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Preliminary communication

σ-ALKYNYL COMPLEXES OF MANGANESE(I) AS LIGANDS. SYNTHESIS AND X-RAY STRUCTURE OF $\{[\eta^2\text{-Bu}^t\text{C}_2\text{Mn(CO)}_3(\text{dppe})]_2\text{Cu}\}(\text{PF}_6)$*

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Summary

The syntheses of complexes of the Group IB metals with η^2-bonded σ-alkynyl compounds of manganese(I) are described. The structure of the salt $\{[\eta^2\text{-Bu}^t\text{C}_2\text{Mn(CO)}_3(\text{dppe})]_2\text{Cu}\}(\text{PF}_6)\cdot\frac{1}{2}\text{Cl}_2\text{CH}_2$ (dppe = 1,2-bis(diphenylphosphino)ethane) has been determined by X-ray crystallography.

Some acetylide complexes of the type $\text{L}_n\text{MC}{\equiv}\text{CR}$ are known to coordinate to several Group IB metal—ligand fragments [1], but to date, no cationic species of the type $[(\text{L}_n\text{MC}_2\text{R})_2\text{M}']^+$ (M′ = Cu, Ag, or Au) have been reported.

We have found that the stable cationic species $\{[\eta^2\text{-Bu}^t\text{C}_2\text{Mn(CO)}_3(\text{dppe})]_2\text{Cu}\}(\text{PF}_6)$ (IIIa) and $\{[\eta^2\text{-Bu}^t\text{C}_2\text{Mn(CO)}_3(\text{dppe})][\text{P(C}_6\text{H}_4\text{Me-2)}_3]\text{Cu}\}(\text{PF}_6)$ (IVa) can be prepared almost quantitatively by means of the reactions shown in Scheme 1.

Complexes analogous to IIIa $\{[\eta^2\text{-Bu}^t\text{C}_2\text{Mn(CO)}_3(\text{dppe})]_2\text{M}\}^+$ with M = Ag (IIIb) or Au (IIIc) can be obtained by direct reaction of a two-fold excess of the σ-alkynyl complex $[\text{Bu}^t\text{C}_2\text{Mn(CO)}_3(\text{dppe})]$ (I) [2] with $[\text{Ag(NCMe)}_4]\text{BF}_4$ [3] or $\text{ClAu(C}_4\text{H}_8\text{S)}$ [4] and TlPF_6 respectively, and, when these silver and gold reagents are treated with a 1/1 mixture of the

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*Dedicated to Prof. R. Usón on the occasion of his 60th birthday.

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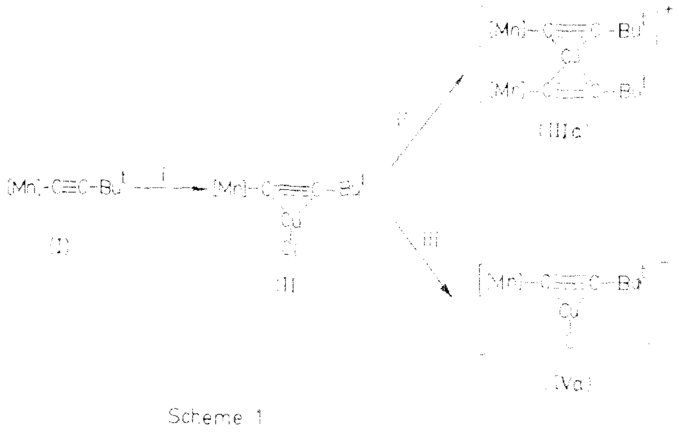

SCHEME 1. [Mn] = *fac*-$Mn(CO)_3(dppe)$, L = $P(C_6H_4Me\text{-}2)_3$ (i) CuCl in Cl_2CH_2; (ii) $[Mn]C{\equiv}CBu^t$ and $TlPF_6$ in Cl_2CH_2; (iii) L and $TlPF_6$ in Cl_2CH_2.

σ-alkynyl (I) and $P(C_6H_4Me\text{-}2)_3$ in Cl_2CH_2, the species analogous to IVa, i.e. $\{[\eta^2\text{-}Bu^tC_2Mn(CO)_3(dppe)][P(C_6H_4Me\text{-}2)_3]M\}^+$ with M = Ag (IVb) or Au (IVc) are formed.

