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Crystal structure of acetyliodotricarbonylcobaltate

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Abstract

The structure of PPN$[Co(CO)_3\{C(O)CH_3\}I]$ (prepared from PPN$[Co(CO)_4]$ (PPN = $Ph_3P{=}N{=}PPh_3$) and methyl iodide) has been determined by low temperature X-ray crystallography. The anion has a trigonal bipyramidal structure with the three carbonyl groups in the equatorial plane of the central cobalt.

Introduction

Acyltetracarbonylcobalt complexes are of interest as intermediates in catalytic carbonylation reactions. The lability of these carbonyl complexes has so far prevented determination of their structures by X-ray crystallography, but the structures of several of the more stable phosphine-substituted derivatives have been determined [1]. For example, the structures of $Co(CO)_3PPh_3\{C(O)CH_2Ph\}$ [2], $Co(CO)_3PPh_3\{C(O)CH_2(2,6\text{-}Cl_2C_6H_3)\}$ [3] and $Co(CO)_3PPh_3\{C(O)OCH_3\}$ [4] are known, and in all three cases the acyl and phosphine ligands occupy axial positions in a trigonal bipyramid. On the basis of spectroscopic evidence, the same type of structure was proposed for the anionic alkoxycarbonyl cobalt complexes $[Co(CO)_3(R)(CO_2R')]^-$ with R = CN, CH_2CO_2Et, R′ = Me which are formed by nucleophilic attack of OR'^- on $Co(CO)_4(R)$ [5].

More recently, we described the synthesis and properties of the first well characterized anionic acyl halide tricarbonyl cobaltate, which was obtained in

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almost quantitative yield by reaction of an excess of methyl iodide with PPN[Co(CO)$_4$] in tetrahydrofuran [6]:

$$\underset{\mathbf{(1)}}{\mathrm{PPN[Co(CO)_4]}} + \mathrm{MeI} \xrightarrow{\mathrm{THF,\ 0\,^\circ C}} \underset{\mathbf{(2)}}{\mathrm{PPN[Co(CO)_3\{C(O)Me\}I]}} \tag{1}$$

On the basis of the IR, ^{1}H- and ^{31}P-NMR, as well as an X-ray crystallographic study, **2** was assigned a trigonal bipyramidal structure with the acetyl and iodide ligands in the axial positions. However, due to the thermal lability of **2** partial decomposition occurred during the X-ray study at room temperature, and we were unable to determine accurate bond lengths or bond angles in **2**. In view of the significance of **2** as a probable intermediate in cobalt/iodide catalyzed carbonylation/hydrocarbonylation of methanol, we have repeated the single crystal X-ray study at low temperature, and are now able to present full structural details for **2**.

Results and discussion

Bond angles and bond distances for **2** are given in Table 1. There seems not to be any specific interaction between the PPN cation (which has the usual geometry) and the cobaltate anion in the crystal, as shown in Fig. 1. Thus, the further discussion concentrates on the anion of **2**, the structure of which is shown in Fig. 2 but Fig. 3 shows the cation.

Table 1

Bond distances (Å) and bond angles (°) in PPN[Co(CO)$_3${C(O)CH$_3$}I] (**2**)

I–Co	2.684(1)	O(1)–C(1)	1.138(4)
Co–C(1)	1.807(3)	O(2)–C(2)	1.135(4)
Co–C(2)	1.804(3)	O(3)–C(3)	1.134(4)
Co–C(3)	1.813(3)	O(4)–C(4)	1.201(4)
Co–C(4)	1.961(3)	C(4)–C(5)	1.521(4)
P(1)–N	1.583(2)	P(2)–N	1.583(2)
P(1)–Ph(1)	1.806(3)	P(2)–Ph(31)	1.800(3)
P(1)–Ph(11)	1.809(3)	P(2)–Ph(41)	1.805(3)
P(1)–Ph(21)	1.806(3)	P(2)–Ph(51)	1.801(3)
C(4)–Co–C(3)	96.9(1)	O(1)–C(1)–Co	177.9(3)
C(4)–Co–C(2)	85.5(1)	O(2)–C(2)–Co	177.6(3)
C(4)–Co–C(1)	89.3(1)	O(3)–C(3)–Co	176.1(3)
C(4)–Co–I	175.9(1)	C(5)–C(4)–O(4)	119.8(3)
C(3)–Co–C(2)	120.2(1)	C(5)–C(4)–Co	117.5(2)
C(3)–Co–C(1)	116.5(1)	O(4)–C(4)–Co	122.6(2)
C(3)–Co–I	87.2(1)		
C(2)–Co–C(1)	123.4(1)		
C(2)–Co–I	92.2(1)		
C(1)–Co–I	89.1(1)		
Ph(21)–P(1)–Ph(11)	108.2(1)	Ph(51)–P(2)–Ph(41)	108.6(1)
Ph(21)–P(1)–Ph(1)	108.2(1)	Ph(51)–P(2)–Ph(31)	106.6(1)
Ph(21)–P(1)–N	109.2(1)	Ph(51)–P(2)–N	106.2(1)
Ph(11)–P(1)–Ph(1)	106.9(1)	Ph(41)–P(2)–Ph(31)	108.3(1)
Ph(11)–P(1)–N	115.5(1)	Ph(41)–P(2)–N	113.7(1)
Ph(1)–P(1)–N	108.7(1)	Ph(31)–P(2)–N	113.0(1)
P(2)–N–P(1)	139.7(2)		

