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Preliminary communication

MANGANESE(I) CARBONYLS WITH σ-BONDED ALKYNYL LIGANDS. THE CRYSTAL STRUCTURE OF $[Co_2(CO)_6][PhC{\equiv}CMn(CO)_4\{P(C_6H_{11})_3\}]$

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Summary

The preparation of some σ-alkynylmanganese(I) carbonyl complexes is described. The crystal structure of the compound $[Co_2(CO)_6][PhC{\equiv}CMn(CO)_4(PCy_3)]$ (Cy = cyclohexyl) has been established by X-ray diffraction.

Octahedral manganese(I) carbonyl derivatives containing σ-bonded alkynyl ligands have been little studied, and as far as we are aware, only the compound $PhC{\equiv}CMn(CO)_5$ [1] and the somehow related acetylide complex $BrMn(CO)_4C{\equiv}CPPh_3$ [2] have been reported. We have found that various new types of σ-alkynyl complexes of manganese(I) can be prepared from halocarbonyls $BrMn(CO)_nL_{5-n}$ or perchlorato complexes $O_3ClOMn(CO)_nL_{5-n}$ by means of the general reactions 1 and 2; the ligands are phosphines, diphosphines or phosphites; R = Ph or Bu^t.

$$BrMn(CO)_nL_{5-n} \xrightarrow[Cl_2CH_2/H_2O]{AgBF_4/HC{\equiv}CR} RC{\equiv}CMn(CO)_nL_{5-n} \quad (1)$$

$$O_3ClOMn(CO)_3L_2 \xrightarrow[THF]{HC{\equiv}CR/KOH} RC{\equiv}CMn(CO)_3L_2 \quad (2)$$

(L_2 = dppe or bipy; R = H or Ph)

The products are fairly stable crystalline solids and, in contrast to the inertness of the "parent" $PhC{\equiv}CMn(CO)_5$ [1], can be used as precursors for other

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TABLE 1

ANALYTICAL, INFRARED, AND MELTING POINT DATA FOR SOME σ-ALKYNYL COMPOUNDS

	Compound	Analysis (Found (calcd.) (%))		IR frequencies [a] (cm^{-1})		m.p. (°C)	Reaction
		C	H	(C—C)	(C—O)		
I	*cis*-$[Mn(CO)_4(PCy_3)(C{\equiv}CPh)]$	65.77 (65.69)	6.91 (6.98)	2106w	2074m; 1983s,br;1949s	162	1
II	*fac*-$[Mn(CO)_3(dppe)(C{\equiv}CPh)]$	69.20 (69.60)	4.48 (4.58)	2097w	2019s,1943s,1920s	168	1
III	*fac*-$[Mn(CO)_3(dppe)(C{\equiv}CH)]$	65.94 (66.20)	4.35 (4.48)	—	2024s,1942s,1918s	166	2
IV	*mer*-$[Mn(CO)_3(PCy_3)_2(C{\equiv}CPh)]$	69.76 (70.48)	9.13 (8.93)	2093w	2009w,1913s,1885m	175	3a
V	$[Mn(CO)(dppe)_2(C{\equiv}CPh)]$	74.65 (74.69)	5.76 (5.44)	2056w	1832m	145	3b

[a] In Cl_2CH_2.

derivatives, by thermally- or UV-promoted replacement of CO by other ligands L such as phosphines or isocyanides, as shown in equations 3a and 3b.

$$PhC{\equiv}CMn(CO)_4(PCy_3) \xrightarrow{L} PhC{\equiv}CMn(CO)_3(PCy_3)(L) \quad (3a)$$

$(L = PCy_3, CNBu^t)$

$$PhC{\equiv}CMn(CO)_3(dppe) \xrightarrow[Cl_2CH_2,\ h\nu]{dppe} PhC{\equiv}CMn(CO)(dppe)_2 \quad (3b)$$

Table 1 lists analytical, infrared and melting point data for some representative compounds made by reactions 1, 2 and 3.

The acetylenic-like nature of compounds $PhC{\equiv}CMn(CO)_nL_{5-n}$ was clearly demonstrated by treating *cis*-$PhC{\equiv}CMn(CO)_4(PCy_3)$ with $Co_2(CO)_8$ in hexane at room temperature (reaction 4). The product $[Co_2(CO)_6][PhC{\equiv}CMn(CO)_4(PCy_3)]$ (VI) could be isolated as dark green crystals (m.p. 126°C dec.) ($\bar{\nu}$(CO)-at 2082w, 2057w, 2035s, 2014m, 1998m, 1984vw, 1968w and 1958w cm^{-1} in hexane. The structure of VI was determined by an X-ray analysis; suitable crystals being obtained from a CH_2Cl_2/EtOH mixture.

