

Preliminary communication

SYNTHESIS OF NEW HALOGEN-BRIDGED CATIONIC DIMANGANESE CARBONYL COMPOUNDS. X-RAY STRUCTURE OF $[\text{Mn}_2(\mu\text{-I})(\text{CO})_8(\mu\text{-Ph}_2\text{PCH}_2\text{PPh}_2)][\text{BF}_4]$

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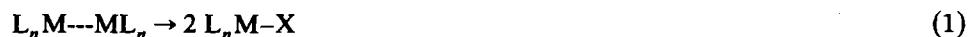
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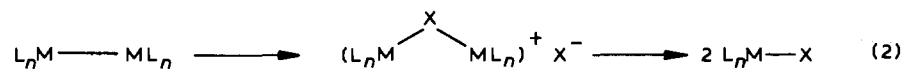
Summary

Binuclear halogen-bridged cationic carbonyl compounds of general formula $[\text{Mn}_2(\mu\text{-X})(\text{CO})_{10-2n}(\mu\text{-}\overline{\text{P}}\overline{\text{P}})_n]^+$, ($n = 1, 2$; $\text{X} = \text{Br}, \text{I}$; $\overline{\text{P}}\overline{\text{P}} = (\text{EtO})_2\text{POP}(\text{OEt})_2$, $\text{Ph}_2\text{PCH}_2\text{PPh}_2$) have been obtained by one or more of the following procedures: (a) halogen abstraction by silver(I) salts, from neutral binuclear compounds containing two terminal halogen ligands; (b) reactions of halogens with $\overline{\text{P}}\overline{\text{P}}$ -bridged derivatives of dimanganese(0) decacarbonyl; (c) reactions of these dimanganese(0) species with the cation $[\text{I}(\text{py})_2]^+$ in an acidic medium. The crystal structure of $[\text{Mn}_2(\mu\text{-I})(\text{CO})_8(\mu\text{-Ph}_2\text{PCH}_2\text{PPh}_2)][\text{BF}_4]$, obtained by the last procedure, has been elucidated by X-ray diffraction.

It is well known that metal–metal bonds in binuclear carbonyl compounds are cleaved by halogens to give the corresponding halides [1], eq. 1:



However, halogenation studies on $(\text{Cp})\text{M}(\text{CO})_3)_2$, ($\text{M} = \text{Mo}, \text{W}$) [2], $(\text{Cp})\text{Fe}(\text{CO})_2)_2$ [3,4], $(\text{Cp})\text{Ru}(\text{CO})_2)_2$ [5], and $\text{Fe}_2(\text{CO})_{6-x}\text{L}_x(\mu\text{-SR})_2$ [6] ($\text{L} = \text{P}$ -donor ligand), revealed that the reaction frequently proceeds through halogen-bridged cationic intermediates (eq. 2), the stabilities of which depend on the nature of the halogen, the metal-ligand fragment and the reaction conditions.



Nevertheless, in the halogenation reactions of dimanganese(0) decacarbonyl or its phosphine and arsine derivatives only neutral, terminal-halogen complexes have been so far observed [7–11].

