) Lindner, E.; Sickinger, A.; Wegner, P. *J. Organomet. Chem.* **1988,** *349,* 75.

(9) Lewis, G. E.; Kraihanzel, C. S. *Inorg. Chem.* **1983,** *22,* 2895.

(10) Boeré, R. T.; Montgomery, C. D.; Payne, N. C.; Willis, C. J. *Inorg. Chem.* **1985,** *24,* 3680.

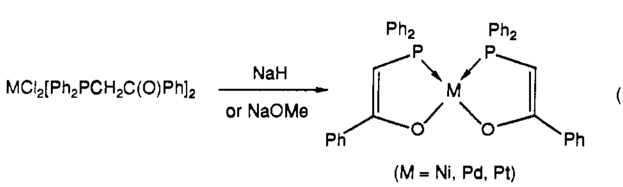
0020-1669/93/1332-4845$04.00/0

Scheme I. Formation of *fac*-[Co{Ph$_2$PCH⋯C(⋯O)R}$_3$], both Directly in Toluene and Indirectly by Toluene Extraction of the Intermediates **4a,b**



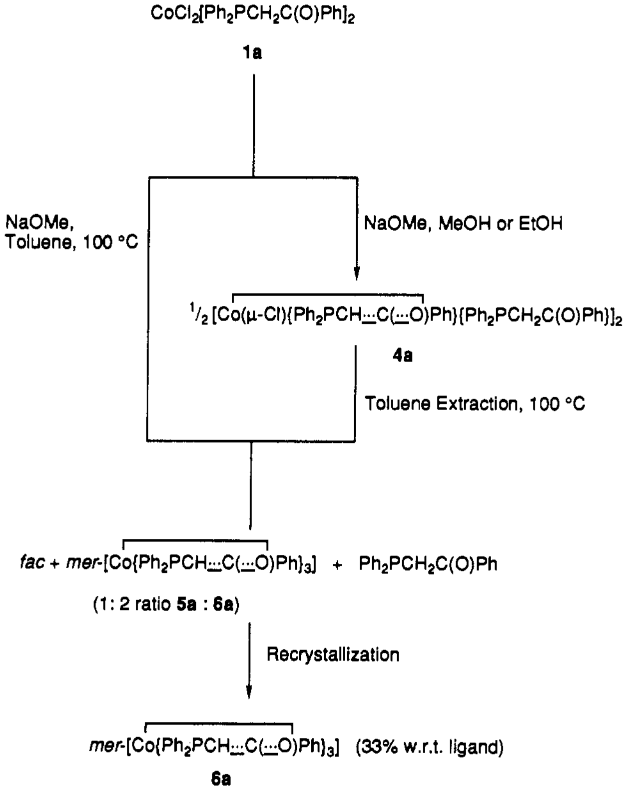
phosphine. The corresponding bromo (**2**) and iodo (**3**) derivatives of **1a** are isolated by facile anion exchange. All the complexes are paramagnetic and pseudotetrahedral with ligand coordination occurring only through the phosphorus center. Such properties mirror those of the well-known PPh$_3$ analogues[11] and of the ether–phosphine complexes of Lindner *et al.*[6] Although octahedral geometries are also readily accessible to cobalt(II), there is no evidence for the additional coordination of the keto function either in the solid state or in dichloromethane, THF, or acetone solutions. However, in methanol a complex–solvent interaction appears to be responsible for the reversible formation of octahedral species.[12]

Formation of *fac*-[Co{Ph$_2$PCH⋯C(⋯O)Ph}$_3$]. We have previously observed the deprotonation of coordinated keto phosphine ligands in the presence of base to form coordinated phosphino–enolate complexes. The reactivity of square planar nickel(II), palladium(II), and platinum(II) systems has been of particular interest (eq 1).[13-15] With the intention of inducing analogous reactivity at tetrahedral cobalt(II), we reacted **1a**, as a toluene slurry, with 2 equiv of NaOMe. Although **1a** is poorly soluble in toluene, the blue slurry rapidly gave way to a deep red solution. Filtration and slow pentane diffusion gave two products, air-stable [Co{Ph$_2$PCH⋯C(⋯O)Ph}$_3$] (**5a**) (ca. 50% yield with respect to ligand) and uncoordinated Ph$_2$PCH$_2$C(O)Ph(L^1) (ca. 50% yield with respect to L^1), Scheme I. In addition, we observed the presence of a blue solid which was insoluble in all common organic solvents. The compound(s) was(were) air-sensitive, decomposing readily in air to give an intractable brown solid. Attempts to characterize the nature of this product, which must contain the remaining cobalt species, were unsuccessful. However, the material is not composed of anhydrous CoCl$_2$, since it would itself react with free L^1 generated along with **5a**.



(1)

Scheme II. Formation of *mer*-[Co{Ph$_2$PCH⋯C(⋯O)Ph}$_3$] (**6a**), both Directly in Hot Toluene and Indirectly by Extraction of the Intermediate **4a** in Hot Toluene



Complex **5a** forms as red crystalline solid which is readily separated from the free ligand by washing with pentane. The complex is diamagnetic and exhibits a singlet peak in the ^{31}P{^{1}H} NMR at δ 27.1 and a ^{1}H NMR singlet at δ 4.75 which can be assigned to the PC*H* protons. These features are indicative of an octahedral low-spin cobalt(III) environment containing three equivalent enolate moities, i.e. in a facial configuration. Crystals of the bulk product proved suitable for X-ray diffraction (see below), and the structure obtained confirmed the *fac*-[Co{Ph$_2$PCH⋯C(⋯O)Ph}$_3$] formulation for **5a** (Figure 1).

The deprotonation of one keto phosphine from **1a** to give, by rearrangement, **5a** with the release of a second free keto phosphine ligand appears to be a general process, Scheme I. Complex **5a** has been isolated in similar yield by the action of stoichiometric or excess NaOMe in toluene, NaH in toluene or THF, and K[OSiMe$_3$] in toluene. Moreover, **2** and **3** also afford **5a** in the presence of base, and in addition the analogous ferrocenyl derivative **5b** has also been characterized.

In view of the general behavior observed in the formation of **5a**, it is therefore surprising to observe significantly different reactivity in methanol. Reaction of **1a** or **1b** with NaOMe in this solvent results in the rapid precipitation of **4a** or **4b**, respectively.

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[11] Cotton, F. A.; Faut, O. D.; Goodgame, D. M. L.; Holm, R. H. *J. Am. Chem. Soc.* **1961**, *83*, 1780.

[12] Braunstein, P.; Kelly, D. G.; Dusausoy, Y.; Bayeul, D.; Tiripicchio, A.; Ugozzoli, F. *Inorg. Chem.*, in press.

[13] Bouaoud, S.-E.; Braunstein, P.; Grandjean, D.; Matt, D.; Nobel, D. *Inorg. Chem.* **1986**, *25*, 3765.

[14] Braunstein, P.; Matt, D.; Nobel, D.; Balegroune, F.; Bouaoud, S.-E.; Grandjean, D.; Fischer, J. *J. Chem. Soc., Dalton Trans.* **1988**, 353.

[15] Moulton, C. J.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1980**, 299.