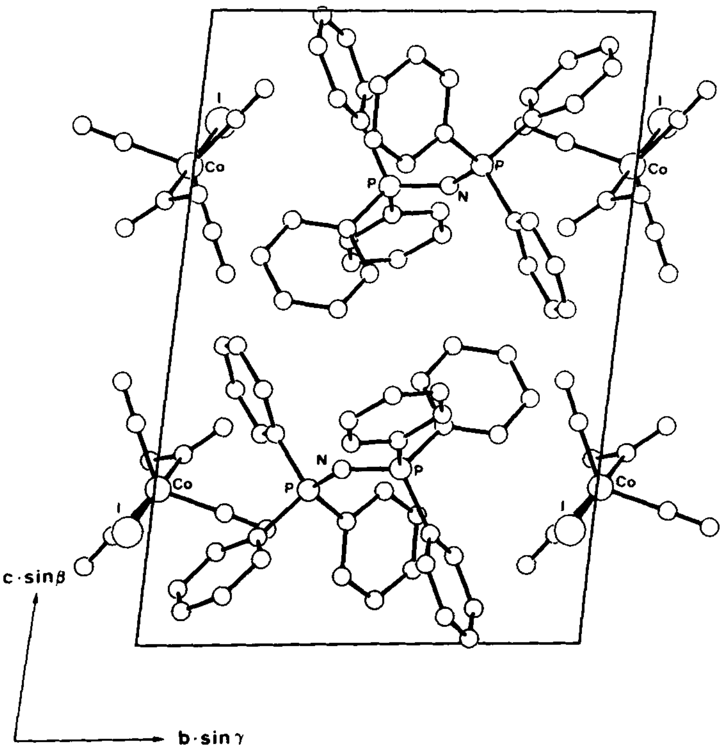

Fig. 1. Unit cell for $\mathrm{PPN[Co(CO)_3\{C(O)CH_3\}I]^-}$.

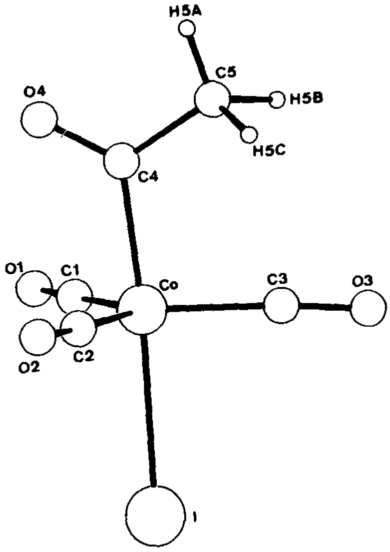

Fig. 2. Structure of $\mathrm{[Co(CO)_3\{C(O)CH_3\}I]^-}$.

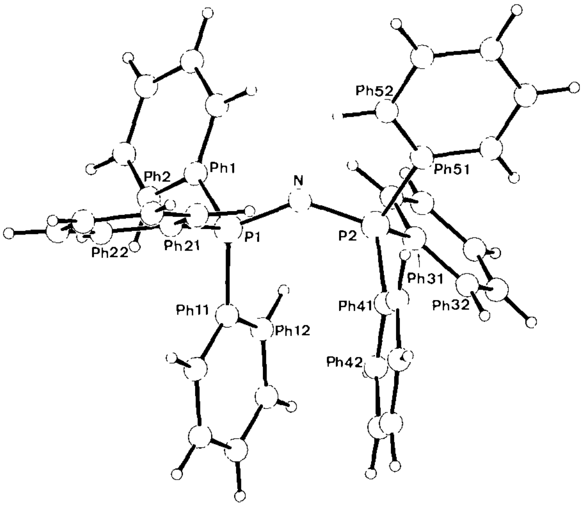

Fig. 3.

