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Preparation and molecular structures of benzyl- and phenylacetylcobalt carbonyls☆

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Dedicated to: Professor László Markó (Veszprém, Hungary) on the occasion of his 70th birthday.

Abstract

The benzyl-type cobalt carbonyl complexes (*para*-^{t}BuC$_6$H$_4$CH$_2$)Co(CO)$_3$PPh$_3$ (**4**) and [*para*-ClC$_6$H$_4$CH$_2$C(O)]Co(CO)$_3$PPh$_3$ (**5**) were prepared and characterized by analyses, spectra and X-ray single-crystal diffraction. The overall structures both of the alkylcobalt-type **4** and the acylcobalt-type **5** display trigonal bipyramidal geometry, with the two noncarbonyl ligands in the two axial positions. The relevance of the stereochemistry of complexes **4** and **5** to the supposed mechanism of the CO insertion/deinsertion on cobalt is discussed. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Molecular structures; Benzylcobalt carbonyls; Phenylacetylcobalt carbonyls

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1. Introduction

Carbon–carbon bond forming processes figure prominently in transition metal-catalyzed carbonylation and in hydroformylation reactions, and are one of the main driving forces behind the explosive development of transition metalorganic chemistry in the last decades [2]. It is surprising, in this context, to note the scarcity of publications on mechanistic speculations about the C–C bond making step (the 'insertion' of CO) in reactions catalyzed by cobalt (Eq. (1)), which is one of the earliest and even nowadays a widely used catalyst for these reactions [3]:

$$\underset{\mathbf{1}}{\mathrm{RCo(CO)_4}} \underset{-\mathrm{CO}}{\overset{+\mathrm{CO}}{\rightleftharpoons}} \underset{\mathbf{2}}{\mathrm{RC(O)Co(CO)_4}} \tag{1}$$

The inventory of experimental and theoretical background behind the generally accepted mechanism of equilibrium (1) consists of:

1. Early experiments of Heck [4] and Markó [5] providing proofs for the intermediacy of alkyl- and acylcobalt tetracarbonyls **1** and **2** in carbonylations catalyzed by cobalt.
2. Kinetic studies of Markó and Ungváry [6] showing quantitative details of reaction (1), of the formation of complexes **1** and of subsequent formation of complexes **2**.
3. Preparative and spectroscopic studies of Cotton and Calderazzo [7] as well as of Flood [8] with alkyl- and acyl- manganese pentacarbonyls, suggesting the migratory character of the CO insertion into the metal–C$_{\mathrm{alkyl}}$ bond (intermediate **3**):

☆ Alkylcobalt carbonyls, Part 13 (for Part 12 see Ref. [1]).

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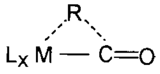


3

4. EHMO calculations of Hoffmann [9] supporting the involvement of **3** in the mechanism.
5. Preparative and isotopic studies on cobalt complexes performed by Markó, Bor et al. [10] providing proofs for
   - 5.1. the equilibrium nature of equation (1) and
   - 5.2. showing that the 'inserted' CO is one of the carbonyl ligands already coordinated to Co.
6. The recent report of Kovács, Szalontai and Ungváry [11] on the spectroscopic detection of *cis*-$MeOC(O)CH_2Co(CO)_3PPh_3$ providing the first direct evidence for the alkyl-migratory character of CO 'insertion' on Co, while all other reports indicate axial-**1** and -**2** as well as *trans*-$RCo(CO)_3PPh_3$ or $RC(O)Co(CO)_3PPh_3$ isomers [1,10b,12].

Consensus has been reached assuming [13] that in all cases, except (6), the primary (equatorial or *cis*) isomers were undergoing a fast rearrangement both in carbonylation or in decarbonylation. The complexity of the picture is shown in Scheme 1.

Prompted by the encouraging results under (5) and (6), we prepared and structurally characterized two benzyl-derived cobalt carbonyls, an alkyl-derivative: *para*-$^tBuC_6H_4CH_2Co(CO)_3PPh_3$ (**4**) and an acyl-derivative: *para*-$ClC_6H_4CH_2C(O)Co(CO)_3PPh_3$ (**5**). The results of this study are reported here.

2. Experimental

Starting materials were of commercial origin, their purity was determined by GLC, and they were distilled, if necessary, before use. Dicobalt octacarbonyl, $Co_2(CO)_8$, was made by the method of Markó et al. [14]. All operations were performed according to standard Schlenk techniques [15].