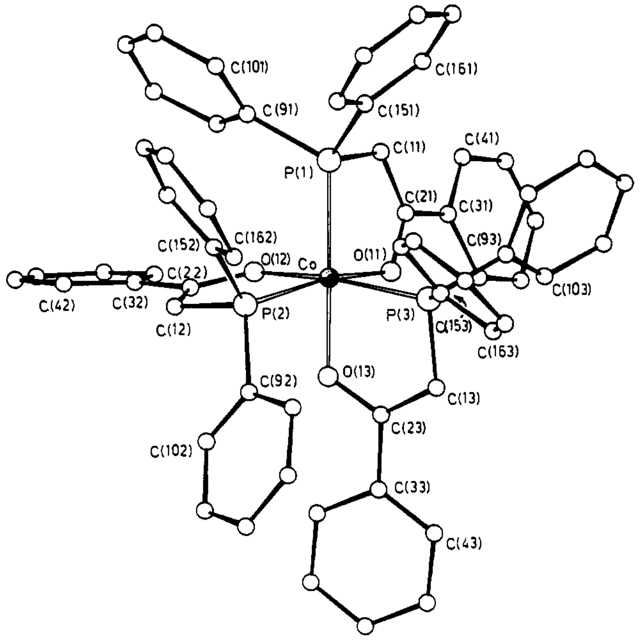

Figure 1. View of the structure of the complex *fac*-[Co{Ph$_2$PCH$\cdots$C($\cdots$O)Ph}$_3$] (**5a**) with the atomic numbering scheme.

Several factors have hampered the characterization of these materials. First, X-ray powder diffraction suggests contamination with NaCl. The relatively high solubility of NaCl in MeOH makes the quantitative precipitation of this material unlikely, and we believe that only traces are present. Purification cannot be achieved to allow full characterization of **4a**,**b** because of the instability of both complexes in common solvents. Rearrangement to **5a**,**b** proceeds over several days in methanol but rapidly on extraction in toluene and other solvents. However, the available evidence suggests they contain cobalt(II) as well as both keto phosphine and phosphino enolate ligands (see Discussion). Such a result is without precedent since coordinated keto phosphine ligands are normally quantitatively converted to enolates in the presence of base.

Formation of *mer*-[Co{Ph$_2$PCH$\cdots$C($\cdots$O)Ph}$_3$]. The reaction of **1a**,**b**, **2**, or **3** with base in toluene, followed by toluene extraction of **4a**,**b** above 0 °C, results in the isolation of a second product and commensurate reductions in the yields of **5a**,**b**. Hence, the reaction of **1a** with NaOMe was fully investigated. In methanol no temperature dependence in the formation of **4a** could be discerned. However, toluene extraction of **4a** and the direct reaction of **1a** with base in toluene both exhibit a marked temperature dependence, Scheme II. Formation of the second product **6a**, characterized as the meridional isomer of **5a**, becomes significant at and above room temperature. By 100 °C a ca. 1:2 ratio of **5a**:**6a** is observed. This temperature dependence appears to be the result of kinetic control during the *formation* of the complexes, since *exchange* between the pure compounds only occurs above 100 °C.

Description of the Crystal Structures of *fac*-[Co{Ph$_2$PCH$\cdots$C($\cdots$O)Ph}$_3$]·C$_7$H$_8$ (5a) and *mer*-[Co{Ph$_2$PCH$\cdots$C($\cdots$O)-Ph}$_3$] (6a). In the crystals of **5a** toluene molecules of solvation are also present. A view of the *fac* and *mer* isomers is shown in Figures 1 and 2, respectively, together with the atom-numbering schemes. Selected bond distances and angles are given in Table I. The cobalt atoms have the anticipated octahedral coordination involving three P and three O atoms from three anionic, chelating Ph$_2$PCH$\cdots$C($\cdots$O)Ph ligands, and both **5a** and **6a** are chiral by virtue of the bidentate nature of the heterodifunctional ligands. As both isomers crystallize in a centrosymmetric space group, both enantiomers are present in the crystals. The five-membered rings are roughly planar in both isomers with a slight deviation of the metal atom with respect to the planar P–C–C–O moiety. The octahedral coordination around the Co atom is slightly more distorted in the *fac* than in the *mer* isomer as the bond angles are in the range 83.1(2)–104.2(1)° in the former and 83.3(1)–96.8(1)° in the latter. No particular strain is caused by the chelating ligands, and their bite angles are favorable to this coordination [in the range 83.8(2)–86.5(1)°]. The Co–P bond distances are very similar in the *fac* isomer [in the range 2.237(3)–2.261(3) Å] but differ remarkably in the *mer* isomer [in the range 2.197(3)–2.310(2) Å], whereas the Co–O distances are similar in both isomers [in the range 1.916(5)–1.940(6) Å (*fac*) and 1.915(4)–1.946(3) Å (*mer*)]. The origin of the differing Co–P bond distances observed in **6a** is unclear. If purely trans influence were responsible, the Co–P(1) bond, which lies opposite an oxygen donor, should have a comparable length to the three Co–P bonds in **5a**. In fact, the Co–P(1) distance in **6a** is significantly shorter than those in **5a**. Moreover, the Co–P(2) and Co–P(3) bonds which are mutually trans should have the same length, but these are also different. Thus, secondary bonding effects, such as interactions between the various phenyl rings and distorsions from regular octahedral geometry generated by ligand chelation, must be considered. The Co–O distances in **5a** and **6a** do not differ remarkably from those reported for Co(III)–O(terminal alcohols) [average value 1.951(17) Å], Co(III)–O(terminal alkoxy) and Co(III)–O(terminal aryloxy) [average values 1.912(26) and 1.894(14) Å, respectively], and Co(III)–O(terminal alkyl carboxylates) [average value 1.906(19) Å].[16] From the values of the O–C, C–C, and C–P bond distances in the chelating ring of both isomers [in the range 1.278(11)–1.317(6), 1.336(13)–1.377(15), and 1.726(9)–1.758(5) Å, respectively], it can be noted that the C–C bond possesses an appreciable double-bond character although a certain degree of delocalization can be observed throughout the P–C$\cdots$C($\cdots$O) system.

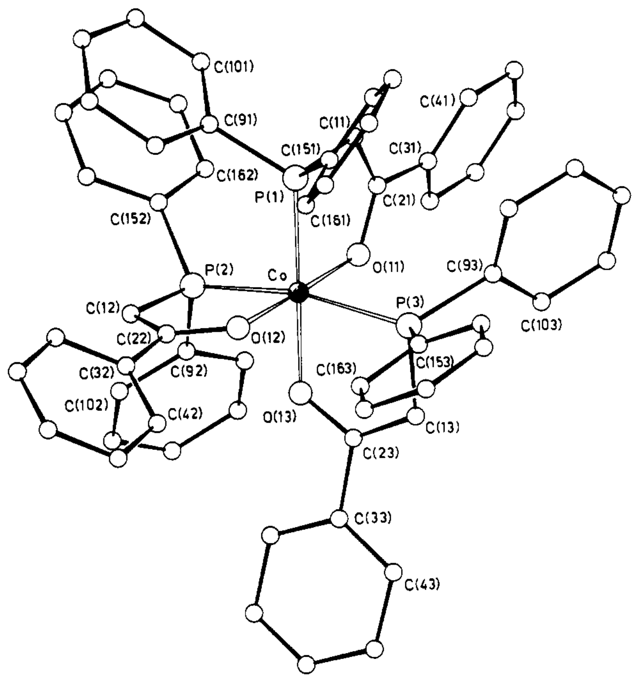

Figure 2. View of the structure of the complex *mer*-[Co{Ph$_2$PCH$\cdots$C($\cdots$O)Ph}$_3$] (**6a**) with the atomic numbering scheme.