In keeping with our previous report [6], the structure of the anion of the **2** is a trigonal bipyramid, with the three carbonyl ligands in the equatorial plane. The arrangement of the axial iodide and acetyl ligands is almost linear, with an I–Co–C(4) angle of 175.9°. There is repulsion between the methyl of the acetyl ligand (C(5)) and one carbonyl ligand (C(3)) which leads to opening of the C(4)–Co–C(3) angle to 96.9° and closing of the C(3)–Co–I angle to 87.3°.

The cobalt–acyl ligand bond distance (Co–C(4)) was found to be 1.961(3) Å, which is within the range reported for comparable bonds in $Co(CO)_3PPh_3\{C(O)OMe\}$ (1.967 Å) [4] and $Co(CO)_3PPh_3\{C(O)CH_2Ph\}$ (1.996 Å) [2]. The lengths of the bonds between the equatorial carbonyls (C(1), C(2), C(3)) and cobalt are all about 1.81 Å, slightly longer than those of 1.78–1.79 Å observed for the related complexes [2,4].

As expected for an anionic species, the bond distance of Co–I in **2** (2.684(1) Å) is larger than the sum of the covalent radii (2.42 Å). The cobalt–iodide bond appears to be rather labile, since concentrated solutions of **2** in THF or acetonitrile tend to decompose with separation of [PPN]I [6].

The IR carbonyl absorptions for **2** (2029w, 1955vs, 1933vs cm^{-1}, THF) suggest that it is structurally related to $[Na(15\text{-crown-}5)][Co(CO)_3(CO_2Me)I]$ (**3**) (1964s, 1952vs cm^{-1}, THF), which was prepared by Tasi et al. by reaction of $Co(CO)_4I$ with $[Na(15\text{-crown-}5)]OMe$ or reaction of $Co(CO)_4(CO_2Me)$ with $[Na(15\text{-crown-}5)]I$. Unfortunately, **3** could not be isolated and characterized [7].

It is noteworthy that the anions of both **2** and **3** are stable in solution only in the presence of large cations. **2** and **3** have been proposed as intermediates in cobalt/iodide catalyzed carbonylation reactions [6,7].

Experimental

A crystal of **2** ($C_{41}H_{33}O_4P_2NCoI$, 851.5 g/mol) of 0.32 × 0.47 × 0.40 mm size was used for the single crystal X-ray study. The data collection was carried out at −150 °C on an Enraf–Nonius CAD-4 diffractometer.

Table 2

Atomic coordinates and equivalent isotropic thermal parameters (Å^2) with standard deviations in parentheses ($U_{eq} = 1/3\Sigma_i\Sigma_j U_{ij} a_i^\star a_j^\star \mathbf{a}_i \mathbf{a}_j$)