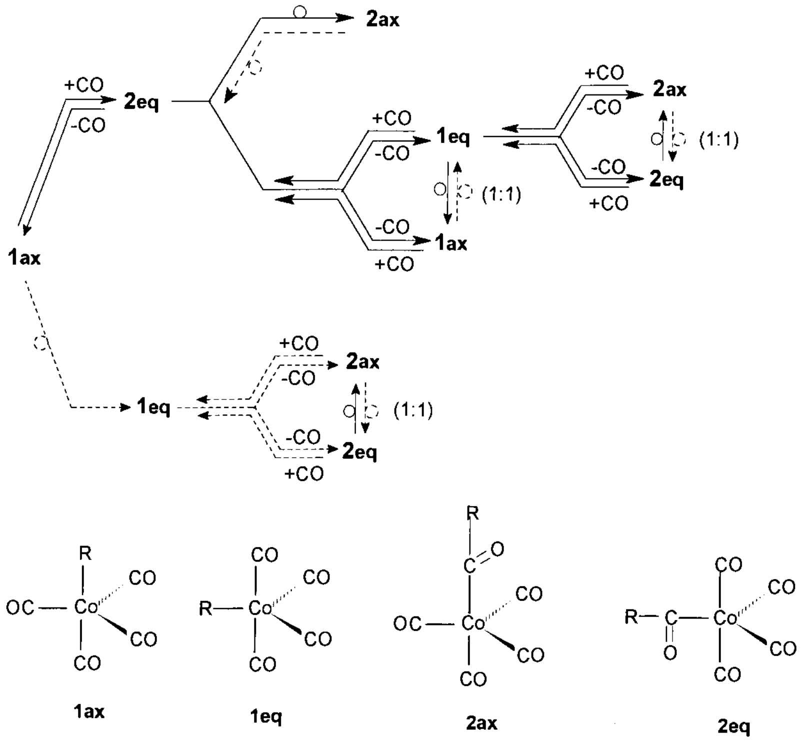
IR spectra were recorded with a Bruker FT-IR IFS113 V spectrometer, ^1H- ^{13}C- and ^{31}P-NMR experiments were performed with a Bruker AMX-400 instrument.

2.1. Preparation of benzyl- and phenylacetylcobalt tetracarbonyls

Essentially the procedures described in Refs. [10,16] were followed.

2.1.1. [*para*-$(CH_3)_3CC_6H_4CH_2$]$Co(CO)_3PPh_3$ (**4**)

$Co_2(CO)_8$ (342 mg, 1 mmol) was reduced to $Na[Co(CO)_4]$ in 20 ml of Et_2O by Na/Hg. This solution of $Na[Co(CO)_4]$ (2 mmol) was filtered into a Schlenk vessel under Ar atmosphere and then cooled to −20°C. To this cold solution, while stirred, *para*-^{t}butylbenzyl chloride (330 mg, 0.39 ml, 2 mmol) was added at once. The formation of a white precipitate (NaCl) was observed immediately. The stirring was continued for 4 h. The gradual development of a yellow and then a brown color was observed. After this period the solution was left



Scheme 1. Full arrows, experimentally proven; dotted arrows, supposed.

Table 1a
FT-IR of the intermediates and of complexes **4** and **5** [(η^3-benzyl)Co(CO)$_3$ (**a**), RCo(CO)$_4$ (**b**) and RC(O)Co(CO)$_4$ (**c**)] (*n*-hexane)

4a	1975 s, 1989 s, 2053 s
4b	2014 vs, 2031 m, 2097 m
4c	1746 m, 2043 s, 2105 m
5a	1972 s, ca. 1990 s, 2054 vs
5b	2013 vs, br, 2035 s, 2099 m
5c	1742 m, 2020 vs, br, 2107 m
4	1957 vs, 1983 s, 2049 m
5	ca. 1725 br, vw, 1964 s, 1988 s, 2051 w

to warm to room temperature (r.t.) and then stirring was continued for 1 h at r.t. A sample was taken (1 ml), and analyzed by IR spectroscopy in the 1600–2200 cm^{-1} range. The analysis showed the disappearance of the strong band of [Co(CO)$_4$]$^-$ and the appearance of a band system which corresponded to a mixture of (η^3-benzyl)Co(CO)$_3$ (**4a**), RCo(CO)$_4$ (**4b**) and RC(O)Co(CO)$_4$ (**4c**) complexes in a ratio of ca. 60:30:10% (in a separate experiment these complexes were characterized by IR, ^{1}H- and ^{13}C-NMR spectra in low-polarity solvents, see Table 1(a–c)). The solution was then filtered and to the filtrate, containing a total of ca. 2 mmol of these mononuclear cobalt complexes triphenylphosphine, P(C$_6$H$_5$)$_3$ (524 mg, 2 mmol) was added at once. Stirring was continued for an additional 3 h during which period a gradual color change from brown to yellow was observed. At this point a sample was taken and analyzed by ^{31}P-NMR spectroscopy. The two bands observed were assigned to RCo(CO)$_3$PR$_3$ (56.2 ppm) and RC(O)Co(CO)$_3$PR$_3$ (47.2 ppm) type complexes on the basis of literature analogies [11a], indicating a ca. 2:1 ratio of these products. Then stirring was continued at r.t. for 6 h during which time the spectroscopic analysis showed a gradual decarbonylation of the acyl-compound. At the end of this period the solvent was evaporated. The crude product was recrystallized from Et$_2$O with layered *n*-hexane. The yield of the analytically pure (twice recrystallized) product was 818 mg (74% as (CH$_3$)$_3$CC$_6$H$_4$CH$_2$Co(CO)$_3$PPh$_3$). This product was characterized by spectra (Table 1(a–c)), elemental analyses and single crystal X ray diffraction.

Anal. Calc. for C$_{32}$H$_{30}$CoO$_3$P: C, 69.6; H, 5.5; Co, 10.7. Found: C, 69.0; H, 5.5; Co, 10.4%.