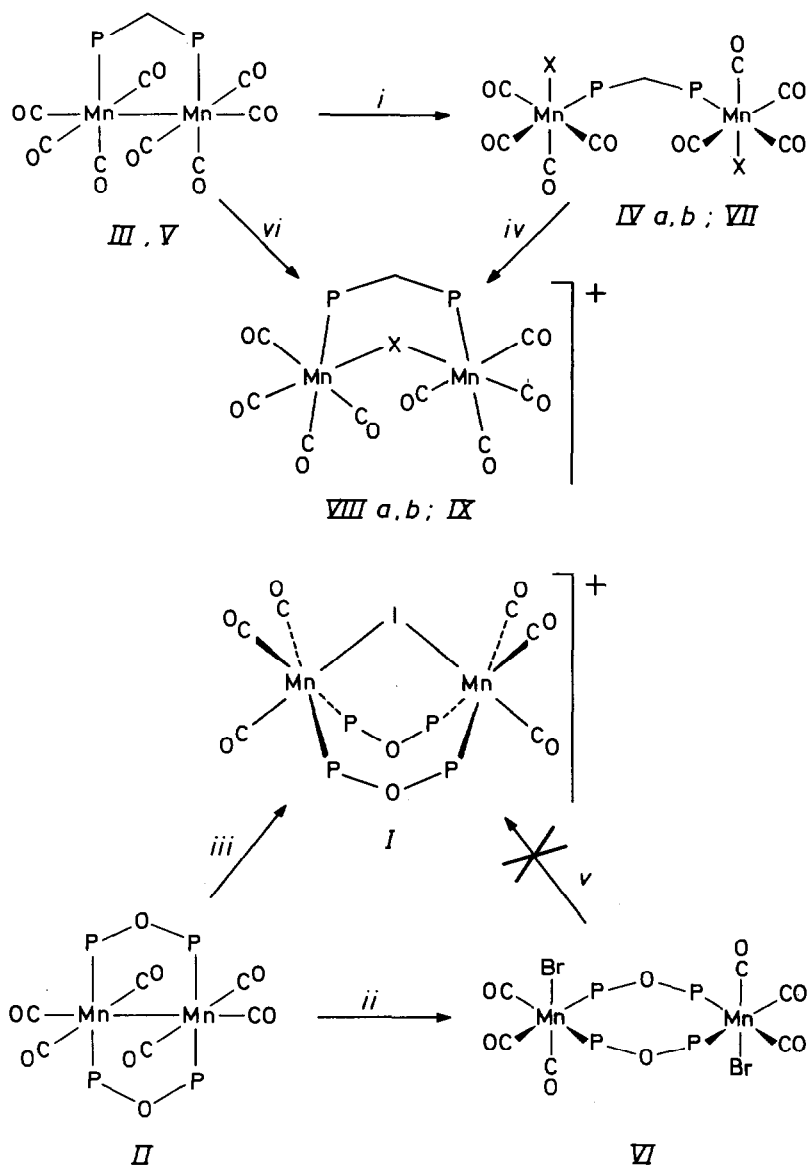
We report here the first observation of a cationic, halogen-bridged carbonyl compound, $[\text{Mn}_2(\mu\text{-I})(\text{CO})_6(\mu\text{-tedip})_2]\text{I}_3$ (I), formed as a result of the iodination of a derivative of dimanganese(0) decacarbonyl, $[\text{Mn}_2(\text{CO})_6(\mu\text{-tedip})_2]$ (II) (tedip = $(\text{EtO})_2\text{POP}(\text{OEt})_2$). We also describe a novel method for selectively obtaining similar iodine-bridged cationic complexes involving use of the cation $[\text{I}(\text{py})_2]^+$ (py = pyridine) as a reagent for adding "I⁺" to a metal–metal bond.

Reaction of Br_2 or I_2 with $\text{Mn}_2(\text{CO})_8(\mu\text{-tedip})$ (III) in light petroleum ether at room temperature (r.t.) affords the neutral complexes $\text{Mn}_2\text{X}_2(\text{CO})_8(\mu\text{-tedip})$ (IVa, IVb) (a: X = Br; b: X = I), which we previously obtained [12] from the reaction of tedip with $\text{XMn}(\text{CO})_5$, (reaction i in Scheme 1); similar results were observed in the halogenation of the related compounds $[\text{Mn}_2(\text{CO})_8(\mu\text{-dppm})]$ (V), [11] and $[\text{Mn}_2(\text{CO})_8(\mu\text{-Me}_2\text{AsC}=\text{C}(\text{AsMe}_2)\text{CF}_2\text{CF}_2)]$, [10]. By contrast, the nature of the product from the halogenation of the bis-substituted complex $[\text{Mn}_2(\text{CO})_6(\mu\text{-tedip})_2]$ (II) strongly depends on which halogen is used (reactions ii and iii in Scheme 1). Thus the bromination in CH_2Cl_2 or light-petroleum ether at 0°C or r.t. leads to the neutral $[\text{Mn}_2\text{Br}_2(\text{CO})_6(\mu\text{-tedip})_2]$ (VI) [12], while iodination at r.t. (light-petroleum ether/ CH_2Cl_2), gives only the stable 1/1 electrolyte $[\text{Mn}_2(\mu\text{-I})(\text{CO})_6(\mu\text{-tedip})_2]\text{I}_3$ (I); analytical and spectroscopic data * support the formulation for this compound; the two tedip bridges probably lie midway between mutually *cis*- and *trans*-positions (i.e. P–Mn–P angle between 90 and 180°, see figure in Scheme 1). Although during the bromination reaction (ii in Scheme 1) an unstable intermediate is observed, its IR spectrum (2055m, 1990s, 1960m, br cm^{-1} in CH_2Cl_2) suggests that it is an isomer of the final neutral product VI rather than a cationic bromide-bridged complex. These results contrast with those reported [11] for bromination of the related $[\text{Mn}_2(\text{CO})_6(\mu\text{-dppm})_2]$ which was found to give the mononuclear species *fac*- $\text{BrMn}(\text{CO})_3(\text{dppm})$, and may be associated with the more effective bridging function of the tedip ligand.

