Journal of Organometallic Chemistry, 372 (1989) 141–150
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 09957

Reductive carbonylation of cobalt(II) in the presence of diphenylphosphine: synthesis and structure of (PPN)[Co(CO)$_3$(PPh$_2$OMe)] and MeCOCo(CO)$_2$(PPh$_2$H)(PPh$_2$OMe)

Sándor Vastag, László Markó,

Institute of Organic Chemistry, Veszprém University, H-8200 Veszprém (Hungary)

and Arnold L. Rheingold

Department of Chemistry, University of Delaware, Newark, DE 19716 (U.S.A.)

(Received November 28th, 1988)

Abstract

Cobalt(II) is reduced to Co(–I) by PPh$_2$H in the presence of CO in MeOH solution containing NaOMe; the complex (PPN)[Co(CO)$_3$(PPh$_2$OMe)] (**1**) was isolated from the reaction product in 12% yield. Alkylation of the cobaltate anion with MeI gave after addition of PPh$_2$H the disubstituted acylcobalt carbonyl complex MeCOCo(CO)$_2$(PPh$_2$H)(PPh$_2$OMe) (**2**). The crystal structures of both complexes were determined: **1** monoclinic, $P2_1/n$, a 10.748(3), b 13.255(2), c 32.123(8) Å, β 93.15(2)°, V 4569(2) Å^3, $Z = 4$, R(F) 0.048. **2** monoclinic, $P2_1/n$, a 14.440(5), b 16.768(6), c 11.526(3) Å, β 102.27(3)°, V 2727(2) Å^3, $Z = 4$, R(F) 0.068. The anion of **1** contains a tetrahedral Co coordination geometry and **2** a trigonal bipyramidal geometry with the PPh$_2$OMe and MeCO groups occupying axial positions.

Introduction

Reductive carbonylation of Co^{II} salts has been successfully applied for the synthesis of a wide variety of Co^{I}, Co^{0}, and Co^{-I} carbonyl complexes under mild conditions. In some cases the low-valent Co species is formed in a disproportionation reaction which also produces Co^{III} [1–4], but in most systems a reductant is needed. This can be a reactant like carbon monoxide which, in the presence of a base, is oxidized to carbonate [1,5,6], alcohol (which is oxidized to the corresponding carbonyl compound) [7,8], or a phosphine for which the oxidation product usually cannot be satisfactorily identified [9–11]. Frequently, additional reducing agents are used: dithionite [12,13], Et_3Al [14], $NaBH_4$ [15–17] or NaH [18] (no reductant was specified in one case [19]).

In continuation of our earlier investigations [8] we now report a reductive carbonylation of Co^{II} in which the secondary phosphine PPh_2H serves as the reducing agent and where the oxidized phosphorus-containing species can be characterized as PPh_2OMe, $OPPh_2H$, and $OPPh_2OMe$.

Results and discussion

As reported earlier [8], if a solution of NaOMe in methanol is added dropwise under CO to a methanol solution of $CoCl_2 \cdot 6H_2O$ and PPh_2H ($Co/P/MeO^- = 1/2/2$) the binuclear complex $Co_2(\mu\text{-}PPh_2)_2(CO)_4(PPh_2H)_2$ (**3**) is formed. It has now been found that if the order of addition is reversed, i.e., the methanol solution of $CoCl_2 \cdot 6H_2O + PPh_2H$ is added dropwise under CO to the methanol solution of NaOMe and the concentration of NaOMe is increased ($Co/P/MeO^- = 1/2/4$), an anionic cobalt carbonyl complex is formed which could be isolated from the reaction mixture in the form of its PPN salt. After recrystallization of the crude product from a MeCN/EtOH solvent mixture, the pale yellow crystals were identified by elemental analysis, IR spectroscopy and a crystal structure determination as $(PPN)[Co(CO)_3(PPh_2OMe)]$ (**1**). This is the first structurally characterized example of a substituted tetracarbonylcobaltate anion. The structure of the anion of **1** is shown in Fig. 1.