2.1.1.1. *X-ray diffraction structure determination of complex (**4**).*

C$_{32}$H$_{30}$CoO$_3$P, crystal dimensions $0.34 \times 0.25 \times 0.18$ mm^3, measured on a Siemens SMART diffractometer with Mo–K$_\alpha$ radiation at $T = 298$ K. Data collection of 12 125 intensities ($2\theta_{\max} = 51.47°$), 8464 independent ($R_{\text{merg}} = 0.0246$), 6796 observed [$F_o \geq 4\sigma(F)$], structure solution with direct methods (Siemens-SHELXS) and refinement on F^2 (Siemens-SHELXTL 5.03) (667 parameters), the hydrogen atom positions were calculated and refined as rigid groups with the 1.2-fold (1.5 for methyl groups) U_{iso}-values of the corresponding C-atoms. $R_1 = 0.0610$, wR_2 (all data) = 0.1815, $w^{-1} = \sigma^2(F_o^2) + (0.1P)^2 + 2.47P$, where $P = [\max(F_o^2) + (2F_c^2)]/3$, maximum residual electron density 0.903 e Å^{-3}.

Drawing was performed with the ORTEP plotting program [17]. The crystal structure determination conditions are given in Table 2, final fractional coordinates and equivalent thermal parameters are shown in Table 3, while selected interatomic distances and angles are collected in Table 4. Tables showing full listings of interatomic distances and angles, anisotropic thermal parameters, final hydrogen coordinates and equivalent thermal parameters are available as supplementary material. For availability of deposited crystallographic data, see Section 4.

2.1.2. *(para-ClC$_6$H$_4$CH$_2$)COCo(CO)$_3$PPh$_3$ (**5**)*

Na[Co(CO)$_4$] (4 mmol) was prepared in 60 ml of Et$_2$O and to this solution 4-chlorobenzylchloride (612 mg, 3.8 mmol) was added under a CO atmosphere at r.t. This solution was stirred and samples were taken after each 1 h and were analyzed by IR spectroscopy. The IR ν(C=O) spectra indicated after 4 h the disappearance of the strong band of [Co(CO)$_4$]$^-$ and a band

Table 1b
^{1}H- and ^{13}C-NMR spectra of the intermediates of complexes **4** and **5** (benzene-d_6)

		C(CH$_3$)$_3$	*p*-C	*m*-CH	*o*-CH	C$_{ipso}$	CH$_2$	CO$_{\text{coord.}}$	CO$_{\text{acyl}}$
4a	^{1}H	1.13		6.23, 6.80	7.24–7.05				
	^{13}C	31.3, 31.2, 30.6, 48.6	121.9	123.4, 125.7	129.5	97.1		204.1	
4b	^{1}H	1.24		7.24–7.05			2.4		
	^{13}C					151.3			
4c	^{1}H	1.19		7.24–7.05			4.20		
	^{13}C								
5b	^{1}H			6.98	6.87		2.9		
	^{13}C		131.6	129.0	129.7	146.0	18.4	198.7	
5c	^{1}H			7.02	6.65		3.73		
	^{13}C		133.7	128.9	131.0	131.8	67.9	196.6	223.7

Table 1c
^{1}H- and ^{13}C-NMR spectra of complexes **4** and **5**[a] (benzene-d_6)

		$C(CH_3)_3$	*p*-C	*m*-CH	*o*-CH	$C_{ipso\ ar}$	CH_2	P–Ph_3	$CO_{coord.}$	CO_{acyl}
4	^{1}H	1.18		6.86–6.97 (m), 7.04–7.13 (m)			3.71 (J_{H-P} 2.46)	7.63 (7.8) 7.23 (8.25) 7.47 (11.3)		
	^{13}C	31.4, 23.1	148.2	130.5	125.8	147.1	14.3 (J_{C-P} 20.1)	133.3, 129.1 (J_{C-P} 9.88), 128.8 (J_{C-P} 11.2), 134.7 (J_{C-P} 43.9)	202.3 (J_{C-P} 23.6)	
	^{31}P							56.2		
5	^{1}H			7.17	7.32		4.23	6.92–6.98 (m), 7.44–7.48 (m)		
	^{13}C		130.9	130.4	131.5	133.9	69.8 (J_{C-P} 25.3)	133.3, 129.1 (J_{C-P} 10.04), 128.9 (J_{C-P} 10.04), 134.7 (J_{C-P} 43.9)	199.9 (J_{C-P} 22.5)	233.5 (J_{C-P} 33.3)
	^{31}P							46.8		

[a] J_{H-P} and J_{C-P} in Hz.

