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PHOSPHIDO COBALT CARBONYL CLUSTERS $P_n[Co(CO)_3]_{4-n}$ ($n = 1, 2, 3$) *

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Summary

The $P_n[Co(CO)_3]_{4-n}$ ($n = 1, 2, 3$) tetrahedral clusters have been prepared and characterized. The very unstable $PCo_3(CO)_9$ can be stabilized in the form of $(CO)_4FePCo_3(CO)_9$

Introduction

Pnicogen derivatives of cobalt carbonyls have been studied in recent years [2—9]. We previously described [2] the preparation of $P_2Co_2(CO)_6$ and $SPCo_3(CO)_9$, and we now present the results of a systematic study of the tetrahedral series $P_n[Co(CO)_3]_{4-n}$ ($n = 1, 2, 3$).

Results and discussion

White phosphorus (P_4) or phosphorus trihalides (PX_3; X = Cl, Br, I) were treated with $Co_2(CO)_8$ in hexane or $[Co(CO)_4]^-$ in THF under various conditions:

$$\left.\begin{array}{l} P_4 + Co(CO)_8 \xrightarrow[\text{1—120 atm CO}]{\text{hexane, 10—50°C}} \\[2ex] PI_3 + Co_2(CO)_8 \xrightarrow[\text{1 atm CO}]{\text{hexane, 25°C}} \\[2ex] PX_3 + Co(CO)_4^- \xrightarrow[\text{1 atm CO, 25°C}]{\text{THF}} \\ \text{(X = Cl, Br, I)} \end{array}\right| \begin{array}{l} \underset{\text{(I)}}{P_3Co(CO)_3} + \underset{\text{(II)}}{P_2Co_2(CO)_6} + \underset{\text{(III)}}{PCo_3(CO)_9} + \\ \underset{\text{(IV)}}{[PCo_3(CO)_8]_3} \end{array} \qquad (1)$$

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* Some details of this work have been presented at a symposium [1] and in a preliminary note [2].

TABLE 1

ν(C—O) FREQUENCIES (cm^{-1}) FOR $P_3Co(CO)_3$ AND $As_3Co(CO)_3$ IN HEXANE

	A_1	E	$\nu(^{13}CO)$
$P_3Co(CO)_3$	2091.4s	2042.7vs	2003.6vw
$As_3Co(CO)_3$ [a]	2080.1s	2032.3vs	1994.3w

[a] Only a low-resolution ν(C—O) spectrum was reported previously [3].

In all cases, compounds I—IV were formed together, and were separated by column chromatography on silica gel with hexane as eluent. Higher temperatures and elevated CO pressures favour formation of compound I, while lower temperatures and 1 atm CO pressure favour compound III.

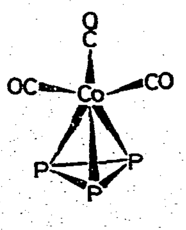
At a ratio of P : Co = 2 : 1, I was the main product. It forms light yellow, hexane-soluble crystals which ignite spontaneously in the air. Its IR spectrum shows two fundamental absorption bands (Table 1) in the terminal C—O stretching frequency range corresponding to the A_1 and E species of the point group C_{3v}. The shape of the spectrum is practically identical with that of the IR spectrum of $As_3Co(CO)_3$ the structure of which is known [3], and the differences in the position of the bands is in agreement with the higher electronegativity of phosphorous as compared to that of arsenic. On the basis of these considerations we suggest for compound I the structure shown below.

At a ratio of P : Co = 1 : 1, the formation of II [2] predominated. This is the most stable compound in the $P_n[Co(CO)_3]_{4-n}$ series.

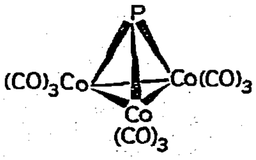
At a P : Co ratio of 1 : 4, IV [10] was the main product although also its "monomer", III could be detected by IR spectroscopy if the samples were taken quickly during and immediately after the reaction. The bands attributed to compound III reached a maximum after ca. 15 min, after which IV began to predominate. The life time of III in solution is less than 10 minutes at room temperature.

The IR ν(C—O) absorption bands of III are presented in Table 2, together with the ν(C—O) spectra of some other non-bridged $ZCo_3(CO)_9$ [10,11] complexes.