These structures appear to represent the first reported examples for cobalt complexes with P,O chelates (Cambridge Crystallo-

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(16) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, T. *J. Chem. Soc., Dalton Trans.* **1989**, S1.

Table I. Selected Bond Distances (Å) and Angles (deg) in the Complexes *fac*-[Co{$Ph_2PCH\cdots C(\cdots O)Ph$}$_3$] (**5a**) and *mer*-[Co{$Ph_2PCH\cdots C(\cdots O)Ph$}$_3$] (**6a**)

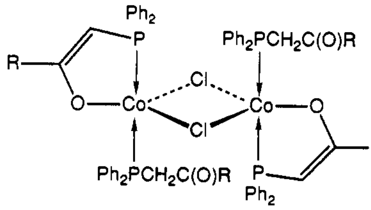
	5a	**6a**
Co–P(1)	2.261(3)	2.197(3)
Co–P(2)	2.237(3)	2.239(2)
Co–P(3)	2.250(3)	2.310(2)
Co–O(11)	1.916(6)	1.925(4)
Co–O(12)	1.940(6)	1.915(4)
Co–O(13)	1.916(5)	1.946(3)
P(1)–C(11)	1.726(9)	1.750(5)
O(11)–C(21)	1.278(11)	1.307(5)
C(11)–C(21)	1.377(15)	1.346(6)
C(21)–C(31)	1.476(13)	1.497(7)
P(2)–C(12)	1.753(10)	1.751(5)
O(12)–C(22)	1.303(11)	1.317(6)
C(12)–C(22)	1.336(13)	1.338(7)
C(22)–C(32)	1.491(14)	1.504(7)
P(3)–C(13)	1.756(9)	1.758(5)
O(13)–C(23)	1.310(11)	1.292(6)
C(13)–C(23)	1.372(13)	1.350(7)
C(23)–C(33)	1.473(13)	1.491(7)
P(1)–Co–P(2)	104.2(1)	96.2(1)
P(1)–Co–P(3)	101.0(1)	96.8(1)
P(2)–Co–P(3)	103.7(1)	167.0(1)
P(1)–Co–O(11)	85.2(2)	86.5(1)
P(1)–Co–O(12)	85.8(2)	92.6(2)
P(1)–Co–O(13)	168.5(2)	179.0(1)
P(2)–Co–O(11)	166.8(2)	94.0(1)
P(2)–Co–O(12)	85.2(2)	86.2(1)
P(2)–Co–O(13)	83.2(2)	83.3(1)
P(3)–Co–O(11)	83.1(2)	86.1(1)
P(3)–Co–O(12)	166.9(2)	93.9(1)
P(3)–Co–O(13)	85.4(2)	83.8(1)
O(11)–Co–O(12)	86.3(3)	179.1(2)
O(11)–Co–O(13)	86.1(3)	92.7(1)
O(12)–Co–O(13)	86.1(2)	88.1(2)
Co–P(1)–C(11)	96.7(4)	98.4(2)
Co–O(11)–C(21)	120.5(6)	116.9(3)
P(1)–C(11)–C(21)	116.4(7)	113.5(4)
O(11)–C(21)–C(31)	115.9(8)	114.0(4)
O(11)–C(21)–C(11)	120.9(8)	124.4(5)
C(11)–C(21)–C(31)	123.2(9)	121.6(4)
Co–P(2)–C(12)	97.6(3)	97.7(2)
Co–O(12)–C(22)	118.8(5)	117.4(3)
P(2)–C(12)–C(22)	115.3(7)	113.9(4)
O(12)–C(22)–C(32)	115.3(8)	112.8(4)
O(12)–C(22)–C(12)	122.9(8)	124.8(5)
C(12)–C(22)–C(32)	121.8(8)	122.4(5)
Co–P(3)–C(13)	97.2(3)	97.0(2)
Co–O(13)–C(23)	120.3(5)	120.3(3)
P(3)–C(13)–C(23)	115.5(7)	114.9(4)
O(13)–C(23)–C(33)	115.5(8)	114.5(5)
O(13)–C(23)–C(13)	120.7(8)	123.0(4)
C(13)–C(23)–C(33)	123.7(9)	122.4(5)

graphic Data Centre). Neutral P,P and P,N complexes are known such as [Co(dppm)$_3$](ClO$_4$)$_3$ and [Co(edpm)$_3$]Br$_3$·3H$_2$O [edpp = (2-aminoethyl)diphenylphosphine].[17,18] However both compounds were generated by ligand exchange from the well-known complex [Co(en)$_2$Cl$_2$]Cl rather than from cobalt(II) phosphine precursors. No structural results have been reported for the former, whereas in the crystal structure of the *fac* isomer of the latter, the Co–P bond lengths [2.231(5), 2.239(4), and 2.242(5) Å], trans with respect to the N atoms, are quite comparable to those found in our *fac* isomer.

Discussion

Although the cobalt(II) complexes [CoX$_2${$Ph_2PCH_2C(O)R$}$_2$] (**1a**, X = Cl, R = Ph; **1b**, X = Cl, R = {(η^5-C_5H_4)Fe(η^5-C_5H_5)}; **2**, X = Br, R = Ph; **3**, X = I, R = Ph) containing keto phosphine ligands react with base (NaH, NaOMe, K[OSiMe$_3$]), corresponding bis(enolato)cobalt(II) complexes were not observed. Instead, the isolation of **5a** and **6a** is notable because cobalt(II) has been oxidized to cobalt(III) in the presence of the normally reducing phosphine ligands. Their structures represent the first reported examples of a P~O chelating system for cobalt(III).

Mechanism of *fac*-[Co{$Ph_2PCH\cdots C(\cdots O)Ph$}$_3$] Formation. Clearly, the isolation of a cobalt(III) product is a general process, and two features of this reactivity are of interest: (i) Why is only half the available ligand deprotonated, even in the presence of excess base? (ii) How and why is cobalt(II) oxidized to cobalt(III)? Some light is shed on the liberation of free ligand by the reactivity of **1a,b** with NaOMe in MeOH or EtOH. Here the addition of base to solutions of **1a,b** instantaneously precipitates NaCl and pale brown or orange cobalt(II) complexes **4a,b**, respectively. In both cases neutral keto (P-bound) and enolato (P~O chelated) phosphine ligands, as well as bridging chlorides, are identified by infrared spectroscopy. These data and the pale colors of the complexes, which typify 5- or 6-coordinate cobalt(II), would be consistent with a dimeric structure of the type suggested as follows:



4a R = Ph
4b R = (η^5-C_5H_4)Fe(η^5-C_5H_5)

Unfortunately, **4a,b** cannot be recrystallized or separated from traces of NaCl. The compounds are poorly soluble in alcohols and react to give **5a,b** in the presence of other solvents, Scheme II. **4a,b** do, however, represent important intermediates. They incorporate the observed 50:50 keto:enolate ratio of the final reaction products and are clearly unstable in solution. The transient presence of such species in other solvent media may, therefore, be important in the isolation of the final cobalt(III) product.