Table 2
Crystal data and structure refinement for complex **4**

Empirical formula	$C_{32}H_{30}CoO_3P$
Formula weight	552.46
Temperature (K)	298(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a (Å)	13.8850(3)
b (Å)	14.1339(2)
c (Å)	15.7905(3)
α (°)	101.1189(8)
β (°)	108.8935(5)
γ (°)	90.0641(7)
V (Å^3)	2870.12(9)
Z	4
$D_{calc.}$ (g cm^{-3})	1.279
Absorption coefficient (mm^{-1})	0.683
$F(000)$	1152
Crystal size (mm)	$0.34\times0.25\times0.18$
θ range for data collection (°)	1.81–25.73
Index ranges	$-8\leq h<16$, $-17\leq k\leq16$, $-14\leq l\leq19$
Reflections collected	12 125
Independent reflections	8464 [$R_{int}=0.0246$]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	8463/0/667
Goodness-of-fit on F^2	1.079
Final R indices [$I>2\sigma(I)$)	$R_1=0.0610$, $wR_2=0.1555$
R indices (all data)	$R_1=0.0764$, $wR_2=0.1816$
Largest difference peak and hole (e Å^{-3})	0.903 and -0.260

system which corresponds approximately to the mixture of 20% $RCo(CO)_4$ (**5b**) and 80% $RC(O)Co(CO)_4$ (**5c**). Then, to the reaction mixture, PPh_3 (1.48 g, 4 mmol) was added at once, with stirring. Vigorous CO evolution was observed for 10–20 min while the reddish brown color of the solution changed to yellow. The resulting solution was then filtered and chilled to − 80°C and an equal volume of cold (− 80°C) *n*-pentane was added. A yellow microcrystalline substance was obtained, yield 1.44 g (68%) which was purified by recrystallization from its saturated solution in Et_2O by diffusion of *n*-hexane, yield 870 mg (41%). The recrystallized material was then characterized.

Anal. Calc. for $C_{29}H_{21}O_4ClCoP$: C, 62.3; H, 3.8; Cl, 6.3; Co, 10.5; P, 5.5. Found: C, 62.5; H, 3.9; Cl, 6.3; Co, 10.4; P, 5.4%.

The spectra of complex **5** together with those of intermediates **5a**, **5b** and **5c** are shown in Table 1(a–c).

2.1.2.1. *X-ray structure determination of complex 5*.

The intensity data for {(4-chlorophenyl)acetyl}cobalt tricarbonyl triphenylphosphine (**5**) were collected at r.t. on a Siemens P4/RA automatic diffractometer with graphite-monochromated Mo–K_α radiation. Details on crystal

Table 3
Atomic coordinates ($\times 10^{-4}$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for complex **4**

	x	y	z	U_{eq} [a]
Co(1)	−5923(1)	−599(1)	−3809(1)	54(1)
P(1)	−6738(1)	−2051(1)	−4187(1)	58(1)
C(1)	−6765(4)	−151(3)	−4743(3)	63(1)
O(1)	−7298(3)	169(3)	−5316(2)	92(1)
C(2)	−4784(4)	−1132(4)	−3855(4)	77(1)
O(2)	−4043(4)	−1465(3)	−3880(4)	129(2)
C(3)	−6182(3)	−308(3)	−2759(3)	62(1)
O(3)	−6365(3)	−132(3)	−2093(3)	90(1)
C(4)	−5101(3)	761(3)	−3481(3)	60(1)
C(5)	−4249(3)	970(3)	−2604(3)	55(1)
C(6)	−4381(3)	1479(3)	−1811(3)	65(1)
C(7)	−3592(4)	1692(3)	−985(3)	68(1)
C(8)	−2627(3)	1376(3)	−902(3)	62(1)
C(9)	−2488(4)	880(3)	−1694(3)	66(1)
C(10)	−3279(3)	682(3)	−2524(3)	63(1)
C(11)	−1755(4)	1593(4)	19(3)	76(1)
C(12)	−799(6)	1103(7)	−25(5)	155(4)
C(13)	−1539(6)	2683(5)	321(4)	114(2)
C(14)	−2107(6)	1219(5)	727(4)	112(2)
C(15)	−6448(3)	−2904(3)	−5082(3)	61(1)
C(16)	−6303(4)	−3868(4)	−5056(4)	79(2)
C(17)	−6100(5)	−4478(4)	−5774(4)	90(2)
C(18)	−6049(5)	−4135(5)	−6510(4)	92(2)
C(19)	−6201(5)	−3190(4)	−6552(4)	90(2)
C(20)	−6396(4)	−2576(4)	−5850(3)	71(1)
C(21)	−8133(4)	−2077(4)	−4603(3)	72(1)
C(22)	−8614(4)	−1266(5)	−4361(4)	91(2)
C(23)	−9676(5)	−1298(7)	−4692(6)	118(3)
C(24)	−10 238(6)	−2119(9)	−5244(6)	135(4)
C(25)	−9750(6)	−2921(8)	−5475(5)	132(3)
C(26)	−8713(5)	−2900(5)	−5163(4)	97(2)
C(27)	−6419(5)	−2672(3)	−3232(3)	74(2)
C(28)	−7131(6)	−2845(4)	−2827(4)	101(2)
C(29)	−6843(11)	−3266(5)	−2062(6)	147(4)
C(30)	−5856(13)	−3516(6)	−1709(5)	157(5)
C(31)	−5130(9)	−3358(5)	−2105(5)	138(4)
C(32)	−5420(6)	−2921(4)	−2869(4)	102(2)
Co(1′)	−7003(1)	3382(1)	−1875(1)	53(1)
P(1′)	−7729(1)	2928(1)	−933(1)	53(1)
C(1′)	−5766(4)	3691(3)	−1063(3)	62(1)
O(1′)	−4952(3)	3893(3)	−576(2)	87(1)
C(2′)	−7890(4)	4297(4)	−2077(3)	69(1)
O(2′)	−8461(3)	4863(3)	−2191(3)	110(2)
C(3′)	−7318(3)	2235(4)	−2643(3)	62(1)
O(3′)	−7546(3)	1511(3)	−3153(3)	86(1)
C(4′)	−6321(4)	3832(4)	−2779(3)	66(1)
C(5′)	−6978(3)	3717(3)	−3752(3)	61(1)
C(6′)	−6918(4)	2935(4)	−4408(3)	73(1)
C(7′)	−7493(4)	2839(4)	−5320(3)	80(2)
C(8′)	−8169(4)	3506(4)	−5624(3)	70(1)
C(9′)	−8237(4)	4284(4)	−4975(3)	76(1)
C(10′	−7656(4)	4387(3)	−4062(3)	73(1)
C(11′)	−8820(5)	3361(5)	−6638(4)	98(2)
C(12′)	−9297(11)	4232(11)	−6861(5)	311(10)
C(13′)	−8106(8)	3236(8)	−7211(5)	177(4)
C(14′)	−9411(13)	2458(11)	−6947(7)	372(12)
C(15′)	−8006(3)	3916(3)	−137(3)	59(1)
C(16′)	−7293(4)	4695(4)	268(3)	72(1)
C(17′)	−7419(5)	5425(4)	934(4)	94(2)
C(18′)	−8281(6)	5387(5)	1190(4)	98(2)
C(19′)	−8994(5)	4645(5)	792(4)	88(2)
C(20′)	−8870(4)	3902(4)	127(3)	72(1)
C(21′)	−7046(3)	2161(3)	−154(3)	56(1)
C(22′)	−7406(4)	1975(4)	524(3)	75(1)
C(23′)	−6906(5)	1381(4)	1102(4)	89(2)
C(24′)	−6059(5)	961(4)	1011(4)	86(2)
C(25′)	−5680(5)	1141(4)	347(4)	85(2)
C(26′)	−6181(4)	1737(3)	−246(3)	68(1)
C(27′)	−8934(3)	2234(4)	−1586(3)	66(1)
C(28′)	−8971(5)	1226(4)	−1745(4)	88(2)
C(29′)	−9837(7)	690(6)	−2349(5)	125(3)
C(30′)	−10 651(7)	1130(9)	−2793(5)	139(4)
C(31′)	−10 645(5)	2116(9)	−2633(5)	125(3)
C(32′)	−9777(4)	2683(5)	−2036(4)	90(2)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