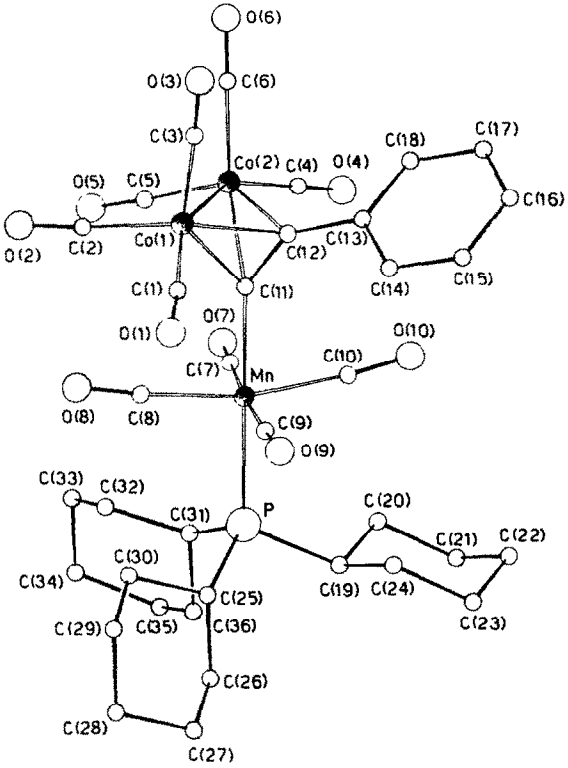

Fig. 1. A view of the compound $[Co_2(CO)_6][PhC{\equiv}CMn(CO)_4(PCy_3)]$. Important bond distances (Å) and angles (°): Co(1)—Co(2) 2.469(3), Co(1)—C(12) 2.002(10), Co(2)—C(12) 1.971(11), Co(1)—C(11) 2.053(9), Co(2)—C(11) 2.045(9), Mn—P 2.362(3), Mn—C(11) 2.063(7), C(11)—C(12),1.313(11); P—Mn—C(11) 178.8(3), Mn—C(11)—C(12) 144.5(8), C(11)—C(12)—C(13) 143.3(9).

Crystal data: $C_{36}H_{38}Co_2MnO_{10}P \cdot \frac{1}{2}C_2H_5OH$, M = 1715.01, monoclinic, space group $P2_1/c$, a 13.545(5), b 18.691(7), c 16.944(9) Å, β 110.89(3)°, V 4008(3) Å^3, Z = 4, D_c 1.421 g cm^{-3}, $F(000)$ 1764, μ(Mo-K_α) 12.06 cm^{-1}. The intensities of 6370 independent reflections were collected on a Siemens AED single-crystal diffractometer (with θ in the range $3 \leqslant \theta \leqslant 24°$); niobium-filtered Mo-$K_\alpha$ radiation and the $\theta/2\theta$ scan technique were used. The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares on the basis of 3402 observed reflections (having $I \geqslant 2\sigma(I)$) to an R value of 0.061. The atomic coordinates for the non hydrogen atoms, the calculated coordinates for the hydrogen atoms, and the thermal parameters are available on request from authors or from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW.

The structure of VI is shown in Fig. 1 together with the more significant bond distances and angles. The structure was mainly as expected, and is similar to that proposed for the known $[Co_2(CO)_6][PhC{\equiv}CFe(\eta\text{-}C_5H_5)(CO)L$ (L = CO, PMe_2Ph) [3], although no X-ray structures have been reported for these species.

In VI the acetylide ligand is σ-bonded to the manganese atom and π-bonded to both cobalt atoms. The Mn—C(11) bond distance (2.063(7) Å) is much longer than in $BrMn(CO)_4C{\equiv}CPPh_3$ (1.981(14) Å) [4] where the acetylide is only σ-bonded to the Mn atom. The interaction with the Co atoms also results in a lengthening of the acetylenic C—C bond (C(11)—C(12) 1.313(11) Å), which is very close to that of the standard ethylenic double bond length (1.337 Å), and in a marked deviation from linearity (Mn—C(11)—C(12) 144.5(8)°). In $BrMn(CO)_4C{\equiv}CPPh_3$ the acetylenic C—C bond length is 1.216(14) Å and the Mn—C—C angle is very close to 180° (176.3°) [4].

An unexpected feature of VI is that the PCy_3 ligand is *trans* to the acetylide ligand, whereas it was *cis* to this ligand in the starting complex. This indicates that in reaction 4 there has been a rearrangement of the $Mn(CO)_4(PCy_3)$ fragment.

The reactions of σ-alkynyl and their derivatives with some nucleophiles and electrophiles and with other metal carbonyls are now under investigation.

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