Two obvious routes are available for cobalt(III) oxidation: (i) by adventitious oxygen; (ii) by cobalt disproportionation. Hypothesis (i) can be excluded because the oxidation appears instantaneous in NaOMe/toluene systems, even under rigorously anaerobic conditions. Moreover, in NaH/THF or toluene, where the insolubility of the base produces a significantly slower formation of **5a**, this product appears to form at comparable rates under nitrogen and in air. In fact, the only significant difference between the two reactions appears to be the partial oxidation of free Ph$_2$PCH$_2$C(O)Ph in air to Ph$_2$P(O)CH$_2$C(O)Ph [^{1}H NMR (CDCl$_3$) δ 4.15, ^2J(PH) = 15 Hz].[19]

In contrast, there is considerable evidence for disproportionation. Spontaneous disproportionation is not observed for cobalt(II) phosphine complexes, however, the literature provides several examples of reactions on related systems in which this does indeed occur. Difluorophenylphosphine forms stable [CoX$_2$(PhPF$_2$)$_2$] complexes when X = I. However, the corresponding bromides disproportionate in the presence of excess ligand, while only disproportionated chloro products can be obtained.[20] Similar reactivity has also been reported with phosphite ligands and cobalt(II) thiocyanate,[21] perchlorate, and tetrafluoroborate salts.[22]

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[17] Ohishi, T.; Kashiwabara, K.; Fujita, J. *Chem. Lett.* **1981**, 1371.
[18] Kinoshita, I.; Kashiwabara, K.; Fujita, J.; Matsumoto, K.; Ooi, S. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 2683.
[19] Braunstein, P.; Coco Cea, S.; DeCian, A.; Fischer, J. *Inorg. Chem.* **1992**, *31*, 4203.
[20] Stelzer, O. *Chem. Ber.* **1974**, *107*, 2329.
[21] Albertin, G.; Pelizzi, G.; Bordignon, E. *Inorg. Chem.* **1983**, *22*, 515.
[22] Socol, S. M.; Verkade, J. G. *Inorg. Chem.* **1986**, *25*, 2658.

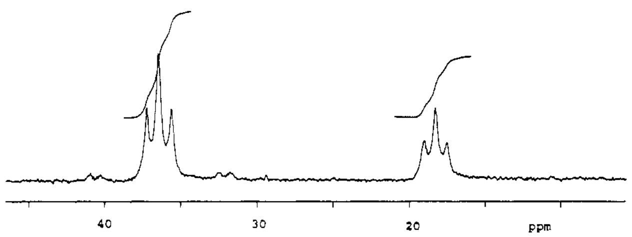
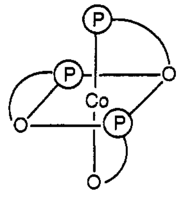


Figure 3. $^{31}P\{^1H\}$ NMR spectrum of *mer*-$[Co\{Ph_2PCH{\cdots}C({\cdots}O)Ph\}_3]$ (**6**) in $CDCl_3/CH_2Cl_2$ at 233 K with signals centered at δ 38.5, 34.3, and 18.0.

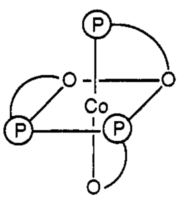
Additionally, cobalt(II) phosphite[21] and phosphine[23] complexes have been shown to disproportionate on reaction with nitrous oxide. Stable cobalt(III) phosphine complexes are formed, with the cobalt(I) species being stabilized by NO coordination. Furthermore, the interaction of the tertiary phosphine complexes $[CoX_2(PR_3)_2]$ with carbon monoxide affords characterizable cobalt(I) complexes. Initial coordination of CO to the cobalt(II) compounds is thought to induce a disproportionation in which the cobalt(III) product is unstable.[24]

While the literature suggests that diphenyl-substituted tertiary phosphines do not spontaneously drive cobalt(II) disproportionation, the additional stability provided by the chelate effect in $[Ph_2PCH{\cdots}C({\cdots}O)Ph]^-$, and by the electron density supplied by the enolate ligand, may be sufficient to shift this balance. Although we have been unable to characterize a cobalt(I) species from our reaction, a deep blue precipitate is formed concurrently with characterized cobalt(III) products. Secondary evidence suggests that this solid does not simply contain $CoCl_2$ and that in fact more complex unstable materials are present. Thus, we believe there is strong evidence to propose that a disproportionation mechanism is involved in the formation of our cobalt(III) complexes.

Formation of *mer*-$[Co\{Ph_2PCH{\cdots}C({\cdots}O)Ph\}_3]$. **6a** is formed in increasing quantities at and above room temperature, and by ca. 100 °C a ca. 2:1 ratio between the *mer* and *fac* isomers is observed.



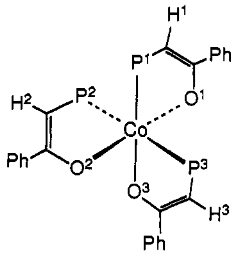
mer



fac

These results suggest **5a** represents the kinetically favored product during *disproportionation* but that there is little thermodynamic difference in stability. It must be stressed that the isolation of **5a** from **1**, **2**, or **3** must be a complex process involving enolate transfer between metal centers as well as disproportionation. Indeed the transfer of enolate ligands between nickel(II) and palladium(II) has previously been reported.[14] While the experimental evidence indicates that these transformations occur rapidly to give cobalt(III) enolates, intermediates must exist which themselves kinetically favor *fac* formation.

The above process represents that observed during $[Co\{Ph_2PCH{\cdots}C({\cdots}O)Ph\}_3]$ formation. In contrast, *exchange* between the pure complexes appears to be a relatively high-energy process, only occuring slowly in refluxing toluene. Pure **5a** or **6a** as well as mixtures of the two compounds do not undergo isomerization until >100 °C. At this point NMR studies indicate the formation of ca. 2:1 *mer*/*fac* mixtures. The high temperature of *fac*–*mer* exchange is perhaps surprising in view of the isolation of stable five-coordinate phosphine complexes such as $[CoCl_3(PR_3)_2]$ (R = Et, Pr).[25] Facile decoordination of one phosphine donor in the octahedral complexes would allow rapid exchange via a five-coordinate transition state. While this process is not excluded as the exchange mechanism, the high temperatures and consequent high activation energies involved are comparable to those of the asymmetric $[Co(acac)_3]$ derivatives. Extensive studies of the latter compounds did indeed point to a dissociative exchange mechanism, thus suggesting that the bond cleavage processes have similar energy in the P,O and O,O chelates.[26] Such a strong metal enolate interaction and consequent concentration of electron density toward the metal center agrees with the observed inactivity of **5a** toward HBF_4 in Et_2O. The elevated temperatures of exchange do, however, allow the isolation and characterization of **6a**. Whereas in an octahedral complex of type *fac*-CoP_3O_3 all three phosphine ligands are equivalent, they are in a different environment in complexes of type *mer*-CoP_3O_3 so that three sets of resonances are expected in NMR spectroscopy. In fact, the ^1H NMR of **6a** exhibits three proton resonances at δ 5.22, 4.89, and 4.83. The downfield resonance was easily assigned to that of the chemically dissimilar H^1 proton. The possibility that the remaining signals represented two equivalent protons, which were exhibiting $^2J(PH)$ coupling, was discounted by comparison of the 200- and 400-MHz spectra of **6a**. Thus the two singlets were assigned to the nonequivalent H^2 and H^3. The room-temperature $^{31}P\{^1H\}$ spectrum of **6a** shows considerable broadening with unresolved peaks at δ 36 (P^2 and P^3) and 17 (P^1), presumably as the result of dynamic processes within the structure. At higher temperatures (ca. 80 °C) these are not resolved to sharper peaks. Hence, the process may be related to a twist isomerization which is blocked by the steric bulk and interactions of the enolate ligands. The spectrum resolves at temperatures below 273 K, Figure 3.