data and experimental parameters are reported in Table 5. Corrections for Lorentzian polarization and absorption (ψ scans) were applied.

The structure was solved by direct methods (SIR-92 [18]) and refined on F_o^2 by the SHELX-97 program package [19]. All atoms in the structure were located in ΔF maps and subsequent refinement cycles. All nonhydrogen atoms were refined anisotropically, while hydrogen atoms were treated isotropically. Drawing was performed with the ORTEP plotting program [17]. Major calculations were carried out on an Alpha 3000/800S computer. Final fractional coordinates and equivalent thermal parameters are given in Table 6, while selected interatomic distances and angles are collected in Table 7. Tables showing full listings of selected interatomic distances and angles, anisotropic thermal parameters, final hydrogen coordinates and equivalent thermal parameters are available as supplementary material (see Section 4).

3. Results and discussion

The main goal of the present work was to obtain alkyl- and acylcobalt type tricarbonyltriphenylphosphine complexes with benzyl-derived organyl ligands, which can be crystallized in satisfactory quality for X-ray crystal and molecular structure determination. This goal has been set in the light of the reports listed under (5) and (6) in Section 1, aiming to get unequivocal structural information about the overall geometry of such complexes, which represent the bulk of the analytically pure products in the crystalline phase. We hope then to use the solution behavior of these complexes as reference for future spectroscopic studies.

In the light of our earlier experience with benzyl-

Table 4
Selected bond lengths (Å) and angles (°) for complex **4**

Bond	Molecule A[a]	Molecule B[a]
Bond lengths		
Co–C(O) av.	1.779	1.782
CO–P	2.2497(13)	2.2313(13)
P–C(Ph) av.	1.825	1.824
Co–C(4)	2.120(4)	2.136(5)
C(1)–O(1)	1.138(5)	1.142(5)
C(2)–O(2)	1.142(6)	1.125(6)
C(3)–O(3)	1.142(6)	1.145(5)
C(8)–C(11)	1.537(6)	1.535(7)
C(4)–C(5)	1.477(6)	1.488(6)
Bond angles		
C(O)–Co–C(O) av.	119.8	119.7
C(O)–Co–C(Ph) av.	87.2	86.8
C(O)–Co–P av.	92.9	93.1
C(4)–Co–P	177.44(14)	179.23(14)
C(Ph)–P–C(Ph) av.	104.1	103.8
O–C(O)–Co av.	178.4	177.5
C(5)–C(4)–Co	116.1(3)	116.5(3)

[a] Atoms of molecule B are indicated in Fig. 1 by (′), e.g. Co(1′)–C(1′).

