Journal of Organometallic Chemistry, 107 (1976) 235—240

$AsCo_3(CO)_9$, ITS CYCLIC TRIMER, $As_3Co_9(CO)_{24}$ AND THE PHOSPHORUS-CONTAINING ANALOG $P_3Co_9(CO)_{24}$*

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(Received August 26th, 1975)

Summary

The $AsCo_3(CO)_9$ trigonal pyramidal cluster, its cyclic "trimer" $As_3Co_9(CO)_{24}$ and the phosphorus-containing analog of the latter, $P_3Co_9(CO)_{24}$ have been prepared and characterized. A reversible equilibrium between the arsenic-containing monomer and trimer was found to depend on $p(CO)$. Such an equilibrium could not be observed in the case of $P_3Co_9(CO)_{24}$.

Introduction

Pnicogenic derivatives of cobalt carbonyls have received increasing attention in recent years [2-8]. The metastable tetrahedral $(Pn)_4$ molecules (Pn = P, As) can be stabilized by replacing one or more of the pnicogen atoms by $Co(CO)_3$ groups: $As_3Co(CO)_3$ [2], $As_2Co_2(CO)_6$ [3] or $P_2Co_2(CO)_6$ [4]. All these compounds are members of the homologous series of $(Pn)_n[Co(CO)_3]_{4-n}$ complexes containing an electron-precise [9] $(Pn)_nCo_{4-n}$ tetrahedral skeleton. The chemistry of this series shows a marked similarity with that of the $E_n[Co(CO)_3]_{4-n}$ type compounds with E = CR ($n = 1, 2$) [10,11], SiR ($n = 1$) [12], SR ($n = 1$) [13], S ($n = 1$) [14], Se ($n = 1$) [15,16] or Te ($n = 1$) [16].

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* Preliminary account of this work was given in a lecture [1].

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Several studies dealt with the electronic structure of the $E_n[Co(CO)_3]_{4-n}$ tetrahedron [10,11,14c,17,18]. The presence of the non-bonding p electron pair of the pnicogen atom(s) in the E = Pn derivatives provides a very useful probe to throw more light upon this question through the study of their reactions as Lewis bases.

It seemed reasonable to assume that the still unknown members of the $(Pn)_n[Co(CO)_3]_{4-n}$ homologous series could be synthesized under suitable conditions and we describe below some work along these lines.

Results and discussion

The reaction of AsX_3 (X = Cl, Br, I) with a three- or four-fold excess of $Na[Co(CO)_4]$ in THF solution gives a mixture from which the deep violet $AsCo_3(CO)_9$ (I) and the deep green $As_3Co_9(CO)_{24}$ (II) can be isolated by column chromatography in rather low (5-10%) yields, together with the well-known [3,4] $As_2Co_2(CO)_6$ (eq. 1).

$$Na[Co(CO)_4] + AsX_3 \xrightarrow[\text{1 atm CO}]{\text{THF, 25°C}} As_2Co_2(CO)_6 + \underset{\text{(I)}}{AsCo_3(CO)_9} + \underset{\text{(II)}}{As_3Co_9(CO)_{24}} \quad (1)$$

X = Cl, Br or I

The low yields make this reaction only moderately useful from the preparative viewpoint, but its analogy with the synthesis of $RCCo_3(CO)_9$ compounds from geminal trihaloalkane derivatives [11] provides preparative evidence for the presence of a trigonal $AsCo_3$ moiety in I and II.

It should be noted that in some cases a further brown, As-containing, cobalt carbonyl (III) was obtained from the reaction mixture of reaction 1. It was characterized by IR ν(C—O) bands at 2109, 2080, 2069vs, 2053, 2045, 2040, 2033, 2026, 2012, 1867, 1858 and 1843 cm^{-1}. Its solution on standing gives some II, but we were not always able to reproduce this result.

Compound I is also formed, along with $As_2Co_2(CO)_6$, II and III, in the reaction of $Co_2(CO)_8$ and $AsCl_3$ in hexane, but the quasi-heterogeneous reaction 2 was much more useful for the preparation of I.

$$Co_2(CO)_8 + AsI_3 \xrightarrow[\text{1 atm CO}]{\text{n-hexane, 25°C}} \underset{\text{(I)}}{AsCo_3(CO)_9} \quad (2)$$

By this method I was obtained in good yields (~30%, based on AsI_3). We explain this finding by the low solubility of AsI_3 in saturated aliphatic hydrocarbons under the reaction conditions, which results in a high Co:P ratio during the reaction.

The infrared spectrum of I in the region of the CO stretching vibrations shows close similarity to those of the non-bridged $ZCo_3(CO)_9$ [4,11,14a,19,20] complexes (Table 1). On this basis, and taking into account the preparative evidence obtained from reaction 1, we suggest for I the pyramidal structure shown in Fig. 1.