Atom	x	y	z	U_{eq}
I	0.2269(1)	0.0494(1)	0.8221(1)	0.021
Co	0.4794(1)	−0.0086(1)	0.7549(1)	0.018
P(1)	0.0060(1)	0.3475(1)	1.2433(1)	0.015
P(2)	0.1310(1)	0.5509(1)	1.2767(1)	0.015
O(1)	0.4471(2)	−0.2640(2)	0.8187(1)	0.020
O(2)	0.4579(2)	0.1021(2)	0.5848(1)	0.024
O(3)	0.5284(2)	0.1385(2)	0.8766(2)	0.037
O(4)	0.6907(2)	−0.1395(2)	0.6576(1)	0.022
N	0.1006(2)	0.4170(2)	1.2757(1)	0.033
C(1)	0.4587(3)	−0.1656(3)	0.7928(2)	0.025
C(2)	0.4633(3)	0.0598(3)	0.6511(2)	0.028
C(3)	0.5139(3)	0.0818(3)	0.8284(2)	0.030
C(4)	0.6601(3)	−0.0569(3)	0.7000(2)	0.022
C(5)	0.7631(3)	0.0177(3)	0.7099(2)	0.027
Ph(1)	−0.0854(2)	0.2576(2)	1.3323(2)	0.016
Ph(2)	−0.2079(3)	0.2259(2)	1.3321(2)	0.021
Ph(3)	−0.2747(3)	0.1559(3)	1.4016(2)	0.023
Ph(4)	−0.2208(3)	0.1174(2)	1.4708(2)	0.022
Ph(5)	−0.0984(3)	0.1475(3)	1.4711(2)	0.024
Ph(6)	−0.0308(3)	0.2180(2)	1.4019(2)	0.021
Ph(11)	−0.1107(2)	0.4426(2)	1.1926(2)	0.018
Ph(12)	−0.2053(3)	0.5205(3)	1.2410(2)	0.022
Ph(13)	−0.2897(3)	0.6016(3)	1.2022(2)	0.026
Ph(14)	−0.2816(3)	0.6054(3)	1.1165(2)	0.030
Ph(15)	−0.1901(3)	0.5271(3)	1.0685(2)	0.031
Ph(16)	−0.1037(3)	0.4461(3)	1.1063(2)	0.023
Ph(21)	0.1008(2)	0.2465(2)	1.1696(2)	0.016
Ph(22)	0.0428(3)	0.1559(2)	1.1464(2)	0.021
Ph(23)	0.1158(3)	0.0799(3)	1.0887(2)	0.027
Ph(24)	0.2462(3)	0.0931(3)	1.0542(2)	0.025
Ph(25)	0.3044(3)	0.1817(3)	1.0779(2)	0.023
Ph(26)	0.2322(3)	0.2598(2)	1.1353(2)	0.020
Ph(31)	0.0030(2)	0.6371(2)	1.3439(2)	0.019
Ph(32)	−0.0203(3)	0.7634(3)	1.3302(2)	0.027
Ph(33)	−0.1176(3)	0.8244(3)	1.3870(2)	0.036
Ph(34)	−0.1907(3)	0.7614(4)	1.4566(2)	0.040
Ph(35)	−0.1690(3)	0.6359(3)	1.4704(2)	0.035
Ph(36)	−0.0715(3)	0.5730(3)	1.4145(2)	0.026
Ph(41)	0.1667(3)	0.6356(2)	1.1732(2)	0.019
Ph(42)	0.0650(3)	0.6949(2)	1.1378(2)	0.021
Ph(43)	0.0916(3)	0.7534(3)	1.0557(2)	0.028
Ph(44)	0.2183(3)	0.7507(3)	1.0086(2)	0.034
Ph(45)	0.3198(3)	0.6903(3)	1.0431(2)	0.034
Ph(46)	0.2937(3)	0.6333(3)	1.1256(2)	0.028
Ph(51)	0.2714(2)	0.5378(2)	1.3212(2)	0.018
Ph(52)	0.3562(3)	0.4309(3)	1.3170(2)	0.024
Ph(53)	0.4633(3)	0.4191(3)	1.3533(2)	0.032
Ph(54)	0.4861(3)	0.5129(3)	1.3926(2)	0.032
Ph(55)	0.4012(3)	0.6183(3)	1.3978(2)	0.038
Ph(56)	0.2944(3)	0.6307(3)	1.3625(2)	0.031

Space group: $P\bar{1}$ No. 2; $F(000) = 856$; a 10.681(6), b 11.219(5), c 16.414(2) Å; α 81.78(2), β 75.98(2), γ 82.22(4)°; V 1878.2 Å^3; D_c 1.51 g cm^{-3}; μ 13.92 cm^{-1}; $Z = 2$; λ(Mo-K_α) 0.71069 Å; absorption correction: none; monochromator: graphite; filter: Zr; method: Ω–2θ; θ-range: 1.3–27.6°; sin θ/λ_{max}: 0.65; measured reflections: 8490 [$\pm h \pm k + l$]; independent reflections: 8281; observed reflections: 7456; refined parameters: 583; $R = 0.031$; $R_w = 0.043$; residual electron density: 0.85 eÅ^{-3}.

Atom coordinates are given in Table 2. Tables of thermal parameters and lists of structure factors can be obtained from the Fachinformationszentrum Energie, Physik, Mathematik GmbH, D-7514 Eggenstein-Leopoldshafen 2 (F.R.G.) if the deposition number CSD52462, the name of the authors, and the journal reference are provided.

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