Table 5
Crystal data and structure refinement for complex **5**

Empirical formula	$C_{29}H_{21}ClCoO_4P$
Formula weight	558.81
Temperature (K)	298(2)
Wavelength (Å)	0.71069
Crystal system	Monoclinic
Space group	*C*2/*c* (no. 15)
Unit cell dimensions	
a (Å)	17.8350(10)
b (Å)	15.3040(10)
c (Å)	19.3090(10)
α (°)	90
β (°)	91.759(7)
γ (°)	90
V (Å^3)	5267.8(5)
Z	8
$D_{calc.}$ (Mg m^{-3})	1.409
Absorption coefficient (mm^{-1})	0.847
F(000)	2288
Crystal size (mm)	0.3 × 0.2 × 0.2
θ range for data collection (°)	2.66–28.5
Index ranges	$-23 \leq h \leq 23$, $0 \leq k \leq 20$, $0 \leq l \leq 25$
Reflections collected	7169
Independent reflections	6646 [$R_{int} = 0.0160$]
Refinement method	Full-matrix least-squares
Data/restraints/parameters	6646/0/410
Goodness-of-fit on F^2	1.068
Final *R* indices [$I > 2\sigma(I)$)	$R_1 = 0.0386$, $wR_2 = 0.1024$
R indices (all data)	$R_1 = 0.0584$, $wR_2 = 0.1105$
Largest difference peak and hole (e Å^{-3})	0.498 and −0.478

Table 6
Atomic coordinates (10^4) and equivalent isotropic displacement parameters (Å$^2 \times 10^3$) for complex **5**

	x	*y*	*z*	U_{eq}[a]
Co	8521(1)	3711(1)	6496(1)	36(1)
P	8135(1)	5115(1)	6497(1)	35(1)
Cl	9314(1)	−1790(1)	5557(1)	107(1)
O(2)	10 099(1)	4157(2)	6746(1)	74(1)
C(2)	9483(1)	4004(2)	6654(1)	46(1)
O(3)	8053(2)	3522(2)	5048(1)	100(1)
C(3)	8224(1)	3598(2)	5617(1)	54(1)
O(1)	7740(1)	3208(1)	7734(1)	75(1)
C(1)	8032(1)	3405(1)	7242(1)	47(1)
O(4)	9463(1)	2240(1)	6483(2)	125(1)
C(4)	8836(1)	2456(1)	6424(1)	53(1)
C(5)	8214(1)	1777(2)	6316(2)	60(1)
C(6)	8485(1)	881(1)	6122(1)	47(1)
C(7)	8787(2)	725(2)	5479(1)	59(1)
C(8)	9040(2)	−95(2)	5304(1)	61(1)
C(9)	8998(1)	−756(1)	5774(1)	56(1)
C(10)	8704(2)	−622(2)	6412(1)	59(1)
C(11)	8452(1)	202(2)	6577(1)	53(1)
C(12)	8505(1)	5796(1)	7207(1)	40(1)
C(13)	8521(1)	5459(2)	7871(1)	54(1)
C(14)	8766(2)	5961(2)	8430(1)	70(1)
C(15)	8994(2)	6797(2)	8334(2)	75(1)
C(16)	8985(2)	7142(2)	7680(2)	84(1)
C(17)	8742(2)	6650(2)	7117(2)	63(1)
C(18)	8389(1)	5686(1)	5709(1)	43(1)
C(19)	7857(2)	5993(2)	5232(1)	64(1)
C(20)	8080(2)	6373(2)	4618(2)	80(1)
C(21)	8819(2)	6448(2)	4480(2)	75(1)
C(22)	9353(2)	6149(2)	4944(2)	72(1)
C(23)	9142(2)	5769(2)	5560(1)	60(1)
C(24)	7125(1)	5280(1)	6551(1)	38(1)
C(25)	6834(1)	6111(2)	6634(1)	49(1)
C(26)	6068(1)	6231(2)	6692(1)	58(1)
C(27)	5593(1)	5526(2)	6664(1)	57(1)
C(28)	5873(1)	4699(2)	6582(1)	55(1)
C(29)	6638(1)	4574(2)	6517(1)	45(1)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

cobalt carbonyls we have chosen (*para*-^{t}butylbenzyl)cobalt tricarbonyl triphenylphosphine (**4**) as representative of the former and [(*para*-chlorophenyl)acetyl]cobalt tricarbonyl triphenylphosphine (**5**) as representative of the latter type.

The preparation of complexes **4** and **5** proceeded smoothly by using metathesis of $[Co(CO)_4]^-$ with the corresponding benzyl halides. The η^3-benzylcobalt tricarbonyl (**a**) η^1-benzylcobalt tetracarbonyl (**b**) η^1-phenylacetylcobalt tetracarbonyl (**c**) type intermediates could be identified spectroscopically on the basis of earlier experience [10,16,20].