6a

Analogy with the proton spectra suggests that P^2 and P^3 become inequivalent as a result of the ligand's cyclic coordination via O^2 (trans to O^1) and O^3 (trans to P^1), respectively. The observed spin system is of the ABX type, and the spectrum may be rationalized on the following basis: Nonequivalent but comparable $J(P^1P^2)$ and $J(P^1P^3)$ couplings of ca. 60 Hz produce the apparent triplet assigned to P^1 at δ 18.0. The phosphorus nuclei P^2 and P^3 are strongly coupled with a $^2J(P^2P^3)$ coupling of 310 Hz. Thus, the signals, which are centered at δ 38.5 and 34.3, are each split into doublets of doublets. As the signal separation is of similar magnitude to the $^2J(P^2P^3)$ coupling they merged. Thus, the resulting pattern for the AB part of the spectrum is that of an apparent triplet and two weak, external doublets.

Conclusion

The formation of cobalt(III) enolato complexes from cobalt(II) keto phosphines by disproportionation is unusual. Furthermore the mechanism provides an insight into the balance bet-

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(23) Alnaji, O.; Peres, Y.; Dahan, F.; Dartiguenave, M.; Dartiguenave, Y. *Inorg. Chem.* **1986**, *25*, 1383.

(24) Bressan, M.; Corain, B.; Rigo, P.; Turco, A. *Inorg. Chem.* **1970**, *7*, 1733.

(25) Jensen, K. A.; Nygaard, B.; Pedersen, C. T. *Acta Chem. Scand.* **1963**, *17*, 1126.

(26) Gordon, J. G., II; Holm, R. H. *J. Am. Chem. Soc.* **1970**, *92*, 5319.

Table II. Experimental Data for the X-ray Diffraction Studies

	5a	**6a**
mol formula	$C_{60}H_{48}CoO_3P_3 \cdot C_7H_8$	$C_{60}H_{48}CoO_3P_3$
mol wt	1061.03	968.89
cryst system	monoclinic	monoclinic
space group	$P2_1/a$	$P2_1/n$
radiatn (Mo Kα) (λ, Å)	Nb-filtered (0.710 73)	graphite-monochromated (0.710 73)
a, Å	23.820(8)	13.592(8)
b, Å	13.096(6)	21.175(6)
c, Å	17.532(6)	16.930(6)
β, deg	97.98(2)	94.23(2)
V, Å^3	5416(4)	4859(4)
Z	4	4
D_{calcd}, g cm^{-3}	1.301	1.324
μ(Mo Kα), cm^{-1}	4.48	4.93
unique tot. no. of data	8553	6727
unique no. of obsd data	3110 [$I > 2\sigma(I)$]	3215 [$I > 3\sigma(I)$]
R^a	0.0575	0.0323
$R_w{}^b$	0.0630	0.0343

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$.

ween the reducing influence of the phosphine ligands and stabilization of high oxidation states provided by the presence of chelating ligands. The structures of *fac*- and *mer*-[Co{$Ph_2PCHC(O)Ph$}$_3$] represent the first reported examples of P~O chelating systems for cobalt complexes.[30]

Experimental Section

A. Reagents and Physical Measurements. All reaction were performed in Schlenk-type flasks under nitrogen. Solvents were purified and dried under nitrogen by conventional methods. Reagent grade materials were used in all cases, except for K[OSiMe$_3$], where Aldrich 80% technical grade was employed. IR spectra were recorded in the 4000–400-cm^{-1} range on a Perkin-Elmer 398 spectrophotometer or Bruker IFS66 FT–IR, while far-infrared spectra were recorded on a Bruker IFS88 FT-FIR machine as polyethene pellets. UV spectra were recorded on a Shimadzu UV260 spectrometer, and magnetic moments were obtained on a Johnson Matthey Faraday balance. ^1H and $^{13}P\{^1H\}$ NMR spectra were recorded at 200.13 and 81 MHz, respectively, on a FT Bruker WP-200SY intrument; an AM 400 was used for the 400.26-MHz spectra.

B. Synthesis. $Ph_2PCH_2C(O)Ph$ (L^1) and $Ph_2PCH_2C(O)[(\eta^5\text{-}C_5H_4)\text{-}Fe(\eta^5\text{-}C_5H_5)]$ (L^2) were prepared by the methods previously described.[13,27]

[CoCl$_2${Ph$_2$PCH$_2$C(O)Ph}$_2$] (1a). $CoCl_2 \cdot 6H_2O$ (0.148 g, 0.63 mmol) was thermally dehydrated to the pale blue anhydrous salt by heating to 120 °C, in vacuo. On cooling, the salt was dissolved in 10 mL of ethanol to give a pale blue solution. Addition of $Ph_2PCH_2C(O)Ph$ (0.380 g, 1.25 mmol) gave a royal blue solution, which after stirring for 2 h was cooled to −20 °C to afford blue **1a** (0.34 g, 74%). The product was filtered out and dried under vacuum: mp 139 °C; IR (KBr) ν(CO) 1675 s cm^{-1}; IR (Nujol) ν(CO) 1670 s cm^{-1}; magnetic moment $\mu_{eff} = 4.4\ \mu_B$; UV–vis (CH_2Cl_2) 668 (ϵ 278), 628 (290), 590 (225) nm; FAB mas spectrum m/e 702.0 (20%, M − HCl − Cl), 379.9 (20%, M − Cl − L^1), 305.1 (100% HL^1). Anal. Calcd for $C_{40}H_{34}Cl_2CoO_2P_2$ (M = 738.5): C, 65.1; H, 4.6. Found: C, 65.2; H, 4.7.

[CoCl$_2${Ph$_2$PCH$_2$C(O)(η^5-C$_5$H$_4$)Fe(η^5-C$_5$H$_5$)}$_2$] (1b). $CoCl_2 \cdot 6H_2O$ (0.097 g, 0.41 mmol) was thermally dehydrated in vacuo and on cooling dissolved in 10 mL of acetone. The ligand $Ph_2PCH_2C(O)[(\eta^5\text{-}C_5H_4)\text{-}Fe(\eta^5\text{-}C_5H_5)]$ (0.337 g, 0.82 mmol) was added to give an immediate blue to brown color change. The solution was stirred for 1 h before the solvent was removed under reduced pressure. **1b**$\cdot 0.5CH_2Cl_2$ was recrystallized by Et_2O diffusion into a CH_2Cl_2 solution of the complex (0.24 g, 59%): mp 138 °C, IR (KBr) ν(CO) 1653 s cm^{-1}; IR (Nujol) ν(CO) 1650 s cm^{-1}. Anal. Calcd for $C_{48}H_{42}Cl_2CoFe_2O_2P_2 \cdot 0.5CH_2Cl_2$ (M = 991.8 + 42.5): C, 57.8; H, 4.3. Found: C, 57.7; H, 4.3.