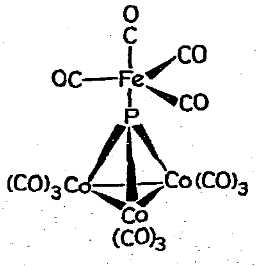
The spectra of all $ZCo_3(CO)_9$ complexes are very similar. This similarity and the ready formation of the known "cyclotrimer" IV [10] from compound III proves that (i) compound III has the same pyramidal structure as $AsCo_3(CO)_9$



(I)



(III)



(V)

TABLE 2

ν(C—O) FREQUENCIES (cm^{-1}) OF SOME $ZCo_3(CO)_9$ COMPLEXES IN HEXANE

	A_1	E	A_1	E	E
$PCo_3(CO)_9$	2105.6w	2066.9vs	2054.0s	2036w	[a]
$SPCo_3(CO)_9$ [10]	2108.1w	2066.1vs	2051.4s	2037.8w	2024vw(sh)
$AsCo_3(CO)_9$ [10]	2101.7w	2054.8vs	2040.9s	2023.1w	2020vw(sh)
$ClCCo_3(CO)_9$ [11]	2108.9m	2062.3vs	2046.1w	2030.3w	2020vw(sh)

[a] This compound could not be obtained pure and this weak band was obscured by bands from other complexes.

[10] or the $XCCo_3(CO)_9$ series [11—13] and (ii) this species is the "monomer" of $[PCo_3(CO)_8]_3$.

Because of its strong tendency towards "cyclotrimerization" compound III could not be isolated. However, its $Fe(CO)_4$ adduct V was prepared since III reacts readily with a THF solution of $Fe_2(CO)_9$ [14], probably according to the following scheme:

$$Fe_2(CO)_9 + THF \xrightarrow[25^\circ C]{N_2} Fe(CO)_4 \cdot THF + Fe(CO)_5 \qquad (2)$$

$$Fe(CO)_4 \cdot THF + PCo_3(Co)_9 \xrightarrow{THF + hexane} \underset{(V)}{(CO)_4FePCo_3(CO)_9} + THF \qquad (3)$$

V was isolated from the reaction mixture in the form of light-sensitive, gleaming black crystals. Its infrared spectrum shows the following bands in the ν(C—O) region: 2111.8w, 2068.6vs, 2057.5s, 2045.9vw, 2040.1vw, 1995.8w, 1985.7w, 1962.0m and 1925.0vw cm^{-1}. The number of observed ν(C—O) bands is in agreement with the selection rules for a compound with the structure shown on p. 62. This structure belongs to point group C_{3v} and requires 4 A_1 + 4 E bands in the terminal ν(C—O) region.

Experimental

All reactions were carried out under CO or N_2. The infrared spectra were run on a VEB Carl Zeiss Jena UR 20 type spectrophotometer using LiF prism and KBr or NaCl cells. The calibration of the IR spectra was performed by the simultaneous recording of a DCl gas spectrum [15].

Preparation of $P_3Co(CO)_3$ (I)

$Co_2(CO)_8$ (2 g, 5.9 mmol), white phosphorus (0.7 g, 23.5 mmol), and 50 ml of dry hexane were placed in a 100 ml rocking autoclave and kept under 120 atm CO pressure at 50°C. After 2 hours the mixture was filtered and the reddish brown hexane solution was chromatographed on a silica gel column and eluted with hexane. The first, light yellow, fraction was concentrated in vacuum, and cooled to —40°C to give light yellow crystals of I, which were dried in a stream of CO. Yield 15 mg. (Found: Co, 24.1; P, 40.8. $P_3CoC_3O_3$ calcd.: Co, 25.00; P, 39.4%). The red-coloured, second fraction eluted by hexane contained II [2].

Preparation of $PCo_3(CO)_9$ (III) and $(CO)_4FePCo_3(CO)_9$ (V)

A solution of $Co_2(CO)_8$ (2 g, 5.9 mmol) and hexane (50 ml) was placed in a double-neck flask containing PI_3 (1.1 g, 2.6 mmol). The heterogeneous mixture was stirred vigorously under CO at 10°C, the progress of the reaction being monitored by recording the infrared spectrum from time to time. After about 15 minutes the bands of $Co_2(CO)_8$ had almost disappeared and the absorption of $PCo_3(CO)_9$ at $\sim$2067 cm^{-1} was the most intense peak. At this point dry THF (50 ml) and crystalline $Fe_2(CO)_9$ (0.55 g, 3 mmol Fe) were added to the solution. After 30 min the black mixture was evaporated to dryness in vacuum and the solid residue was extracted with hexane. The dark brown hexane solution was chromatographed on a silica gel column and the first, deep red fraction was concentrated in vacuum. Chilling the solution to —40°C gave V as gleaming black crystals, which were filtered off and dried in a stream of N_2. The complex was handled in darkness. Yield 25 mg. (Found: Fe, 8.6; Co, 27.5; P, 4.56. $FeCoPC_{13}O_{13}$ calcd.: Fe, 8.89; Co, 28.17; P, 4.93%).

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