

1994b). Software used to prepare material for publication: *SHELXL93*.

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Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: FG1231). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Tricarbonyl(trifluoromethyl)(triphenylphosphine)cobalt

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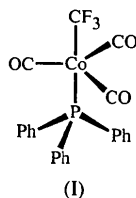
Abstract

The title compound, [Co(CF₃)(C₁₈H₁₅P)(CO)₃], has a trigonal bipyramidal geometry with the trifluoromethyl and triphenylphosphine ligands occupying the *trans*-axial positions. The three carbonyl ligands occupy the

planar equatorial positions. Both the trifluoromethyl and triphenylphosphine ligands are in a staggered conformation relative to the carbonyl ligands in the equatorial plane. The structure of the title compound is similar to other alkylcobalt tricarbonyl triphenylphosphines. Important bond distances include Co—CF₃ 1.953 (6), Co—P1 2.235 (1), mean Co—CO 1.752 and mean P1—C 1.822 Å.

Comment

The interconversion of alkyl and acyl functional groups through carbonylation/decarbonylation reactions of transition metal organometallic compounds plays an important role in many catalytic processes (Abel, Stone & Wilkinson, 1995). This interconversion can frequently be accelerated by oxidation (Fernandez, Prock & Giering, 1994) or reduction (Amatore, Bayachou, Verpeaux, Pospisil & Fiedler, 1995), and a project is currently underway examining the reductively induced decarbonylation of (CF₃CO)Co(CO)₃(PPh₃). This reaction is known to occur thermally, giving the stable trifluoromethyl complex (CF₃)Co(CO)₃(PPh₃) (Hieber, Beck & Lindner, 1961). The perfluorinated complexes are preferred for study due to their enhanced stability compared with the unsubstituted alkyl and aryl complexes. During the course of the current study, (CF₃CO)Co(CO)₃(PPh₃) was thermally decarbonylated in tetrahydrofuran to yield the title complex, (I), which was subsequently isolated as colorless single crystals through slow evaporation of the solvent. As its structure had not previously been reported and in the interest of learning more about its properties, the X-ray crystal structure of the trifluoromethyl complex was determined.



The structures of three other alkylcobalt tricarbonyl triphenylphosphine complexes have been reported, namely, (HCF₂CF₂)Co(CO)₃(PPh₃) (Wilford & Powel, 1967), (PhCH₂OOCCH₂)Co(CO)₃(PPh₃) (Galamb, Palyi, Cser, Furmanova & Struchkov, 1981) and (ClCH₂)Co(CO)₃(PPh₃) (Galamb, Palyi, Boese & Schmid, 1987). All three previously reported structures, as well as the present one, display the expected trigonal bipyramidal geometry with the alkyl and triphenylphosphine ligands occupying the *trans*-axial positions. The trigonal bipyramidal geometry is displayed in Fig. 1. Bond distances around the Co atom are quite normal when compared with those reported in BIDICS

(1969–1981) and the Cambridge Structural Database (Orpen *et al.*, 1989). The three carbonyl groups lie in the equatorial plane with a mean deviation from the least-squares plane of less than 0.022 Å. The F atoms around C1 are arranged in a staggered conformation relative to the carbonyl ligands [torsion angle F1—C1—Co—C2 59.2(5)°]. Distortions are observed in the angles around the P atom, with a maximum deviation from an ideal tetrahedral angle of 5.7°. However, the mean angle about the P atom is 109.3°. This type of distortion has been previously observed in other complexes containing phosphine ligands (Mullica, Oliver, Sappenfield & Grossie, 1986; Mullica, Sappenfield & Hampden-Smith, 1991). The enlarged tetrahedral angles (mean Co—P1—C11/C21/C31 114.2°) are probably due to the steric bulk of the ligands. The phosphine ligand has its organic substituents in a staggered orientation relative to the carbonyl ligands [torsion angle C2—Co—P1—C11—36.3(3)°]. The phenyl rings of the triphenylphosphine group are regular with only minimal angular distortion and are almost planar; the maximum deviation from the best plane is 0.098 Å.