Table III. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Thermal Parameters (Å^2 × 10^4) with Esd's in Parentheses for the Non-Hydrogen Atoms of *fac*-[Co($Ph_2PCHC(O)Ph$)$_3$]$\cdot C_6H_5Me$ (**5a**)

	x/a	y/b	z/c	$U_{eq}{}^a$		x/a	y/b	z/c	$U_{eq}{}^a$
Co	701(1)	2017(1)	2602(1)	384(4)	C(112)	−767(6)	1109(10)	−8(7)	702(53)
P(1)	1363(1)	3130(2)	3149(1)	432(10)	C(122)	−1275(6)	1565(11)	121(7)	797(56)
P(2)	426(1)	2659(2)	1427(1)	419(9)	C(132)	−1274(5)	2305(10)	650(6)	693(50)
P(3)	−27(1)	2380(2)	3248(1)	422(8)	C(142)	−770(4)	2636(9)	1091(6)	595(46)
O(11)	941(3)	1177(5)	3482(3)	438(24)	C(152)	465(4)	4006(8)	1147(6)	497(38)
O(12)	1313(2)	1395(4)	2143(4)	410(23)	C(162)	10(5)	4676(8)	1065(6)	588(48)
O(13)	253(2)	871(4)	2204(3)	431(22)	C(172)	90(6)	5706(9)	876(7)	735(56)
C(11)	1626(4)	2369(8)	3920(5)	546(40)	C(182)	597(7)	6062(10)	773(7)	822(61)
C(21)	1360(4)	1444(8)	3978(5)	442(41)	C(192)	1053(6)	5380(10)	838(7)	782(60)
C(31)	1540(4)	697(8)	4594(5)	482(44)	C(202)	993(5)	4367(9)	1014(6)	597(44)
C(41)	2021(5)	789(10)	5122(7)	743(50)	C(13)	−422(4)	1267(7)	3002(5)	490(40)
C(51)	2171(5)	98(11)	5692(8)	888(64)	C(23)	−213(4)	637(7)	2483(5)	437(33)
C(61)	1844(6)	−746(11)	5764(7)	838(61)	C(33)	−493(4)	−314(7)	2186(5)	445(38)
C(71)	1359(5)	−868(10)	5239(7)	775(56)	C(43)	−952(4)	−717(8)	2470(7)	685(47)
C(81)	1215(5)	−177(9)	4668(6)	620(48)	C(53)	−1195(5)	−1619(10)	2177(8)	880(63)
C(91)	1967(4)	3450(8)	2641(5)	459(37)	C(63)	−981(5)	−2104(9)	1590(8)	860(56)
C(101)	2088(4)	4422(8)	2416(6)	560(46)	C(73)	−524(5)	−1732(10)	1314(7)	859(56)
C(111)	2552(5)	4604(9)	2045(7)	658(50)	C(83)	−285(5)	−812(8)	1598(6)	702(45)
C(121)	2902(5)	3822(10)	1934(7)	681(52)	C(93)	129(4)	2453(7)	4283(5)	445(33)
C(131)	2799(4)	2867(10)	2147(6)	649(50)	C(103)	155(4)	1584(9)	4723(6)	613(44)
C(141)	2337(4)	2668(8)	2534(6)	552(38)	C(113)	282(5)	1609(10)	5516(7)	754(53)
C(151)	1211(4)	4380(8)	3522(6)	505(43)	C(123)	383(5)	2546(12)	5879(7)	840(59)
C(161)	1343(5)	4586(11)	4298(7)	763(58)	C(133)	350(5)	3415(11)	5448(7)	773(51)
C(171)	1248(7)	5548(14)	4579(10)	1041(81)	C(143)	221(4)	3369(9)	4655(6)	596(47)
C(181)	1025(7)	6304(11)	4100(12)	1077(82)	C(153)	−508(4)	3462(8)	3074(5)	456(35)
C(191)	866(6)	6109(10)	3336(10)	869(71)	C(163)	−1040(5)	3413(9)	3281(7)	734(47)
C(201)	973(4)	5166(9)	3067(7)	628(51)	C(173)	−1406(5)	4219(11)	3187(8)	924(60)
C(12)	941(4)	2065(8)	956(5)	518(39)	C(183)	−1236(6)	5096(11)	2892(7)	826(59)
C(22)	1326(4)	1515(7)	1408(5)	385(35)	C(193)	−713(6)	5188(10)	2679(7)	850(59)
C(32)	1805(4)	997(8)	1100(6)	472(39)	C(203)	−353(4)	4363(9)	2780(7)	663(48)
C(42)	1945(5)	1190(11)	378(7)	838(61)	C(14)	1196(9)	8473(15)	2211(11)	1654(72)
C(52)	2382(6)	675(13)	103(8)	1005(77)	C(24)	1716(10)	8394(18)	2768(13)	1725(79)
C(62)	2697(5)	−8(12)	548(10)	977(81)	C(34)	1952(8)	8924(13)	3280(10)	1256(56)
C(72)	2581(5)	−196(11)	1252(9)	820(58)	C(44)	2488(9)	8759(17)	3785(11)	1611(72)
C(82)	2140(5)	298(9)	1540(7)	685(52)	C(54)	2748(9)	7910(18)	3669(12)	1688(75)
C(92)	−255(4)	2215(8)	945(5)	442(39)	C(64)	2454(9)	7308(15)	3000(12)	1601(70)
C(102)	−272(4)	1464(8)	406(6)	561(43)	C(74)	1997(9)	7417(16)	2492(11)	1624(73)

[a] Equivalent Isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table IV. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Thermal Parameters (Å^2 × 10^4) with Esd's in Parentheses for the Non-Hydrogen Atoms of *mer*-[Co(Ph$_2$PCHC(O)Ph)$_3$] (**6a**)