We have used two other methods to obtain selectively this type of cationic halogenide complex: In one of them the halogen bridge is formed by nucleophilic attack of a terminally coordinated halogen atom on another metal fragment from which the halogen ligand has been removed (usually with Ag^+ salts or AlX_3). Such a method has been previously employed to synthesize halogen-bridged cationic complexes of Fe [13,14], Mo [15] and the only known related manganese cations $[(\text{CO})_5\text{Mn}(\mu\text{-X})\text{Mn}(\text{CO})_5]^+$ [16]. Thus, addition of one equivalent of AgClO_4 to a solution of IVa,b or $[\text{Mn}_2\text{I}_2(\text{CO})_8(\mu\text{-dppm})]$ (VII), (iv in Scheme 1), affords, respectively, the cationic species $[\text{Mn}_2(\mu\text{-X})(\text{CO})_8(\mu\text{-tedip})][\text{ClO}_4]$ (VIIIa,b) and $[\text{Mn}_2(\mu\text{-I})(\text{CO})_8(\mu\text{-dppm})][\text{ClO}_4]$ (IX). However, the analogous reaction with the hexacarbonyl compound $[\text{Mn}_2\text{Br}_2(\text{CO})_6(\mu\text{-tedip})_2]$ (VI) (see v in Scheme 1) does not produce the corresponding bromide-bridged cationic complex, probably because of the strong barrier to the necessary geometric reorganisation.

The other synthetic procedure has not previously been described and we think

* 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).



SCHEME 1. (i) Br_2 or I_2 ; light-petroleum ether or CH_2Cl_2 ; r.t.; (ii) Br_2 ; CH_2Cl_2 ; r.t., 4 h; (iii) 2 equiv. I_2 ; light-petroleum ether/ CH_2Cl_2 (4/1); r.t.; 15 min; (iv) 1 equiv. AgClO_4 ; CH_2Cl_2 ; r.t.; 30 min; (v) $\text{X} = \text{Br}$; 1 equiv. AgClO_4 ; CH_2Cl_2 or toluene; r.t.; (vi) 1 equiv. $[\text{I}(\text{py})_2][\text{BF}_4]$ and 2 equiv. $\text{HBF}_4 \cdot \text{OEt}_2$; CH_2Cl_2 ; 0°C ; 15 min.

that it may have general application. It involves the insertion of a formally monopositive iodine atom into a metal-metal bond. Thus the reaction of V in CH_2Cl_2 at 0°C with $[\text{I}(\text{py})_2][\text{BF}_4]$ [17] in the presence of two equivalents of $\text{HBF}_4 \cdot \text{OEt}_2$ (to remove the pyridine ligand) gives high yields of $[\text{Mn}_2(\mu\text{-I})(\text{CO})_8(\mu\text{-dppm})][\text{BF}_4]$ (IX) (vi in Scheme 1); the spectroscopic data for the product are identical to those of the product from the halogen-abstraction reaction (iv in