TABLE 1

ν(C—O) STRETCHING FREQUENCIES OF SOME $ZCo_3(CO)_9$ COMPLEXES, $As_3Co_9(CO)_{24}$ AND $P_3Co_9(CO)_{24}$ IN HEXANE SOLUTION

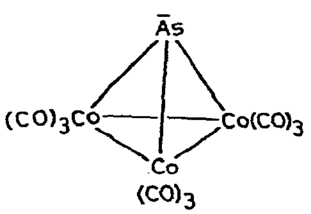
Compound	Stretching frequencies (cm^{-1})							Ref.
	ν_1A_1	ν_4E	ν_2A_1	ν_6E	ν_5E [a]			
$AsCo_3(CO)_9$	2101.7 w	2054.8 vs	2040.9 s	2023.1 w	2020 vw(sh)			this work
$PhCCo_3(CO)_9$	2101.4 m	2054.2 vs	2039.9 s	2020.9 w	[b]			11
$ClCCo_3(CO)_9$	2108.9 m	2062.3 vs	2046.1 s	2030.3 w	2020 vw(sh) [c]			11
$SPCo_3(CO)_9$	2108.1 w	2066.1 vs	2051.4 s	2037.8 w	2024 vw(sh) [c]			4
$SCo_3(CO)_9$	2103.4 w	2049.5 s	2037.5 m	2023.5 w	[d]			14a
$As_3Co_9(CO)_{24}$	2075.5 s	2064.7 s	2048.5 w	2044.4 m	2025.6 m	2018.5 vw	2012.7 vw	this work
$P_3Co_9(CO)_{24}$	2078.5 vs	2067.1 s	2051.0 m	2046.6 m	2027.6 m	2020.7 w	2015.0 w	this work

[a] Assignment according to refs. 19, 20. [b] This band was not reported in earlier literature and neither could it be observed with an authentic sample, in the course of this work. [c] Measured in the course of this work. [d] Not observed by ref. 14a.

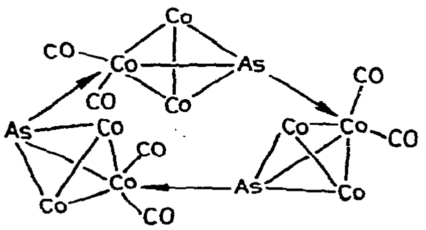
The practically identical values of the ν(C—O) absorptions for I and $PhCCo_3(CO)_9$ suggest that As$\leqslant$ and PhC$\leqslant$ groups are very similar from the viewpoint of electron donor—acceptor capacities when they are on the apex. This similarity is much less pronounced with the analogous binuclear couple $As_2Co_2(CO)_6$ [4] and $(PhC_2Ph)Co_2(CO)_6$ [21].

The deep violet complex I is rather stable in the solid state under carbon monoxide, but its hexane solution under nitrogen readily turns green and carbon monoxide is evolved. From the green solution compound II may be crystallized. This suggests that despite the expected electron-reservoir properties [11, 17,18] of the $AsCo_3$ moiety in I the apical arsenic atom has significant nucleophilic character due to its lone electron pair. Under nitrogen or at a decreased CO partial presssure an S_N reaction [22] thus takes place between $AsCo_3(CO)_9$ molecules leading to the more stable II.

The deep green polynuclear cluster II, which has a rather low solubility in apolar organic solvents, was prepared previously [23]. It was formulated earlier



(I)



(II)

Fig. 1. Suggested structure of compound I.

Fig. 2. Structure of II, according to ref. 23b. CO ligands of non-substituted CO atoms are omitted.

as $[AsCo_3(CO)_9]_x$ [23a], but recently its structure was found by X-ray analysis to be a cyclic trimer with the formula $[AsCo_3(CO)_8]_3$ [23b].

The $As_3Co_9(CO)_{24}$ cyclic trimer (Fig. 2) contains a six membered ring consisting of alternating Co and As atoms. Thus the cluster may be regarded as an inorganic heterocycle stabilized by $Co(CO)_3$ fragments. Each arsenic atom replaces one of the axial carbonyl groups in the neighbouring monomer and the other two non-substituted $Co(CO)_3$ groups lie symmetrically below and above the plane of the Co_3As_3 ring. The idealized structure would belong to point group C_{3h}.

The cyclotrimerization of I was found to be a reversible process depending on the carbon monoxide pressure (3). This was proved by converting trimer II

$$\underset{(I)}{3AsCo_3(CO)_9} \rightleftharpoons \underset{(II)}{As_3Co_9(CO)_{24}} + 3CO \qquad (3)$$

to monomer I in about 80% yield by treating it for 6—7 hours at room temperature with 15—20 atmospheres of carbon monoxide and monitoring the reaction in a high pressure cell by infrared spectroscopy.