The spectroscopic properties of the products are in accord with the structures shown in Scheme 1, and the monomeric nature of compound II is assumed by analogy with that of the analogous complex $\{[\eta^2\text{-}PhC_2Mn(CO)_3\text{-}(dppe)]CuCl\}$ which was established by X-ray crystallography [5]. The copper compound IIIa was unambiguously characterized by an X-ray diffraction study* and the structure is shown in Fig. 1 together with some significant bond distances and angles. The C(1), C(2), Mn(1), and Cu atoms, and the C(1′), C(2′), Mn(2), and Cu form planes with a dihedral angle between them of 71(1)°. As a result, steric interaction between the two $Mn(CO)_3(dppe)$ moieties makes the C(1)—Cu—C(1′) (158.4(5)°) angle larger than the C(2)—Cu—C(2′) (146.6(5)°) angle. The acetylenic C—C bond lengths, e.g. C(1)—C(2) 1.244(18) Å, are in the range expected for a C—C triple bond slightly elongated and, while the Mn—C—C angle is very close to 180° (Mn(1)—C(1)—C(2) 170.5(10)), the C—C—Bu^t is more deviated from linearity (C(1)—C(2)—C(3) 164.0(14)°).

Compound II also reacted with the tungsten carbyne $[W(\equiv CR)(CO)_2\text{-}(\eta^5\text{-}C_5H_5)]$ (R = $C_6H_4Me\text{-}4$) [6] and $TlPF_6$ to form $\{[Bu^tC_2Mn(CO)_3\text{-}(dppe)][W(\equiv CR)(CO)_2(\eta^5\text{-}C_5H_5)]Cu\}(PF_6)$ (V). Therefore II is a source of a cationic fragment of the general type $\{[\eta^2\text{-}RC_2Mn(CO)_3(dppe)]Cu\}^+$, the ability of such fragments to coordinate with other molecules such as isocyanides, acetylenes, other σ-alkynyl complexes and carbynes is now being studied.

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*Crystal data for IIIa: $C_{78}H_{66}O_6P_4Mn_2CuPF_6 \cdot \frac{1}{2}CH_2Cl_2$, F_W = 1494.09 monoclinic, *a* 25.441(4), *b* 14.862(3), *c* 20.892(4) Å; β 114.00(3)° V 7216(4) $Å^3$, $P2_1/n$, D_X 1.375 g cm^{-3}, Z = 4, F(000) 3076, $\lambda(Mo\text{-}K_\alpha)$ 0.71069 Å, $\mu(Mo\text{-}K_\alpha)$ 8.61 cm^{-1}. Room temperature, $R(R_W)$ = 0.074(0.081) for 5088 intensities with $I \geqslant 2.5\sigma(I)$.

The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW (Great Britain). Any request should be accompanied by a full literature citation for this communication.