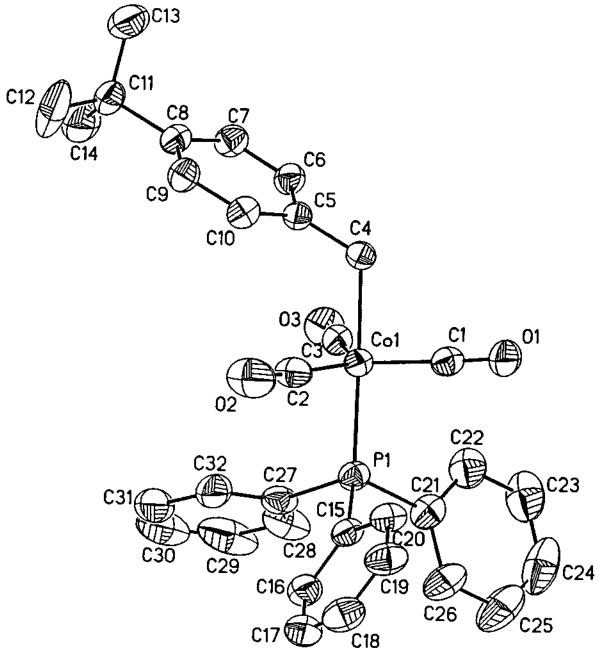
The X-ray diffraction crystal and molecular structure determinations show that the overall molecular geometries of complexes **4** (Fig. 1) and **5** (Fig. 2) are nearly ideal trigonal bipyramidal with the two noncarbonyl ligands in the axial positions. The P–Co–C_{alkyl}

and P–Co–C_{acyl} axes are slightly bent (**4**: 177.44(14)° and 179.23(14)° **5**: 175.90(7)°) as has been observed also for the known alkyl- [1,6,10b,12a,b,d,e] and acylcobalt carbonyl [10b,12b,c] structures, e.g. $RCo(CO)_3PPh_3$, R = $ClCH_2$: 177.6(1)° [12b], R = ${}^{i}PrOC(O)CH_2$: (two independent molecules) 176.2(2)° and 178.1(2)° [21]; $RC(O)Co(CO)_3PPh_3$, R = $ClCH_2$: 174.5(1)° [12b], = 2,6-dichlorophenylCH_2: 178.9(1)° [10b], R = ${}^{n}BuO$: 177.1(1)° [12c]. The three carbonyl groups are nearly coplanar, with a slight bending towards the organic ligand (**4**: C_{alkyl}–Co–C_{coord} av. 87.0°; **5**: C_{acyl}–Co–C_{coord} av. 87.1°), a phenomenon which was predicted on the basis of a sophisticated analysis of the IR ν(C=O) stretching vibrations of $MeCo(CO)_4$ [22].

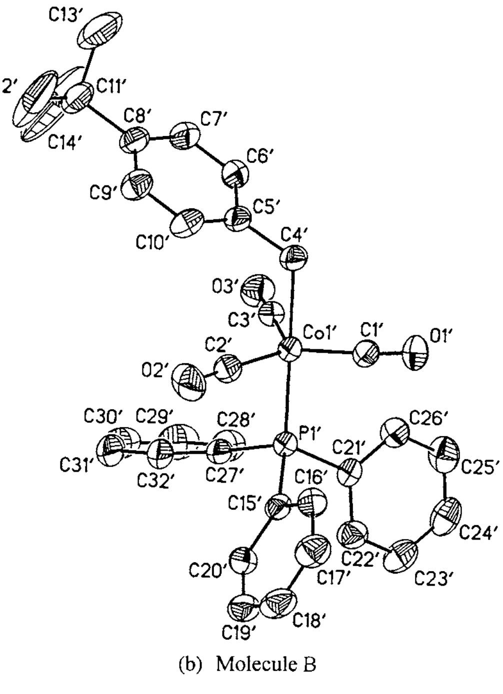
The crystal structure of complex **4**, has the fairly interesting feature of two independent molecules in the unit cell. This effect may be correlated to the surprising stereochemistry observed for the crystals of $ROC(O)CH_2Co(CO)_3PPh_3$ complexes [12d,21], however, the organic ligand in **4** is symmetric and thus direct comparison with the ester derivatives is not possible. This point merits additional efforts using asymmetrically (*ortho*- and/or *meta*-) substituted benzyl derivatives.

Table 7
Selected bond lengths (Å) and angles (°) for complex **5**

Bond lengths			
Co–C(3)	1.769(2)	Co–C(1)	1.771(2)
Co–C(2)	1.791(2)	Co–C(4)	2.008(2)
Co–P	2.2564(5)	P–C(18)	1.823(2)
P–C(24)	1.8251(18)	P–C(12)	1.829(2)
Cl–C(9)	1.736(2)	O(2)–C(2)	1.132(3)
O(3)–C(3)	1.139(3)	O(1)–C(1)	1.137(3)
O(4)–C(4)	1.168(3)	C(4)–C(5)	1.530(3)
C(5)–C(6)	1.505(3)	C(5)–H(5A)	1.06(3)
C(5)–H(5B)	1.05(4)		
Bond angles			
C(3)–Co–C(1)	127.87(11)	C(3)–Co–C(2)	116.43(11)
C(1)–Co–C(2)	114.87(10)	C(3)–Co–C(4)	85.23(10)
C(1)–Co–C(4)	87.07(10)	C(2)–Co–C(4)	88.94(9)
C(3)–Co–P	90.68(8)	C(1)–Co–P	95.35(7)
C(2)–Co–P	93.03(7)	C(4)–Co–P	175.90(7)
C(18)–P–C(24)	104.67(9)	C(18)–P–C(12)	105.00(10)
C(24)–P–C(12)	102.28(9)	C(18)–P–Co	111.81(7)
C(24)–P–Co	115.66(7)	C(12)–P–Co	116.13(6)
O(2)–C(2)–Co	177.3(2)	O(3)–C(3)–Co	178.1(3)
O(1)–C(1)–Co	177.7(2)	O(4)–C(4)–C(5)	120.6(2)
O(4)–C(4)–Co	122.30(19)	C(5)–C(4)–Co	117.10(15)
C(6)–C(5)–C(4)	114.54(19)	C(6)–C(5)–H(5A)	111.0(15)
C(4)–C(5)–H(5A)	108.0(15)	C(6)–C(5)–H(5B)	112(2)
C(4)–C(5)–H(5B)	108(2)	H(5A)–C(5)–H(5B)	103(3)