It should be mentioned that the compound claimed to be I in a patent [8] is most probably II, or at least a mixture of I and II, according to the IR data given there.

We made efforts to prepare the phosphorus-containing analogs of I and II by reactions similar to 1 and 3. The reaction of PX_3 (X = Cl, Br, or I) in THF with $[Co(CO)_4]^-$ led only to the formation of the known [4] $P_2Co_2(CO)_6$ and IV, a dark green crystalline substance (eq. 4). The expected "monomeric" $PCo_3(CO)_9$ could not be observed.

$$Na[Co(CO)_4] + PX_3 \xrightarrow[\text{1 atm CO}]{\text{THF, 25°C}} P_2Co_2(CO)_6 + \underset{(IV)}{P_3Co_9(CO)_{24}} \qquad (4)$$

IV was characterized by elemental analyses and ν(C—O) IR spectra. We suggest a structure analogous to that of II on the basis of: (i) the nature of the reaction in which it is formed, (ii) the green colour in solution, similar to that of II, (iii) the very close similarity of the IR spectrum to that of II.

We also tried to prepare $PCo_3(CO)_9$ from IV under CO pressure (as in the case of reaction 3) but did not observe its formation even under 200 atm CO at 100°C for 2 days. This negative result was not wholly unexpected, in view of the enhanced stability of P—Co bands as compared to that of As—Co bonds.

Experimental

All reactions were carried out under CO or N_2, with careful exclusion of moisture. The infrared spectra were run on a VEB Carl Zeiss Jena UR 20 type spectrophotometer using LiF prisms and KBr or NaCl cells. The high pressure infrared cell was made by MÁFKI (Hungarian Oil and Gas Reasearch Institute) [24]. The calibration of the infrared spectra was performed by the simultaneous recording of a DCl spectrum [25].

1. *Preparation of $AsCo_3(CO)_9$ (I) and $As_3Co_9(CO)_{24}$ (II) from $Na[Co(CO)_4]$*

The solution of 2 g $Co_2(CO)_8$ (5.9 mmol) in 50 ml dry THF was shaken with 100 g sodium amalgam (1% Na content) untill it became colourless. After filtration 0.53 g (2.9 mmol) $AsCl_3$ (Co:As, 4:1) dissolved in 2.9 ml THF was added slowly. The colourless solution turned gradually dark brown and carbon monoxide was evolved. After gas evolution stopped (~3 h) the reaction mixture was evaporated in vacuum and the solid residue was extracted with hexane. The reddish brown hexane solution was chromatographed on a silica gel column. The first fraction was red $As_2Co_2(CO)_6$ [3] (identified by its IR spectrum [4] and the preparation of its mono-PPh_3 derivative [3,4]). The second (violet-coloured) fraction was concentrated in a stream of carbon monoxide. Cooling the concentrated solution in dry ice gave deep violet crystals of $AsCo_3(CO)_9$. The crystals were filtered off and dried under carbon monoxide. Yield 3 mg, 1.4%. (Found Co, 34.6, $AsCo_3C_9O_9$ calcd.: Co, 35.29%.)

The green coloured third fraction was eluted from the silica gel column with a hexane/benzene (7:3) mixture. The solvent was evaporated to dryness at reduced pressure and the deep green solid residue was recrystallized from hexane. The crystals were dried in vacuo. Yield: 17 mg, 8%. (Found Co, 36.5; As, 15.4. $As_3Co_9C_{24}O_{24}$ calcd. Co, 37.2; As, 15.75%.)

2. *Preparation of $AsCo_3(CO)_9$ (I) from $Co_2(CO)_8$*

0.37 g (1.1 mmol) $Co_2(CO)_8$ were dissolved in 20 ml hexane and 0.3 g (0.66 mmol) AsI_3 added (Co:As, 3.3:1). The heterogeneous mixture was stirred vigorously under CO untill all $Co_2(CO)_8$ has been used up (20-25 minutes, control by IR spectroscopy). The mixture was filtered, and the filtrate concentrated by evaporating most of the solvent in a stream of CO. $AsCo_3(CO)_9$ was crystallized from the concentrated solution by chilling to —78°C. The violet crystals were dried after filtration in a stream of CO. Yield: 85 mg, 30%.

If the preparation is carried out under N_2 or Ar complex I undergoes substantial trimerization.

3. *Conversion of the cyclic trimer $As_3Co_9(CO)_{24}$ (II) into $AsCo_3(CO)_9$ (I)*

About 3 ml hexane solution of II obtained as described in 1. was transferred to the high pressure infrared cell and stirred under 15—20 atm CO pressure. The reaction was followed by recording the infrared spectrum from time to time. After 450 min the absorption bands characteristic for I became dominant and those of II almost disappeared. The green colour of the solution turned to violet. The experiment was performed in a 200 ml rocking autoclave for preparative purposes (50 ml staurated hexane solution of II, 50 atm CO, room temperature, overnight), an 80% yield, based on IR data, was obtained.