	x/a	*y/b*	*z/c*	U_{eq}[a]
Co	8639(1)	8071(1)	6845(1)	400(2)
P(1)	9026(1)	9031(1)	7250(1)	417(5)
P(2)	10191(1)	7735(1)	6768(1)	448(5)
P(3)	6949(1)	8185(1)	6844(1)	488(4)
O(11)	8606(2)	7855(1)	7947(2)	429(12)
O(12)	8674(2)	8299(2)	5753(2)	466(12)
O(13)	8311(2)	7215(1)	6501(2)	504(12)
C(11)	8946(3)	8915(2)	8267(3)	454(19)
C(21)	8731(3)	8316(2)	8458(3)	429(19)
C(31)	8654(4)	8118(3)	9300(3)	475(20)
C(41)	8515(5)	8547(3)	9876(4)	893(20)
C(51)	8476(5)	8371(4)	10656(4)	966(36)
C(61)	8585(5)	7769(4)	10865(4)	909(34)
C(71)	8716(8)	7345(4)	10319(5)	1521(52)
C(81)	8745(7)	7520(3)	9528(4)	1231(44)
C(91)	10218(4)	9391(2)	7089(3)	475(19)
C(101)	10878(4)	9534(3)	7719(3)	622(23)
C(111)	11749(5)	9834(3)	7595(4)	817(30)
C(121)	11968(5)	9992(3)	6847(5)	916(34)
C(131)	11323(5)	9859(3)	6220(4)	789(29)
C(141)	10438(4)	9558(3)	6329(3)	610(21)
C(151)	8240(3)	9680(2)	6899(3)	436(19)
C(161)	7942(4)	9741(2)	6099(3)	508(20)
C(171)	7433(4)	10271(3)	5832(4)	654(24)
C(181)	7209(4)	10737(3)	6344(4)	696(25)
C(191)	7480(4)	10681(3)	7130(4)	647(26)
C(201)	7990(4)	10159(3)	7405(3)	533(21)
C(12)	10322(4)	7954(2)	5784(3)	514(20)
C(22)	9501(4)	8194(2)	5415(3)	448(19)
C(32)	9431(4)	8364(2)	4550(3)	481(19)
C(42)	8592(4)	8228(3)	4082(3)	684(25)
C(52)	8533(6)	8347(3)	3280(4)	895(33)
C(62)	9321(6)	8616(3)	2952(4)	886(35)
C(72)	10143(5)	8763(3)	3406(4)	838(29)
C(82)	10214(4)	8640(3)	4210(3)	667(25)
C(92)	10349(3)	6887(3)	6859(3)	472(19)
C(102)	10914(4)	6565(3)	6344(3)	684(25)
C(112)	11065(5)	5927(3)	6413(4)	857(31)
C(122)	10650(5)	5589(3)	6989(4)	743(27)
C(132)	10091(4)	5899(3)	7502(4)	706(26)
C(142)	9942(4)	6536(3)	7439(3)	604(24)
C(152)	11230(4)	7997(3)	7410(3)	542(20)
C(162)	11206(4)	7929(3)	8226(4)	668(25)
C(172)	11995(6)	8111(3)	8728(4)	888(29)
C(182)	12830(6)	8343(4)	8426(5)	1031(37)
C(192)	12861(5)	8401(3)	7634(5)	962(35)
C(202)	12071(4)	8238(3)	7118(4)	727(23)
C(13)	6637(4)	7405(2)	6572(3)	615(22)
C(23)	7400(4)	7046(2)	6370(3)	507(18)
C(33)	7254(4)	6436(3)	5937(3)	577(22)
C(43)	6330(5)	6184(3)	5754(4)	860(27)
C(53)	6209(7)	5643(4)	5312(4)	1135(43)
C(63)	7003(8)	5347(4)	5041(4)	1147(43)
C(73)	7914(7)	5584(3)	5217(4)	974(33)
C(83)	8056(5)	6129(3)	5665(3)	728(23)
C(93)	6415(3)	8387(2)	7768(3)	525(18)
C(103)	6048(4)	7923(3)	8231(4)	805(26)
C(113)	5638(5)	8085(4)	8923(4)	1007(32)
C(123)	5584(5)	8685(4)	9155(4)	938(34)
C(133)	5953(4)	9156(3)	8715(4)	847(27)
C(143)	6371(4)	9000(3)	8020(3)	635(23)
C(153)	6211(4)	8633(3)	6100(3)	595(20)
C(163)	6434(4)	8556(3)	5321(3)	772(25)
C(173)	5890(5)	8832(4)	4707(4)	959(30)
C(183)	5096(6)	9186(4)	4864(5)	1152(39)
C(193)	4852(5)	9275(4)	5627(5)	1153(37)
C(203)	5399(4)	8997(3)	6242(4)	835(27)

[a] Equivalent Isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

[CoBr$_2${Ph$_2$PCH$_2$C(O)Ph}$_2$] (2). **1a** (0.333 g, 0.45 mmol) and NaBr (0.93 g, 9.0 mmol) were stirred in dichloromethane (25 mL). Over *ca.* 1 d the solution changed from blue to deep green. After a further 3 d the solution was filtered and the solvent subsequently removed in vacuo to yield **2** as a deep green solid (0.32 g, 85%): mp 109–110 °C; IR (KBr) ν(CO) 1669 s cm^{-1}; IR (Nujol) ν(CO) 1666 s cm^{-1}; magnetic moment μ_{eff} = 4.4 μ_B; UV–vis (CH$_2$Cl$_2$) 685 (ϵ 320), 655 (340), 610 sh nm. Anal. Calcd for C$_{40}$H$_{34}$Br$_2$CoO$_2$P$_2$ (*M* = 827.4): C, 58.1; H, 4.1. Found: C, 58.4; H, 4.0.

[CoI$_2${Ph$_2$PCH$_2$C(O)Ph}$_2$] (3). This complex was prepared by a route analogous to that of **2**, using **1a** (0.228 g, 0.31 mmol) and NaI (0.139 g, 0.93 mmol) in dichloromethane (25 mL). The reaction mixture was stirred for 4 d to produce a green-brown solution. **3** was isolated as a brown solid on filtration and removal of solvent in vacuo (0.22 g, 76%): mp 121 °C; IR (KBr) ν(CO) 1668 s cm^{-1}; IR (Nujol) ν(CO) 1669 s cm^{-1}; magnetic moment μ_{eff} = 4.5 μ_B; UV–vis (CH$_2$Cl$_2$) 760 (ϵ 370), 721 (640), 687 (620), 643 (385) nm. Anal. Calcd for C$_{40}$H$_{34}$CoI$_2$O$_2$P$_2$ (*M* = 921.4): C, 52.1; H, 3.7. Found: C, 52.3; H, 3.8.

[Co(μ-Cl){Ph$_2$PCH⋯C(⋯O)Ph}{Ph$_2$PCH$_2$C(O)Ph}]$_2$ (4a). **1a** (0.329 g, 0.45 mmol) was dissolved in methanol (10 mL) to give a red-brown solution. A 0.77-mL volume (0.45 mmol) of NaOMe in methanol (0.58 M solution) was added against a flow of nitrogen to immediately precipitate a pale brown solid. It was filtered out, and a second crop of solid was obtained on cooling to –20 °C (combined yield 0.266 g). Addition of excess base does not result in the precipitation of further material or the deprotonation of a second phosphine moiety. X-ray powder studies confirmed the presence of NaCl, suggesting that the solid isolated was a mixture of **4a** and NaCl (mp 240 °C): IR (KBr) ν(CO) 1672 m, 1512 s, 1484 s cm^{-1}; FIR (polyethene) ν(Co–Cl) 231 m, 221 m cm^{-1}.

[Co(μ-Cl){Ph$_2$PCH⋯C(⋯O)(η^5-C$_5$H$_4$)Fe(η^5-C$_5$H$_5$)}{Ph$_2$PCH$_2$C(O)(η^5-C$_5$H$_4$)Fe(η^5-C$_5$H$_5$)}]$_2$ (4b). **1b** (0.24 g, 0.25 mmol) was dissolved in methanol (10 mL) to give a red-brown solution. A 0.44-mL volume (0.25 mmol) of NaOMe in methanol (0.58 M solution) was added against a flow of nitrogen to immediately precipitate an orange solid (yield 0.160 g). X-ray powder studies confirmed the presence of NaCl, suggesting that the product isolated was a mixture of **4b** and NaCl: mp dec >300 °C; IR (KBr) ν(CO) 1645 m, 1506 s, 1480 s cm^{-1}; FIR (polyethene) ν(Co–Cl) 231 m, 223 m cm^{-1}.

***fac*-[Co{Ph$_2$PCH⋯C(⋯O)Ph}$_3$] (5a).** **1a** (0.120 g, 0.16 mmol) was slurried in 25 mL of toluene. NaOMe (0.36 mL) was added from a 0.47 M MeOH solution to immediately afford a deep red solution. After 0.5 h the solution was concentrated to 5 mL and filtered. **5a** was precipitated by slow pentane diffusion along with free L^1. The flocculent free ligand was removed as a pentane suspension to give **5a** (0.048 g, 44% with respect to L^1): mp 257 °C; IR (KBr) ν(CO) 1521, 1486 s cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.73–7.03 (m, 45 H, aromatic), 4.75 (s, 3H, CH); ^{13}P{^{1}H} NMR (CDCl$_3$/CH$_2$Cl$_2$) δ 27.1 (s); UV–vis (CH$_2$Cl$_2$) 550 sh nm; FAB mass spectrum *m/e* 969.2 (80%, M + 1), 666.1 (60% M + 1 – L^1). Anal. Calcd for C$_{60}$H$_{48}$CoO$_3$P$_3$ (*M* = 968.9): C, 74.4; H, 5.0. Found: C, 73.5; H, 5.1.