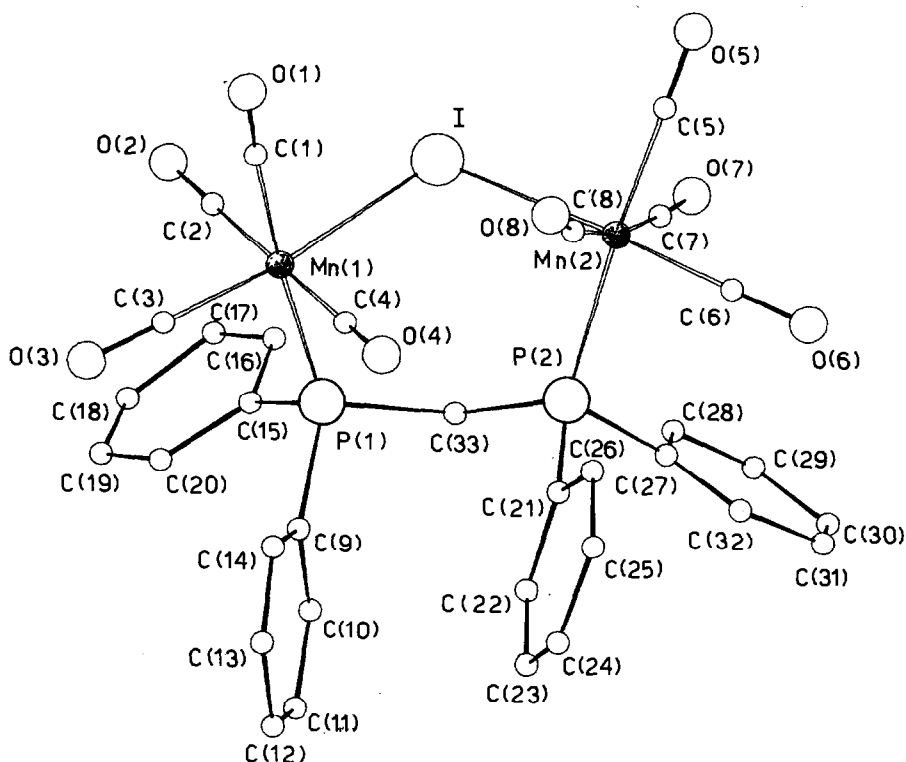


Fig. 1. View of the cation $[\text{Mn}_2(\mu\text{-I})(\text{CO})_8(\mu\text{-Ph}_2\text{PCH}_2\text{PPh}_2)]^+$ with the atom numbering scheme. Important bond distances (Å) and angles ($^\circ$): Mn(1)–I 2.689(3), Mn(1)–P(1) 2.350(4), Mn(2)–I 2.666(2), Mn(2)–P(2) 2.361(4), Mn(1)–C(carbonyls) in the range 1.78(1)–1.86(1), Mn(2)–C(carbonyls) in the range 1.78(1)–1.87(1); Mn(1)–I–Mn(2) 113.9(1), I–Mn(1)–P(1) 90.4(1), I–Mn(2)–P(2) 91.9(1).

Scheme 1); in addition the structure of IX was fully elucidated by an X-ray diffraction study.

Crystal data : $\text{C}_{33}\text{H}_{22}\text{BF}_4\text{IMn}_2\text{O}_8\text{P}_2$, M 932.06, orthorhombic, space group $P2_12_12_1$, a 11.256(7), b 28.191(13), c 11.155(8) Å, V 3540(4) Å³, Z = 4, D_c 1.749 g cm⁻³, $F(000)$ 1832, $\mu(\text{Mo-K}\alpha)$ 17.05 cm⁻¹. The intensities of 4357 independent reflections were determined on a Siemens AED diffractometer (with θ in the range 3–27 $^\circ$); 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 3277 observed reflections (with $I \geq 2\sigma(I)$) to R and R_w values of 0.047 and 0.062 respectively*.

* Selected spectroscopic data for new compounds. (IR data in cm⁻¹, measured in CH₂Cl₂; ¹H NMR data in ppm relative to internal TMS; ³¹P{¹H} data in ppm relative to external 85% H₃PO₄)

Compound I: $\nu(\text{CO})$: 2064s,sh, 2056vs, 2004s, 1971s; ¹H NMR (CDCl₃): 4.3 (m,OCH₂,2H), 1.5(t,7Hz,CH₃,3H); ³¹P{¹H} NMR (CD₂Cl₂, -60 $^\circ$ C): 149.25. Compound VIIIa: $\nu(\text{CO})$: 2126m, 2105ms, 2059s,sh, 2046vs, 2007s; ¹H NMR (CDCl₃): 4.6(m,OCH₂,2H), 1.5(t,7Hz,CH₃,3H); ³¹P{¹H} NMR (CDCl₃): 140.8. Compound VIIIb: $\nu(\text{CO})$: 2118m, 2105ms, 2040vs, 2010s. ¹H NMR (CDCl₃): 4.6(m,OCH₂,2H), 1.5(t,7Hz,CH₃,3H); ³¹P{¹H} NMR (CDCl₃): 141.1. Compound IX (BF₄⁻ salt): $\nu(\text{CO})$: 2144m, 2102ms, 2047s, 2034vs, 1997s; ¹H NMR (CDCl₃): 7.34(m,br,Ph,2OH), 4.4(t,12.5Hz,CH₂,2H); ³¹P{¹H} NMR (CH₂Cl₂,ext.lock D₂O): 33.4

Satisfactory elemental (C,H) analysis were obtained for all the above compounds, which also showed the expected molar conductivities in Me₂CO or MeNO₂ for 1/1 electrolytes.

The structure of the cation of IX is shown in Fig. 1 together with some important bond distances and angles. In the binuclear cation the iodine atom bridges the two metals as well as the dppm ligand through the two P atoms. Each metal completes its slightly distorted octahedral coordination with four carbon atoms from carbonyl groups.

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