To our knowledge, the transformation of PPh_2H into PPh_2OMe is an unprecedented reaction. As it produces two reduction equivalents per mole of phosphine the stoichiometry of the formation of the $[Co(CO)_3(PPh_2OMe)]^-$ anion can be formally represented by eq. 1.

$$Co^{2+} + 1.5PPh_2H + 3MeO^- + 3CO \rightarrow [Co(CO)_3(PPh_2OMe)]^- + 1.5MeOH + 0.5PPh_2OMe \quad (1)$$

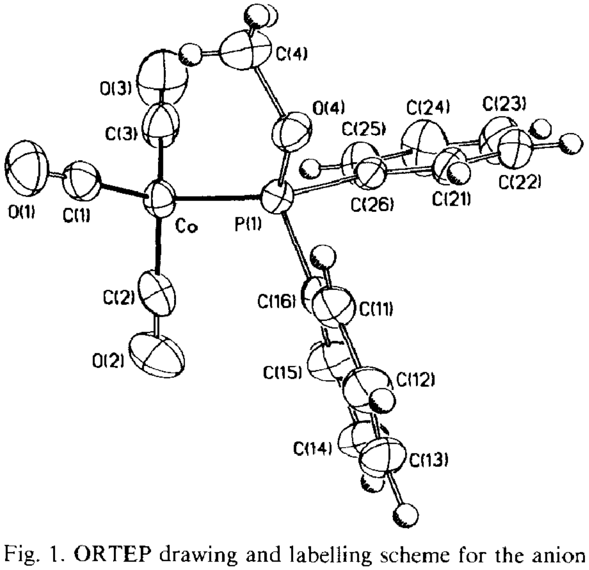
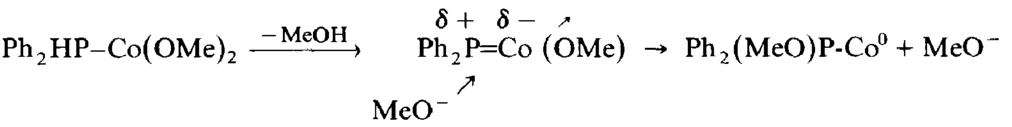


Fig. 1. ORTEP drawing and labelling scheme for the anion of **1** with 40% thermal ellipsoids.

Experiments using the molar ratios defined by eq. 1 gave, however, lower yields of **1** obviously due to possible side reactions. To get some information about the mechanism of formation of the $Co(CO)_3(PPh_2OMe)^-$ anion, some additional experiments were carried out. First it was found that PPh_2H does not react with NaOMe in methanol solution to give PPh_2OMe. Therefore, the new ligand has to be formed within the coordination sphere of the metal. In a second test it was clarified that complex **3**, which is formed in the same system under somewhat different conditions [8], is not an intermediate of the process since it does not react with NaOMe in methanol under CO to give $Co(CO)_3(PPh_2OMe)^-$. This proves that the PPh_2OMe ligand is not formed by a nucleophilic attack of MeO^- at a diphenylphosphido bridge.

Performing an experiment under conditions identical with those used in the preparation of **1**, but under Ar instead of CO and analysing the reaction product by GLC and mass spectroscopy, $OPPh_2H$ and $OPPh_2OMe$ were detected as volatile components. The composition of the (volatile) organic part of the reaction mixture did not change after treatment with CO, but the IR spectrum showed the expected formation of the $Co(CO)_3(PPh_2OMe)^-$ anion. These results support two conclusions. First, that PPh_2OMe is formed from PPh_2H within the coordination sphere of Co and remains bonded to the metal; a somewhat speculative mechanism for this



$$Ph_2HP\text{-}Co(OMe)_2 \xrightarrow{-MeOH} \underset{MeO^- \nearrow}{\overset{\delta+\;\;\delta-\;\nearrow}{Ph_2P{=}Co\,(OMe)}} \rightarrow Ph_2(MeO)P\text{-}Co^0 + MeO^- \qquad (2)$$

is suggested in eq. 2. Second, that the reduction of Co^{2+} to Co^{-1} is not accomplished at the cost of PPh_2OMe formation alone, but also via the more usual formation of phosphine oxides (both from PPh_2H and PPh_2OMe). Water, introduced into the system in the form of $CoCl_2 \cdot 6H_2O$, presumably plays a role in these latter redox processes [20] as shown in eq. 3:

$$R_3P + H_2O + Co^{2+} \rightarrow R_3PO + 2H^+ + Co^0 \qquad (3)$$

In order to search for other well characterized derivatives of the primary anionic product obtained by reductive carbonylation, the crude reaction product was treated with $HgCl_2$ and MeI. Changes in the IR spectra suggested that in the first case a complex of type $Hg[Co(CO)_3L]_2$ was formed [21], but this complex could not be isolated in pure form. We were more successful with the reaction between MeI and the cobaltate anion. Although the first reaction product was an oil and could, once again, only be identified through its IR spectrum as an alkyl complex of type $RCo(CO)_3L$ [22], it could be transformed in a second step by the addition of PPh_2H into a disubstituted acylcobalt carbonyl which was isolated in the form of pale yellow crystals and characterized by elemental analysis, IR spectroscopy and a crystal structure determination as $MeCOCo(CO)_2(PPh_2H)(PPh_2OMe)$ (**2**). Complex **2** is the first example for the structure of a disubstituted acylcobalt carbonyl derivative. The structure of complex **2** is shown in Fig. 2.

The coordination geometry at the Co atom in **1** is tetrahedral with an average angle at the Co cluster of 109.4°. The Co–P(1) bond length of 2.127(2) Å is unusually short: the equivalent bond in **2** is 2.208(3) Å which may be regarded as a

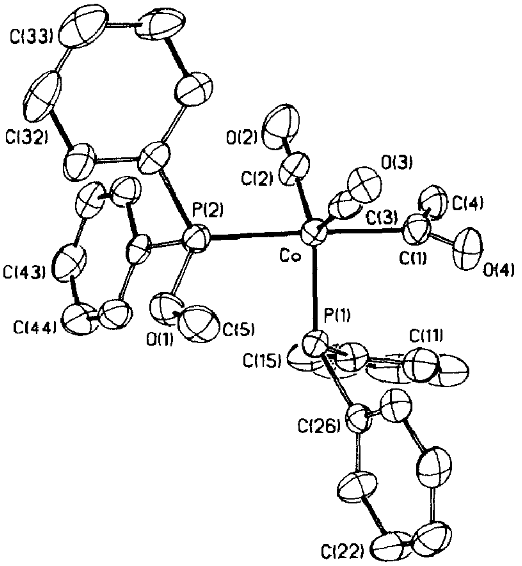


Fig. 2. ORTEP drawing and labelling scheme for **2** with 40% thermal ellipsoids.

"normal" Co–PR_3 distance. The shortness of this bond may reflect a considerable transfer of negative charge to the phosphine. In **2**, the coordination geometry at the Co atom is trigonal bipyramidal with axial PPh_2OMe and COMe groups. The P(2)–Co–C(3) angle is 178.1(3)° and the equatorial angles are all near 120°. We were unable to crystallographically locate the hydrogen atom of the secondary phosphine, but its presence is clearly indicated by the C(16)–P(1)–C(26) bond angle of 101.1(3)°.

Experimental

General procedures

Diphenylphosphine was prepared from PPh_3 by the method of ref. 23. If not under CO, reactions were conducted under a prepurified Ar atmosphere. IR spectra were recorded on a Carl Zeiss IR 75 spectrophotometer, liquid samples were analyzed with a Hewlett–Packard 5830A gas chromatograph and a JEOL IMS(01) SG-2GC-MS instrument.

Preparation of $(PPN)[Co(CO)_3(PPh_2OMe)]$ (1)

NaOMe (0.432 g, 8 mmol) was dissolved under CO in methanol (10 ml) in a 50-ml two-necked flask equipped with a magnetic stirrer. To this was added dropwise over a period of 1.5 h PPh_2H (740 μl, 4 mmol) and $CoCl_2 \cdot 6H_2O$ (476 mg, 2 mmol) dissolved in methanol (10 ml). During the addition, absorption of CO (25–30 ml) was observed and measured with a gas buret. After CO absorption stopped, methanol was removed in vacuo and the residue dissolved in MeCN (10 ml). Following the addition of PPN^+Cl^- (1146 mg, 2 mmol) the reaction mixture was filtered to remove NaCl, the filtrate was evaporated to dryness in vacuo and the residue dissolved in ethanol (10 ml). The clear solution was cooled to −18°C, the mother liquor removed by a syringe and the solid precipitate washed with benzene.