4. *Preparation of $P_3Co_9(CO)_{24}$ (IV)*

A solution of $NaCo(CO)_4$ was prepared from 2 g (5.9 mmol) $Co_2(CO)_8$ as described in Experiment 1. To this solution 0.3 ml (3.5 mmol) PCl_3 dissolved in 3 ml THF was added slowly. After 3 hours the black reaction mixture was evaporated in vacuum and the solid residue was extracted with hexane. The dark brown solution was chromatographed on a silica gel column. The first, red-coloured, fraction eluted with hexane was $P_2Co_2(CO)_6$ [4].

The green second fraction was eluted with a hexane/benzene (7:3) mixture. The solvent was evaporated to dryness in vacuum and the black solid residue was recrystallized from hexane. Yield: 30 mg, 9.7%. (Found Co, 41.6; P, 7.1. $P_3Co_9C_{24}O_{24}$ calcd.: Co, 40.93; P, 7.18%.)

Acknowledgement

We acknowledge stimulating discussions and correspondence with Prof. Lawrence F. Dahl (Madison, Wisc., U.S.A.), who informed us about unpublished structural data and agreed to publication of the formula given in Fig. 2.

References

1 IX. Komplexkémiai Kollokvium (IXth Colloquium on Coordination Chemistry of the Hungarian Chemical Society), Esztergom, May 1974.
2 A.S. Foust, M.S. Foster and L.F. Dahl, J. Amer. Chem. Soc., 91 (1969) 5631.
3 A.S. Foust, M.S. Foster and L.F. Dahl, J. Amer. Chem. Soc., 91 (1969) 5633.
4 A. Vizi-Orosz, G. Pályi and L. Markó, J. Organometal. Chem., 60 (1973) C25.
5 A.S. Foust and L.F. Dahl, J. Amer. Chem. Soc., 92 (1970) 7337.
6 G.L. Simon and L.F. Dahl, J. Amer. Chem. Soc., 95 (1973) 2175.
7 W.R. Cullen, D.J. Patmore and J.R. Sams, Inorg. Chem., 12 (1973) 867.
8 C.E. Morrel and L.B. Taranko, Ger., Offen. 2 260 534 (1973).
9 D.M.P. Mingos, Nature Phys. Sci., 236 (1972) 99.
10 R.S. Dickson and P.J. Faser, Advan. Organometal. Chem., 12 (1974) 323.
11 G. Pályi, F. Piacenti and L. Markó, Inorg. Chim. Acta Rev., 4 (1970) 109.
12 S.F.A. Kettle and I. Khan, Proc. Chem. Soc., (1962) 82; J. Organometal. Chem., 5 (1966) 588.
13 E. Klumpp, G. Bor and L. Markó, Chem. Ber., 100 (1967) 1451.
14 (a) L. Markó, G. Bor, E. Klumpp, B. Markó and G. Almásy, Chem. Ber., 96 (1963) 955; (b) C.H. Wei and L.F. Dahl, Inorg. Chem., 6 (1967) 1229; (c) C.E. Strouse and L.F. Dahl, Discuss. Faraday Soc., 47 (1969) 93.
15 C.E. Strouse and L.F. Dahl, J. Amer. Chem. Soc., 93 (1971) 6032.
16 C.E. Strouse and L.F. Dahl, 157th ACS National Meeting, Minneapolis, Abstr. of Papers, 1969, INOR 180.
17 B.R. Penfold and B.H. Robinson, Accounts Chem. Res., 6 (1973) 73.
18 B.H. Robinson, Proc. Symp. Hydroformylation and Related Reactions, Veszprém, 1972, p. 67.
19 G. Bor, Proc. Symp. Metal Carbonyls, Inorg. Chim. Acta, Ed., 1969, p. 56.
20 G. Pályi and G. Váradi, J. Organometal. Chem., 86 (1975) 119.
21 G. Bor, Chem. Ber., 96 (1963) 2644; J. Organometal. Chem., 94 (1975) 181.
22 P. Chini, Pure Appl. Chem., 23 (1970) 489.
23 (a) A.S. Foust, Diss. Abstr. Int. B, 31 (1970) 1134; (b) R.S. Gall, A.S. Foust, P.J. Pollick, A. Wojcicki and L.F. Dahl, Abstr. Amer. Crystallograph. Meeting, Berkeley, Calif., March 1974, L.F. Dahl, personal communication.
24 Z. Décsy, K. Bélafi-Réthy and B. Heil, MÁFKI Közleményei, 13 (1972) 9.
25 G. Bor, Acta Chim. Budapest, 34 (1962) 315.