(a) Molecule A



(b) Molecule B

Fig. 1. ORTEP view of complex **4** with atom labels and 30% probability thermal ellipsoids. The hydrogen atoms are omitted for clarity.

In alkyl- and acylcobalt carbonyls the $C_{organic}$–Co

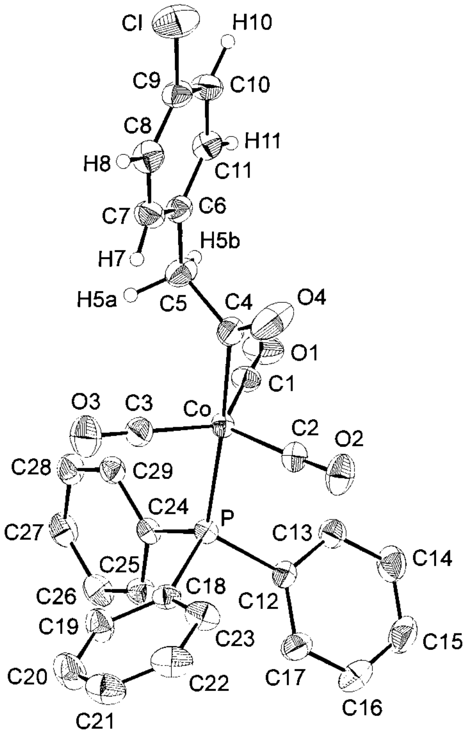


Fig. 2. ORTEP view of complex **5** with atom labels and 30% probability thermal ellipsoids. The hydrogen atoms of the triphenylphosphine ligand are omitted for clarity.

and Co–P distances are the most sensitive to structural changes in the organic ligand or in the phosphine. The C_{alkyl}–Co separation in **4** is slightly longer than the average in numerous alkylcobalt complexes (2.120(4) and 2.136(5) Å vs. 2.1 Å), probably due to the 'tension' generated by the bulky organic ligand. Similarly the Co–P distances (2.2213(13) and 2.2313(13)) also show a slight increment with respect to the average of the alkylcobalt complexes (2.212 Å), approaching the value observed for butoxycarbonylcobalt tricarbonyl triphenylphosphine (2.229(1) Å [12c]). In the acylcobalt derivative **5** these trends are different. The C_{acyl}–Co bond is significantly shorter (by ca. 0.1 Å) than the ca. 2.1 Å values observed for alkylcobalt carbonyls [10b,12], but fairly similar to values found at the acyl complexes cited above, with Co–C_{acyl} distances ranging from 1.967 to 1.999 Å. The Co–P distances show even less consistency: the 2.2564(5) Å value found in the present study is similar only to the values found at the (2,6-dichlorophenyl)acetyl- (2.259(1) Å [10b]) and chloroacetylcobalt (2.254(1) Å [12b]) complexes, but significantly longer than the Co–P distances found at the butoxycarbonyl (2.229(1) Å [12c]) or the alkyl-derivatives (av. 2.212 Å). Generally it can be deduced that the negative inductive effect in the organic group causes shortening of the Co–C_{acyl} distance and increases the Co–P distance, with the exception of **4** and of the alkoxycarbonyl derivative, which merits a separate study.

We can conclude that the structural rearrangement of the supposed primary *cis*-alkyl/acylcobalt tricarbonyl phosphine complexes [6,7,8,11a,12a,13] should be fast (or at least faster than the formation of the crystalline phase) also in the case of the benzylcobalt family. On the other hand we regard the results obtained in the present work as a solid basis for solution studies in an attempt at extending the highly interesting observations of Kovács et al. [11a] to additional alkyl- and acylcobalt carbonyls. It should be pointed out [23] that the benzyl-type (present work and Refs. [10,16]) as well as the alkoxycarbonylmethyl-type ($ROC(O)CH_2Co(CO)_3L$, L = CO, PR'_3; [6,11a,12a,d,21,24]) complexes possess a great structural advantage: CO insertion studies are not complicated by β-H elimination and connected isomerization [6,12a,25,26] reactions [27].

4. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-119403 (**4**) and CCDC-119397 (**5**). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: int. code +(1223) 336-033; e-mail: deposit@chemcrys.cam.ac.uk).

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