Recrystallization from MeCN/EtOH (1/10) gave light yellow crystals of complex **1**, yield 206 mg (0.23 mmol, 11.5% based on Co). Analysis. Found: C, 68.4; H, 4.9; Co, 6.7; N, 1.4; P, 10.4. $C_{52}H_{43}CoNO_4P_3$ calcd.: C, 69.57; H, 4.79; Co, 6.57; N, 1.56; P, 10.36%. IR spectrum (ν(CO)) in MeCN: 1934m, 1847s cm^{-1}.

Preparation of $MeCOCo(CO)_2(PPh_2H)(PPh_2OMe)$ (2)

Complex **1** (206 mg, 0.23 mmol) was dissolved under Ar in absolute THF (10 ml) in a Schlenk tube and MeI (14.3 μl, 0.23 mmol) was added with a syringe. The white, shiny precipitate that formed was filtered off after 1 h. The filtrate was evaporated to dryness in vacuo and the residue dissolved in hexane (10 ml) (IR bands in the ν(CO) region: 2042w, 1970s, 1966s, and 1935vw cm^{-1}). On adding PPh_2H (50 μl, 0.29 mmol) to the hexane solution, the ν(CO) bands shifted to 1982m and 1927s cm^{-1}, and a new (organic carbonyl) band appeared at 1658w cm^{-1}. After completion of the reaction, the solution was cooled to $-18°C$ overnight. Light yellow crystals of complex **2** deposited, yield 45 mg (0.08 mmol, 35%). Analysis. Found: C, 60.8; H, 4.7; Co, 10.9; P, 10.3. $C_{29}H_{27}CoO_4P_2$ calcd.: C, 62.15; H, 4.82; Co 10.52; P, 11.06%.

Table 1

Crystallographic data for **1** and **2**

	1	**2**
formula	$C_{52}H_{43}NO_4P_3Co$	$C_{28}H_{26}O_4P_2Co$
crystal system	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$
a (Å)	10.748(3)	14.440(5)
b (Å)	13.255(2)	16.768(6)
c (Å)	32.123(8)	11.526(3)
β (deg)	93.15(2)	102.27(3)
V (Å^3)	4569(2)	2727(2)
Z	4	4
D_x (g cm^{-3})	1.305	1.333
μ(Mo-K_α, cm^{-1})	5.21	7.73
T (K)	293	292
color	yellow	yellow
size (mm)	0.36 × 0.37 × 0.40	0.26 × 0.29 × 0.36
scan method	Wyckoff	$\theta/2\theta$
scan limits (deg)	4–45	4–50
reflections collected	6422	4648
independent reflections	5975	4086
observed reflections ($\geq 5\sigma F_0$)	3658	2430
R(int)	0.031	0.039
$R(F)$	0.048	0.068
$R(wF)$	0.051	0.071
GOF	1.218	1.937
Δ/σ (final)	0.096	0.073
$\Delta(\rho)$ (e Å^{-3})	0.29	1.01
N_0/N_v	7.85	8.41

Identification of PPh_2H oxidation products

The procedure described for the preparation of **1** was used with the difference that the reaction was performed under Ar. The MeCN solution obtained (10 ml) was analyzed by gas chromatography and GC-MS, and the two main components (ratio 5/1) of the product were identified as $OPPh_2OMe$ (m/e = 232 (parent ion), 202, 199, 155, 139, 109, 77) and $OPPh_2H$ (m/e = 202 (parent ion), 201, 124, 77). Following this the solution was treated with CO which resulted in the formation of the $Co(CO)_3(PPh_2OMe)^-$ anion (IR control). The composition of the organic phase did not change under this treatment as shown by a repeated analysis by gas chromatography.

Table 2

Atomic coordinates ($\times 10^4$) and isotropic thermal parameters (Å $\times 10^3$) for **1**