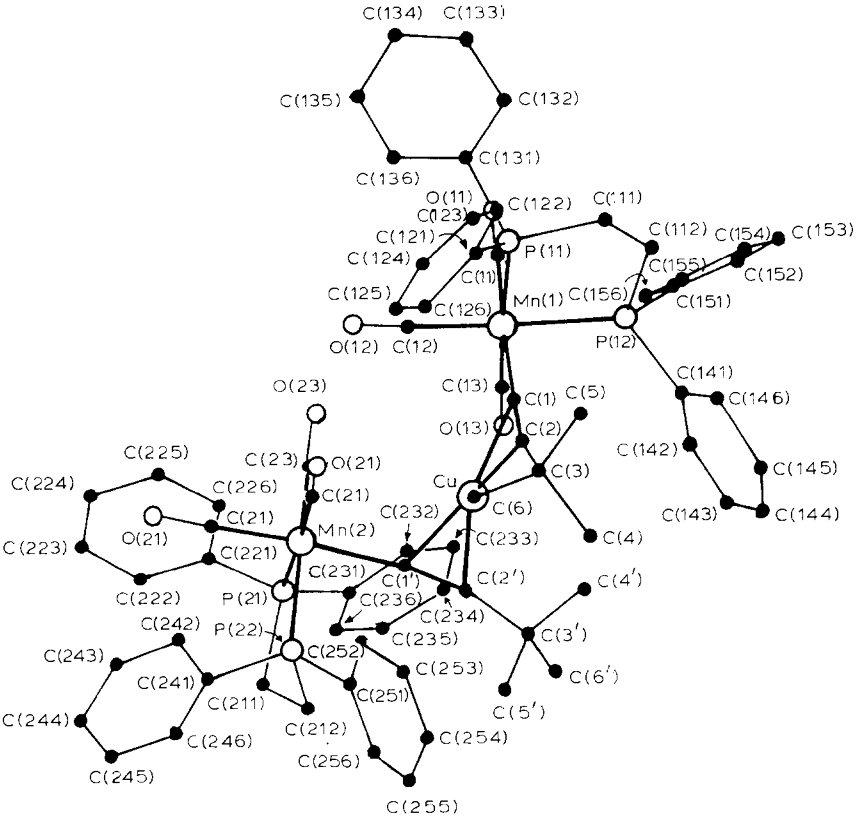

Fig. 1. A view of the molecule $\{[\eta^2\text{-Bu}^t\text{C}_2\text{Mn(CO)}_3\text{(dppe)}]_2\text{Cu}\}^+$ (IIIa), with some significant bond distances (Å) and angles (°). Cu—C(1) 2.078(13); Cu—C(1′) 2.086(11), Cu—C(2) 2.078(12); Cu—C(2′) 2.080(14); Mn(1)—C(1) 2.032(12); C(1)—C(2) 1.244(18); Mn—Cu (average) 3.472(2); Mn—P (average) 2.332(2); C(1)—Cu—C(2) 34.8(5); C(1′)—Cu—C(2′) 34.3(5); C(1)—Cu—C(1′) 158.4(5); C(2)—Cu—C(2′) 145.6(5); Mn(1)—C(1)—C(2) 170.5(10); C(1)—C(2)—C(3) 164.0(14). The dihedral angle between the planes C(1)CuC(2) and C(1′)CuC(2′) is 71(1)°.

Selected spectroscopic data: IR (cm^{-1}) in Cl_2CH_2. ^{1}H NMR (δ) and $^{31}\text{P}\{^1\text{H}\}$NMR (ppm to high frequency of external H_3PO_4, J in Hz) in Cl_3CD. Compound II IR: ν_{max}(CO) 2025s, 1947s, 1940s; ν(C≡C) 1983w; NMR: ^{1}H, 0.59(s, 9H, CMe_3), 3.06, 2.84(m, 4H, CH_2CH_2), 7.39—7.76(m, 20H, C_6H_5): ^{31}P, 75.8. IIIa IR: ν_{max}(CO) 2029s, 1947sh, 1937s, ν(C≡C) 1970w; NMR: ^{1}H, 0.43(s, 9H, CMe_3), 3.04(br, 4H, CH_2CH_2), 7.36(br, 20H, C_6H_5); ^{31}P, 73.8. (IIIb) NMR: ^{1}H, 0.47(s, 9H, CMe_3), 3.00, 3.20(br, 4H, CH_2CH_2); ^{31}P, 74.8. IIIc NMR: ^{1}H, 0.45(s, 9H, CMe_3), 2.95, 3.15(br, 4H, CH_2CH_2); ^{31}P, 76.0. IVa IR: ν_{max}(CO) 2024s, 1947s, 1935s, ν(C≡C) 2000; NMR: ^{1}H, 0.18(s, 9H, CMe_3), 2.49(s, 9H, $Me\text{C}_6\text{H}_4\text{P}$), 3.28, 3.06 (br, 4H, CH_2CH_2), 7.41(br, 20H, C_6H_5); ^{31}P, 72.3(s, 2P, dppe), −8.6(s, 1P, $\text{PC}_6\text{H}_4\text{Me-4}$). IVb NMR: ^{1}H, 0.29(s, 9H, CMe_3), 2.52(s, 9H, $Me\text{C}_6\text{H}_4\text{P}$), 3.24, 3.01(br, 4H, CH_2CH_2); ^{31}P, 73.0(s, 2P, dppe), −11.4 [d.d., 1P, $\text{P(C}_6\text{H}_4\text{Me-4)}_3$, $J(^{107}\text{Ag—P})$ 583.3, $J(^{109}\text{Ag—P})$ 673.7]. IVc NMR: ^{1}H, 0.28(s, 9H, CMe_3), 2.62(s, 9H, $Me\text{C}_6\text{H}_4\text{P}$), 2.96, 3.19(br, 4H, CH_2CH_2); ^{31}P, 74.3(s, 2P, dppe), 21.1(s, 1P, $\text{P(C}_6\text{H}_4\text{Me-2)}_3$). V NMR: ^{1}H, 0.32(s, 9H, CMe_3), 2.36(s, 3H, Me-4), 5.89 (s, 5H, C_5H_5), 3.1(m br., 4H, CH_2CH_2), 7.42 (v. br., 24 H, $\text{C}_6\text{H}_5\text{+C}_6\text{H}_4$).

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