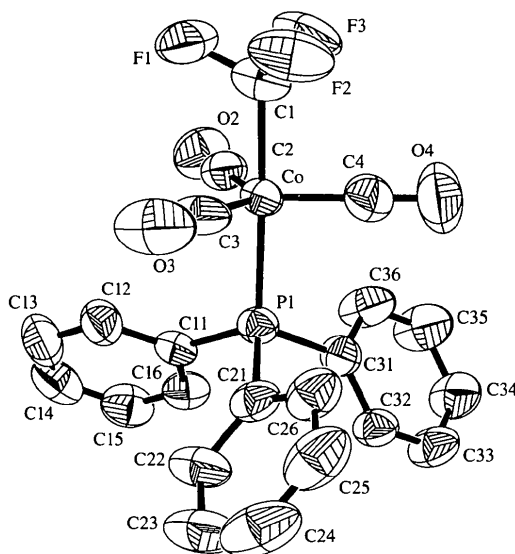


Fig. 1. The molecular structure of (I) showing the atomic numbering scheme, with 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

Experimental

The trifluoroacetyl complex $(\text{CF}_3\text{CO})\text{Co}(\text{CO})_3(\text{PPh}_3)$ was prepared according to the method of Heck & Breslow (1962). This compound was dissolved in tetrahydrofuran, where it underwent slow thermal decarbonylation at room temperature to the trifluoromethyl complex $(\text{CF}_3)\text{Co}(\text{CO})_3(\text{PPh}_3)$. Subsequent slow evaporation of the solvent by diffusion through a rubber septum resulted in crystallization of the title compound as clear colorless single crystals.

Crystal data

$[\text{Co}(\text{CF}_3)(\text{C}_{18}\text{H}_{15}\text{P})(\text{CO})_3]$
 $M_r = 474.26$
 Monoclinic
 $P2_1/c$
 $a = 9.823(2) \text{ \AA}$
 $b = 19.600(2) \text{ \AA}$
 $c = 11.384(2) \text{ \AA}$
 $\beta = 93.26(2)^\circ$
 $V = 2188.3(6) \text{ \AA}^3$
 $Z = 4$
 $D_x = 1.44 \text{ Mg m}^{-3}$
 $D_m = 1.48(3) \text{ Mg m}^{-3}$
 D_m measured by flotation
 in heptane and bromotrichloromethane

Data collection

Enraf–Nonius CAD-4F
 diffractometer
 ω – 2θ scans
 Absorption correction:
 by integration
 $T_{\min} = 0.822$, $T_{\max} = 0.906$
 4214 measured reflections
 3835 independent reflections
 2549 reflections with
 $F > 4\sigma(F)$

Refinement

Refinement on F
 $R = 0.051$
 $wR = 0.065$
 $S = 1.590$
 2549 reflections
 272 parameters
 H atoms were placed in
 calculated positions
 $w = 1/[\sigma^2(F) + 0.0004F^2]$
 $(\Delta/\sigma)_{\max} = 0.578$

Mo $K\alpha$ radiation
 $\lambda = 0.71073 \text{ \AA}$
 Cell parameters from 25
 reflections
 $\theta = 10.18$ – 16.43°
 $\mu = 0.897 \text{ mm}^{-1}$
 $T = 292 \text{ K}$
 Clear prism
 $0.26 \times 0.20 \times 0.12 \text{ mm}$
 Colorless

$R_{\text{int}} = 0.0466$
 $\theta_{\max} = 25^\circ$
 $h = 0 \rightarrow 11$
 $k = 0 \rightarrow 23$
 $l = -13 \rightarrow 13$
 3 standard reflections
 frequency: 120 min
 intensity decay: 0.6%

$\Delta\rho_{\max} = 0.429 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.406 \text{ e \AA}^{-3}$
 Extinction correction:
 SHELXTL-Plus (Sheldrick,
 1989)
 Extinction coefficient:
 0.0001(1)
 Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. Selected geometric parameters ($\text{\AA}$, $^\circ$)

