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Preliminary communication

Phosphido cobalt carbonyl clusters: $Co_2(CO)_6P_2$ and $Co_3(CO)_9PS$

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SUMMARY

Two phosphido cobalt carbonyl clusters $Co(CO)_6P_2$ and $Co_3(CO)_9PS$ have been prepared and characterised.

Very few phosphorus-group derivatives of cobalt carbonyls bearing no organic ligands on the Group VB element are known; examples are $As_3Co(CO)_3$ [1] (I), $Co_2(CO)_6As_2$ [2] (II), $Co_4(CO)_{12}Sb_4$ [3] (III), $Bi[Co(CO)_4]_3$ [4] (IV) and the $Sb[Co(CO)_3(PPh_3)]_4^+$ [4] cation.

We wish to report now the preparation of $Co_2(CO)_6P_2$ (V) and $Co_3(CO)_9PS$ (VI)[*] by the reactions

$$Na[Co(CO)_4] + PX_3 \xrightarrow{\text{THF, } 25^\circ} \text{(V)}$$

$$Na[Co(CO)_4] + SPX_3 \xrightarrow{\text{THF, } 25^\circ} \text{(VI)}$$

(where X = Cl or Br) with rather low (1–10%) yields.

(V) was separated from the reaction mixture by chromatography on silica gel and eluted by hexane (red oil). Its IR[**] ν(C–O) spectrum (n-hexane, 2100.6 m, 2066.3 vs, 2045.5 s, 2041.5 s, 2028.5 mw cm^{-1}) as well as that of its mono-triphenylphosphine derivative $Co_2(CO)_5(PPh_3)P_2$ (reddish brown crystals), (n-hexane; 2072.4 s, 2027.1 s, 2020.5 s, 2006.8 w, 1984.2 m) show complete analogy with the high resolution ν(C–O) spectra[***] of (II) (n-hexane; 2093.4 m, 2058.5 vs, 2039.0 s, 2033.5 s, 2021.4 mw cm^{-1}) and $Co_2(CO)_5(PPh_3)As_2$ [2] (n-hexane; 2066.7 s, 2021.9 s, 2016.3 s, 1999.6 w, 1978.4 m),

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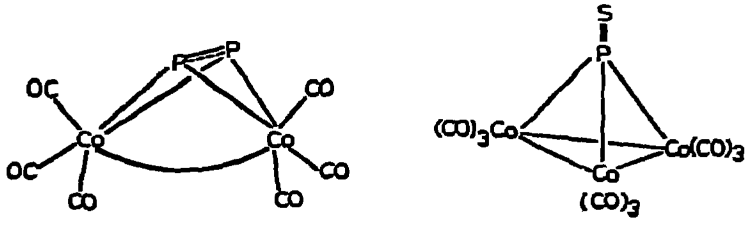
[*] All new compounds gave satisfactory analyses.

[**] Spectra were recorded with simultaneous DCl calibration[5], the error is ± 0.5 cm^{-1}.

[***] Only a low resolution ν(C–O) spectrum of (II) was reported[2].

respectively, as well as with the spectra of the $Co_2(CO)_6$ (acetylene)[6] and $Co_2(CO)_5(PR_3)$-(acetylene)[7] complexes. On the basis of these analogies we suggest the structure shown in Fig. 1 for (V). This complex may thus be regarded as the first metal-carbonyl-stabilised derivative of the P_2 molecule, and the second example[14] of an organocobalt complex containing "naked" phosphorous.

(VI) was also eluted by hexane from silica gel (dark violet crystals). Its ν(C—O) spectrum (n-hexane; 2108.1 w, 2066.1 s, 2051.4 m, 2037.8 w) is analogous with that of the non-bridged $Co_3(CO)_9Z$ (VII) (Z may be CY[8] (Y = H, alkyl, aryl, halogen, etc.), S[9], Se[10], Te[10] or GePh[11]) or $Co_2Fe(CO)_9S$[9b,12] complexes. The ν(P—S) band is shifted to a rather high[13] wave number (810 cm^{-1} (KBr)) which may be expected by comparing with ν(C—Y) absorptions of compounds (VII) (Z = CY[8]). On this basis we suggest for (V) the structure shown in Fig. 1.



(V) (VI)

Fig. 1.

REFERENCES

1 A.S. Foust, M.S. Foster and L.F. Dahl, *J. Amer. Chem. Soc.*, 91 (1969) 5631.
2 A.S. Foust, M.S. Foster and L.F. Dahl, *J. Amer. Chem. Soc.*, 91 (1969) 5633.
3 A.S. Foust and L.F. Dahl, *J. Amer. Chem. Soc.*, 92 (1970) 7337.
4 W.R. Cullen, D.J. Patmore and J.R. Sams, *Inorg. Chem.*, 12 (1973) 867.
5 G. Bor, *Acta Chim. (Budapest)*, 34 (1962) 315.
6 G. Bor, *Chem. Ber.*, 96 (1963) 2644.
7 G. Váradi, G. Pályi and L. Markó, unpublished results.
8 G. Pályi, F. Piacenti and L. Markó, *Inorg. Chim. Acta, Rev.*, 4 (1970) 109.
9 (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.
10 C.E. Strouse and L.F. Dahl, *15th Amer. Chem. Soc. Nat. Meeting, Minneapolis, Abstr. Papers* 1969, INOR. 180.
11 R. Ball, M.J. Bennett, E.H. Brooks, W.A.G. Graham, J. Hoyano and M.S. Illingworth, *Chem. Commun.*, (1970) 592.
12 S. Khattab, L. Markó, G. Bor and B. Markó, *J. Organometal. Chem.*, 1 (1964) 373.
13 J. Goubeau, *Angew. Chem.*, 81 (1969) 343.
14 G.L. Simon and L.F. Dahl, *J. Amer. Chem. Soc.*, 95 (1973) 2175.