	x	y	z	U [a]
Co	3002.9(8)	1394.6(7)	2230(1)	39.8(4)
P(1)	2144(2)	567(1)	952(2)	41.1(8)
P(2)	2653(2)	752(1)	3753(2)	42.7(9)
O(1)	2764(4)	−211(4)	3785(5)	54(3)
O(2)	2118(7)	2824(5)	2908(7)	99(4)
O(3)	5059(6)	1151(6)	3082(7)	43(3)
O(4)	3917(5)	1731(4)	343(6)	69(3)
C(1)	3304(6)	1941(6)	828(7)	49(4)
C(2)	2451(7)	2250(7)	2607(8)	56(4)
C(3)	4312(10)	1225(5)	2738(7)	61(4)
C(4)	2741(7)	2665(6)	307(8)	62(4)
C(5)	3669(7)	−557(6)	3757(10)	66(4)
C(11)	1615(5)	1237(4)	−1308(6)	70(5)
C(12)	986	1612	−2233	102(6)
C(13)	52	1751	−2139	138(8)
C(14)	−252	1516	−1120	113(7)
C(15)	378	1142	−195	76(5)
C(16)	1312	1002	−289	50(4)
C(21)	2124(3)	−724(4)	−593(6)	65(4)
C(22)	2544	−1304	−1180	79(5)
C(23)	3529	−1365	−970	66(4)
C(24)	4094	−847	−174	61(4)
C(25)	3674	−267	414	47(3)
C(26)	2689	−205	204	41(3)
C(31)	3260(5)	572(4)	6203(6)	67(5)
C(32)	3752	798	7331	84(6)
C(33)	4287	1497	7478	88(6)
C(34)	4331	1971	6497	82(5)
C(35)	3840	1745	5368	69(5)
C(36)	3304	1046	5221	48(4)
C(41)	1124(4)	1524(3)	4341(5)	57(4)
C(42)	170	1622	4369	64(4)
C(43)	−479	1018	3947	78(5)
C(44)	−174	316	3497	74(5)
C(45)	781	218	3469	62(4)
C(46)	1430	822	3891	44(3)

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

Table 3

Atomic coordinates ($\times 10^4$) and isotropic thermal parameters ($Å^2 \times 10^3$) for **2**

	x	y	z	U^{a}
Co	7782.5(7)	6945.7(4)	1294.0(2)	50.2(3)
P(1)	7902(1)	8477(1)	1490.6(4)	43.6(5)
P(2)	3496(1)	1810(1)	1201.5(4)	41.9(5)
P(3)	1278(1)	3170(1)	1154.8(4)	41.4(5)
O(1)	6736(4)	5920(3)	1993(1)	91(2)
O(2)	10337(4)	6410(4)	1160(1)	109(2)
O(3)	6170(6)	6832(4)	542(2)	140(3)
N	2106(4)	2192(3)	1176(1)	48(2)
O(4)	6841(3)	8927(3)	1792(1)	58(1)
C(1)	7158(5)	6320(4)	1710(2)	60(2)
C(2)	9300(6)	6610(4)	1210(2)	68(2)
C(3)	6811(7)	6875(5)	847(2)	80(3)
C(4)	5608(7)	8555(8)	1746(3)	77(3)
C(11)	9177(3)	9214(3)	2224(1)	58(2)
C(12)	10249	9514	2456	74(3)
C(13)	11406	9470	2279	73(3)
C(14)	11490	9125	1872	74(3)
C(15)	10418	8825	1640	69(2)
C(16)	9261	8870	1816	44(2)
C(21)	7933(4)	10495(3)	1228(1)	62(2)
C(22)	7949	11262	931	82(3)
C(23)	7969	11021	508	98(4)
C(24)	7972	10013	383	105(4)
C(25)	7956	9246	680	71(3)
C(26)	7936	9487	1102	46(2)
C(31)	5206(3)	1144(3)	1815(1)	68(2)
C(32)	5673	1028	2226	82(3)
C(33)	4994	1384	2553	73(3)
C(34)	3848	1856	2470	73(3)
C(35)	3380	1972	2059	59(2)
C(36)	4060	1616	1731	45(2)
C(41)	4596(3)	256(3)	767(1)	65(2)
C(42)	4596	−698	584	83(3)
C(43)	3511	−1278	564	85(3)
C(44)	2427	−904	727	81(3)
C(45)	2427	50	910	61(2)
C(46)	3512	630	931	46(2)
C(51)	4553(3)	2739(3)	542(1)	63(2)
C(52)	5276	3475	361	82(3)
C(53)	6013	4122	613	82(3)
C(54)	6025	4032	1046	72(3)
C(55)	5301	3295	1227	59(2)
C(56)	4565	2649	974	44(2)
C(61)	66(3)	2180(2)	1762(1)	51(2)
C(62)	−790	2083	2071	63(2)
C(63)	−1524	2904	2174	67(2)
C(64)	−1402	3823	1968	71(3)
C(65)	−546	3920	1659	58(2)
C(66)	188	3099	1556	40(2)
C(71)	−429(3)	4002(3)	576(1)	67(2)
C(72)	−1011	4092	178	76(3)
C(73)	−721	3418	−136	78(3)
C(74)	151	2655	−52	94(3)
C(75)	733	2565	345	73(3)
C(76)	443	3239	659	45(2)