Co—C1	1.953(6)	C3—O3	1.175(7)
C1—F1	1.352(8)	Co—C4	1.763(6)
C1—F2	1.344(8)	C4—O4	1.177(8)
C1—F3	1.358(7)	Co—P1	2.235(1)
Co—C2	1.751(5)	P1—C11	1.818(5)
C2—O2	1.172(7)	P1—C21	1.823(5)
Co—C3	1.742(5)	P1—C31	1.824(5)
C1—Co—C2	88.1(3)	Co—C1—F3	114.3(4)
C1—Co—C3	88.0(3)	F1—C1—F3	103.5(5)
C2—Co—C3	124.2(3)	F2—C1—F3	103.1(5)
C1—Co—C4	89.4(3)	Co—C2—O2	178.6(5)
C2—Co—C4	115.4(3)	Co—C3—O3	178.6(5)
C3—Co—C4	120.1(3)	Co—C4—O4	175.8(5)
C1—Co—P1	178.3(2)	Co—P1—C11	114.0(2)
C2—Co—P1	91.8(2)	Co—P1—C21	114.1(2)
C3—Co—P1	90.6(2)	C11—P1—C21	105.2(2)
C4—Co—P1	92.1(2)	Co—P1—C31	114.5(2)
Co—C1—F1	114.8(4)	C11—P1—C31	104.0(2)
Co—C1—F2	115.4(4)	C21—P1—C31	103.8(2)
F1—C1—F2	104.2(5)		

A conoscopic examination between two crossed polarizers on a Zeiss Photomicroscope II confirmed the optical quality and nature of the crystal. Due to a most satisfactory refinement, it was deemed unnecessary to continue further iterations [see $(\Delta/\sigma)_{\max}$ under refinement]. The structure was checked for additional symmetry by the *MISSYM* program (Gabe, Le Page, Charland, Lee & White, 1989).

Data collection: *CAD-4 Manual* (Enraf–Nonius, 1988). Cell refinement: *CAD-4 Manual*. Data reduction: *SDP* (Enraf–Nonius, 1985). Program(s) used to solve structure: *SHELXTL-Plus* (Sheldrick, 1989) (heavy-atom Patterson method). Program(s) used to refine structure: *SHELXTL-Plus*. Molecular graphics: *SHELXTL-Plus* and *XP* (Siemens, 1994). Software used to prepare material for publication: local *CIFGEN* program.

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Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: FR1018). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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(Benzyl sym-dibenzo-16-crown-5 ether)-lead(II) Dinitrate

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Abstract

The title complex, (17-benzyloxy-2,5,8,15,19-pentaoxa-tricyclo[18.4.0.0^{9,14}]tetracos-9,11,13,20,22,24-hexaene-κ⁶O)bis(nitrato-*O, O'*)lead(II), [Pb(NO₃)₂(C₂₆H₂₈O₆)], prepared from benzyl sym-dibenzo-16-crown-5 ether and Pb(NO₃)₂ in aqueous CHCl₃/MeOH at room temperature, has decacoordinate geometry for the Pb²⁺ ion, with bonds to the five ring O atoms, the side-arm ether O atom and two O atoms of each of the two coordinated nitrate ions. The four Pb—O bond lengths for the nitrate ligands are considerably shorter than those for the crown ether.

Comment

While crystal structures of metal complexes of simple crown and cryptand lariat ethers are well documented (Vögtle & Weber, 1989), corresponding complexes with C-pivot lariat ethers remained unknown until the recent report (Liu, Lin, Young, Shgu & Ueng, 1996) that C-pivot hydroxy- and 2'-methoxyethyl benzyl sym-dibenzo-16-crown-5 ethers form complexes with Na⁺ and Pb²⁺ ions, respectively. These results provide concrete evidence of side-arm participation in C-pivot lariat crown–metal complexation.

The structure of the title complex, (I), formed from benzyl sym-dibenzo-16-crown-5 ether and Pb(NO₃)₂, is shown in Fig. 1. Of the six lariat donor atoms, the side-arm O6 atom is the closest to the metal [2.658 (5) Å]. The lengths of the other five Pb—O bonds in the macrocycle are in the range 2.725 (6)–2.901 (5) Å. That the Pb—O bond for the side-arm is significantly shorter than those for the ring may be attributed to the flexibility of the side-arm. Two nitrate anions also serve as bidentate donors, making Pb²⁺ decacoordinate, and the four nitrate Pb—O bond lengths are considerably shorter than the others. The coordination geometry may be described as two superimposed trigonal bipyramids. The first is formed by atoms O3, O6 and O13 in equatorial sites, and O5 and O11 in axial sites; the second has O2, O4 and O14 equatorial, and O1 and O10 axial. The structure is similar to that of the pentanitratocerate(III) ion (Al-Karaghoulis & Wood, 1970), but more distorted.