***fac*-[Co{Ph$_2$PCH⋯C(⋯O)(η^5-C$_5$H$_4$)Fe(η^5-C$_5$H$_5$)}$_3$] (5b).** **1b** (0.240 g, 0.25 mmol) was slurried in 10 mL of methanol. NaOMe (0.44 mL) was added from a 0.58 M MeOH solution to immediately afford an orange precipitate of **4b**. Extraction with toluene (10 mL) produced a red solution, which on slow pentane diffusion precipitated free L^2. The remaining solution was evaporated to dryness and consisted of **5b** along with traces of L^2 (0.085 g, 44% with respect to L^2): mp 62 °C, IR (KBr) ν(CO) 1503 s, 1453 s cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.82–6.95 (m, 30 H, aromatic), 4.78 and 4.50 (two t, AA′BB′ spin system, 12 H, 3C$_5$H$_4$), 4.21 (s, 3 H, 3CH), 4.16 (s, 15 H, 3C$_5$H$_5$); ^{31}P{^{1}H} (CDCl$_3$/CH$_2$Cl$_2$) δ 31.9 (s); FAB mass spectrum *m/e* 1293 (70% M), 882 (90%, M + 1 – L^2). Anal. Calcd for C$_{72}$H$_{60}$CoFe$_3$O$_3$P$_3$ (*M* = 1292.7): C, 66.9; H, 4.7. Found: C, 67.3; H, 4.9.

***mer*-[Co{Ph$_2$PCH⋯C(⋯O)Ph}$_3$] (6a).** **1a** (0.721 g, 1.00 mmol) was slurried in 25 mL of methanol to give a pale brown solution. Addition of 2.0 mmol of NaOMe (0.50 M MeOH solution) produced an immediate pale brown precipitate of **4a**. Removal of MeOH afforded a pale brown solid. Extraction with hot toluene (>100 °C) instantly gave a red solution. Concentration, filtration, and slow pentane diffusion yielded **5a** and **6a** in a 1:2 ratio along with L^1 (yield 0.310 g, 49%, with respect to L^1). **5a** and **6a** were separated from the ligand by washing with pentane after which **6a** was purified by repeated recrystallization from toluene/pentane: mp 268 °C; IR (KBr) ν(CO) 1521 s, 1517 s, 1507 s, 1483 s, 1479 s, 1473 s cm^{-1}; ^{1}H NMR (CDCl$_3$) (200 MHz) δ 7.99–6.74 (m, 45 H, aromatic), 5.23 (s, 1 H, CH), 4.91 (s, 1 H, CH), 4.85 (s, 1 H, CH); ^{1}H NMR (CDCl$_3$) (400 MHz) δ 7.95–6.67 (m, 45 H, aromatic), 5.22 (s, 1 H, CH), 4.89 (s, 1 H, CH), 4.83 (s, 1 H, CH); ^{31}P{^{1}H} NMR

($CDCl_3/CH_2Cl_2$) (303 K) δ 36 and 17 (br); $^{31}P\{^1H\}$ NMR ($CDCl_3/CH_2Cl_2$) (233 K) ABX pattern with δ 38.5 (dd, 1 P, $^2J(PP)$ = 60 and 310 Hz), 34.3 (dd, 1 P, $^2J(PP)$ = 60 and 310 Hz), 18.0 (apparent t, 1 P, $^2J(PP)$ = 60 Hz); UV–vis (CH_2Cl_2) 570 sh nm; FAB mass spectrum *m/e* 969.3 (100% M + 1), 666.2 (80%, M + 1 – L^1). Anal. Calcd for $C_{60}H_{48}CoO_3P_3$ (*M* = 968.9): C, 74.4; H, 5.0. Found: C, 74.1; H, 5.0.

C. X-ray Crystal Structure Determinations of *fac*-[$Co\{Ph_2PCH\cdots C(\cdots O)Ph\}_3$]·$C_7H_8$ (5a) and *mer*-[$Co\{Ph_2PCH\cdots C(\cdots O)Ph\}_3$] (6a).

The crystallographic data for both compounds are summarized in Table II. Data were collected at room temperature on a Siemens AED (**5a**) and Enraf-Nonius CAD-4 (**6a**) single-crystal diffractometer using the niobium-filtered (**5a**) and graphite-monochromated (**6a**) Mo Kα radiation. All reflections with θ in the range 3–24° (**5a**) and 3–23° (**6a**) were measured; of 8553 (**5a**) and 6727 (**6a**) independent reflections, 3110 (**5a**), having $I > 2\sigma(I)$ and 3215 (**6a**), having $I > 3\sigma(I)$, were considered observed and used in the analysis. No absorption correction was applied. Only the observed reflections were used in the structure solution and refinement.

The structures were solved by Patterson and Fourier methods. A toluene molecule of solvation was found in the ΔF map of **5a**. The refinements were carried out by blocked-matrix least-squares calculations first with isotropic and then with anisotropic thermal parameters in the last cycles for all the non-hydrogen atoms (except the carbon atoms of the solvent in **5a**). All hydrogen atoms (except those of the solvent molecule) were placed at their geometrically calculated positions and refined "riding" on the corresponding carbon atoms. In all stages of both refinements unit weights were used. The atomic scattering factors, corrected for the real and imaginary parts of anomalous dispersion, were taken from ref 28. All calculations were carried out on the CRAY X-MP/12 computer of the "Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale" (CINECA, Casalecchio Bologna) and on the Gould Powernode 6040 of the "Centro di Studio per la Strutturistica Diffrattometrica" del CNR, Parma, Italy, using the SHELX-76 and SHELXS-86 systems of crystallographic computer programs.[29] The final atomic coordinates for the non-hydrogen atoms are given in Tables III (**5a**) and IV (**6a**).

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Supplementary Material Available: Crystallographic data, coordinates for hydrogen atoms, thermal parameters for the non-hydrogen atoms, and complete bond distances and angles for **5a** and **6a** (Tables S-I–S-VII (11 pages). Ordering information is given on any current masthead page.

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(27) Braunstein, P.; Gomes Carneiro, T. M.; Matt, D.; Balegroune, F.; Grandjean, D. *J. Organomet. Chem.* **1989**, *367*, 117.

(28) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.

(29) Sheldrick, G. M. SHELX-76 Program for crystal structure determination. University of Cambridge, England, 1976. Sheldrick, G. M. SHELXS-86 Program for the solution of crystal structures. University of Göttingen, 1986.

(30) Note added in proof: The isolation of cobalt(III) enolates from cobalt(II) phosphine complexes is especially notable in view of the related cobalt(II) phenoxide system derived from tris(2,4,6-trimethoxyphenyl)phosphine. Its reaction with $[Rh(COD)(THF)_2]^+/Ag^+$ results in oxidation of Co(II) to Co(III). See: Dunbar, K. R.; Quillevéré, A. *Organometallics* **1993**, *12*, 618.