Table 3 (continued)

	x	y	z	U [a]
C(81)	2623(4)	4748(3)	850(1)	57(2)
C(82)	3377	5604	885	73(3)
C(83)	3637	6045	1274	79(3)
C(84)	3142	5631	1628	80(3)
C(85)	2388	4776	1593	63(2)
C(86)	2129	4334	1204	46(2)

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

Crystal structure determinations

Crystallographic data are collected in Table 1. Crystals of both **1** and **2** were found to diffract only moderately well with limited high-angle data available. The space groups were uniquely defined by the systematic absences. Data were collected at ambient temperatures using a Nicolet R3m diffractometer with Mo-K_α radiation (λ 0.71073 Å) and monochromatized by a graphite crystal. Corrections for a linear decay in reflection intensities (5% for **1** and 3% for **2**), but none for absorption (low coefficients and uniform crystal dimensions) were applied to the data.

The structure of **1** was solved from a Patterson synthesis and **2** by direct methods. The hydrogen atom bonded to P(1) in **2** could not be located and was ignored. The remaining hydrogen atoms in both structures were treated as idealized isotropic contributions (d(C–H) 0.95 Å). All non-hydrogen atoms were anisotropically refined. Phenyl rings were constrained to ideal planar hexagons (d(C–C) 1.395 Å). All computations used SHELXTL (5.1) software (G. Sheldrick, Nicolet XRD, Madison, WI, U.S.A.). Atomic coordinates for **1** and **2** are given in Tables 2 and 3,

Table 4

Selected bond distances and angles for **1**

Bond distances (Å)			
Co–P(1)	2.127(2)	O(1)–C(1)	1.166(7)
Co–C(1)	1.738(6)	O(2)–C(2)	1.166(8)
Co–C(2)	1.726(6)	O(3)–C(3)	1.168(9)
Co–C(3)	1.731(7)	O(4)–C(4)	1.414(9)
P(1)–O(4)	1.648(4)	P(2)–N	1.575(4)
P(1)–C(16)	1.825(4)	P(3)–N	1.571(4)
P(1)–C(26)	1.832(4)		
Bond angles (deg)			
P(1)–Co–C(1)	104.3(2)	Co–P(1)–O(4)	119.2(1)
P(1)–Co–C(2)	104.5(2)	Co–P(1)–C(16)	118.4(1)
P(1)–Co–C(3)	108.8(2)	Co–P(1)–C(26)	119.9(1)
C(1)–Co–C(2)	113.9(3)	O(4)–P(1)–C(16)	96.8(2)
C(1)–Co–C(3)	111.8(3)	O(4)–P(1)–C(26)	100.1(2)
C(2)–Co–C(3)	112.9(3)	C(16)–P(1)–C(26)	97.8(2)
Co–C(1)–O(1)	178.5(5)	P(1)–O(4)–C(4)	119.1(5)
Co–C(2)–O(2)	178.0(5)	P(2)–N–P(3)	143.2(3)
Co–C(3)–O(3)	179.0(7)		

Table 5

Selected bond distances and angles for **2**

Bond distances (Å)			
Co–P(1)	2.204(2)	C(3)–O(3)	1.1075(15)
Co–P(2)	2.208(3)	P(1)–C(16)	1.814(7)
Co–C(1)	1.985(9)	P(1)–C(26)	1.824(7)
Co–C(2)	1.739(11)	P(2)–C(36)	1.820(7)
Co–C(3)	1.878(13)	P(2)–C(46)	1.811(7)
C(1)–O(4)	1.196(12)	P(2)–O(1)	1.624(6)
C(1)–C(4)	1.513(13)	O(1)–C(5)	1.436(12)
C(2)–O(2)	1.163(14)		
Bond angles (deg)			
P(1)–Co–P(2)	91.9(1)	Co–C(2)–O(2)	176.9(9)
P(1)–Co–C(1)	86.3(3)	Co–C(3)–O(3)	176.2(9)
P(1)–Co–C(2)	117.6(3)	Co–P(1)–C(16)	117.3(3)
P(1)–Co–C(3)	120.0(3)	Co–P(1)–C(26)	121.7(2)
P(2)–Co–C(1)	178.1(3)	Co–P(2)–O(1)	117.7(3)
P(2)–Co–C(2)	90.5(4)	Co–P(2)–C(36)	116.5(3)
P(3)–Co–C(3)	93.6(3)	Co–P(2)–C(46)	115.5(2)
C(1)–Co–C(2)	90.8(4)	O(4)–C(1)–C(4)	116.1(9)
C(1)–Co–C(3)	86.8(4)	C(16)–P(1)–C(26)	101.1(3)
C(2)–Co–C(3)	122.1(4)	C(36)–P(2)–C(46)	102.8(3)
Co–C(1)–O(4)	123.8(7)	P(2)–O(1)–C(5)	119.1(6)
Co–C(1)–C(4)	120.1(7)		

respectively, and selected bond distances and angles in Tables 4 and 5. Copies of the structure factor tables may be obtained from one of us (A.L.R.).

References

1 M.P. Schubert, J. Am. Chem. Soc., 55 (1933) 4563.
2 J. Halpern and M. Pribanic, J. Am. Chem. Soc., 93 (1971) 96.
3 L. Markó, G. Gervasio, P.L. Stanghellini and G. Bor, Transition Met. Chem., 10 (1985) 344.
4 L. Markó and G. Bor, J. Organomet. Chem., 3 (1965) 162.
5 A. A. Blanchard and P. Gilmont, J. Am. Chem. Soc., 62 (1940) 1192; R.J. Clark, S.E. Whiddon and R.E. Serfass, J. Organomet. Chem., 11 (1968) 637.
6 G. Albertin, E. Bordignon, A.A. Orio and G. Rizzardi, Inorg. Chem., 14 (1975) 944.
7 P. Rigo, M. Bressan and A. Morvillo, J. Organomet. Chem., 93 (1975) C34; 105 (1976) 263.
8 G.L. Geoffroy, W.C. Mercer, R.R. Whittle, L. Markó and S. Vastag, Inorg. Chem., 24 (1985) 3771.
9 G. Aklan, C. Forster, E. Hergovich, G. Speier and L. Markó, Veszprémi Vegyip. Egy. Közl., 12 (1971) 131; Chem. Abstr., 80 (1974) 77750.
10 M. Basato, M. Bressan and P. Rigo, J. Organomet. Chem., 232 (1982) 81.
11 A. Del Zotto and P. Rigo, J. Organomet. Chem., 315 (1986) 165.
12 W. Hieber and E.O. Fischer, Z. Anorg. Allg. Chem., 269 (1952) 292; W. Hieber, E.O. Fischer and E. Böckly, ibid., 269 (1952) 308.
13 G. Bor and B. Mohai, Acta Chim. Acad. Sci. Hung., 8 (1956) 335.
14 P. Szabó and L. Markó, J. Organomet. Chem., 3 (1965) 364.
15 C. Carriedo, P. Gomez-Sal, P. Royo, S. Martinez-Carrera and S. Garcia-Blanco, J. Organomet. Chem., 301 (1986) 79.
16 N. Satyanarayana and M. Periasamy, J. Organomet. Chem., 333 (1987) C33.
17 D.J. Elliot, D.G. Holah and A.N. Hughes, Inorg. Chim. Acta, 142 (1988) 195.
18 J.J. Brunet, C. Sidot and P. Caubere, J. Organomet. Chem., 204 (1981) 229.

19 M. Bressan, B. Corain, P. Rigo and A. Turco, Inorg. Chem., 9 (1970) 1733.
20 C.W. Weston, G.W. Bailey, J.H. Nelson and H.B. Jonassen, J. Inorg. Nucl. Chem., 34 (1972) 1752.
21 J. Newman and A.R. Manning, J. Chem. Soc. Dalton Trans., (1972) 241.
22 V. Galamb, G. Pályi, F. Cser, M.G. Furmanova and Y.T. Struchkov, J. Organomet. Chem., 209 (1981) 183.
23 W. Gree, R.A. Shaw and B.C. Smith, Inorg. Synth., 9 (1976) 19.