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Preliminary communication

NEW TETRAETHYLDIPHOSPHITE-BRIDGED DINUCLEAR MANGANESE(I) CARBONYL COMPLEXES; SYNTHESIS OF μ-HYDRIDE-BROMIDE COMPOUNDS $Mn_2(\mu\text{-}H)(\mu\text{-}Br)(CO)_{8-2n}(tedip)_n$ (n = 1, 2; tedip = $(EtO)_2POP(OEt)_2$). CRYSTAL STRUCTURES OF $Mn_2(\mu\text{-}Br)_2(CO)_4(tedip)_2$ AND $Mn_2(\mu\text{-}H)(\mu\text{-}Br)(CO)_4(tedip)_2$

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Summary

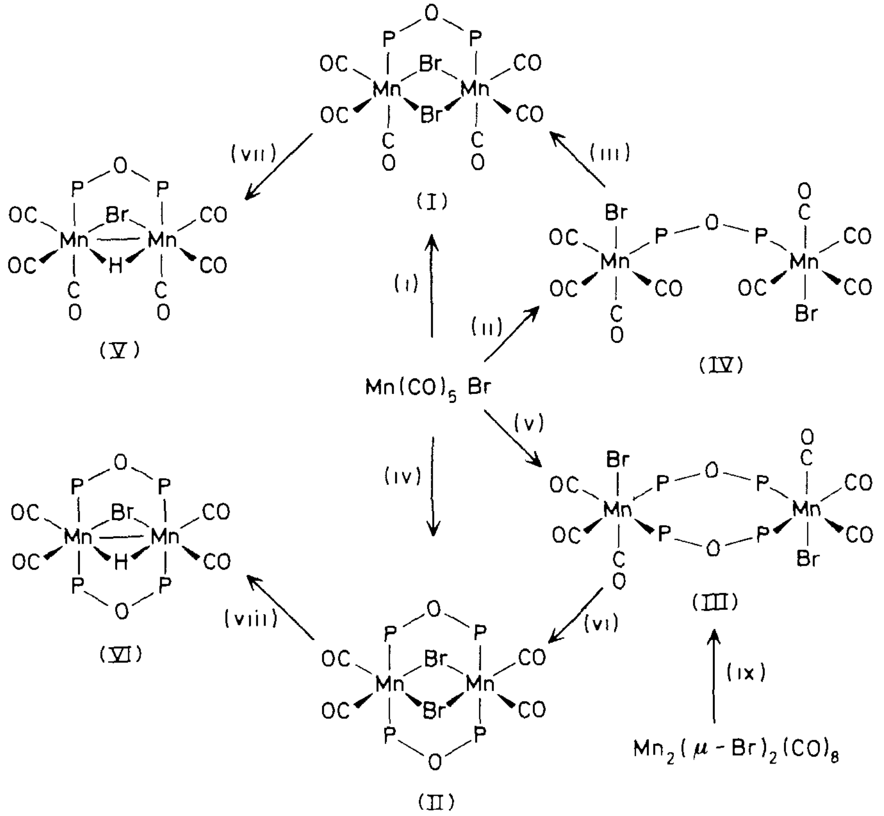
Carbonyl replacement reactions of $MnBr(CO)_5$ with the bridging ligand $(EtO)_2POP(OEt)_2$ (tedip) give $Mn_2Br_2(CO)_{10-2n}(\mu\text{-tedip})_n$ (n = 1, 2), or $Mn_2(\mu\text{-}Br)_2(CO)_{8-2n}(\mu\text{-tedip})_n$ (n =1, 2); the latter complexes are reduced by Na/Hg to afford, after acidification, red crystals of the doubly bridged complexes $Mn_2(\mu\text{-}H)(\mu\text{-}Br)(CO)_{8-2n}(\mu\text{-tedip})_n$ (n = 1, 2). The crystal structures of $Mn_2(\mu\text{-}Br)_2(CO)_4(tedip)_2$ and $Mn_2(\mu\text{-}H)(\mu\text{-}Br)(CO)_4(tedip)_2$ have been determined.

Introduction

Phosphorus donor ligands of the type R_2PXPR_2, where X is a methylene [1] or amino [2] group, have been extensively used because of their ability to bridge two transition metal centers, though the formation of four-membered chelate rings in their complexes is also known [1,2]. Tetraethyldiphosphite (tedip), which belongs to the same class of ligands, predominantly shows the bridging mode of coordination, forming bimetallic species, although so far only a few such complexes have been reported [3—6]. We have now synthesized new dibromide bridged dinuclear manganese(I) carbonyl complexes containing also bridging tetraethyldiphosphite, $Mn_2(\mu\text{-}Br)_2(CO)_{8-2n}(\mu\text{-tedip})_n$ (n = 1, 2), which are precursors of new μ-hydride derivatives containing the $Mn(\mu\text{-}H)(\mu\text{-}Br)Mn$ ring, which were obtained by reduction without disruption of the $Mn_2(\mu\text{-tedip})_n$ moiety.

Results and discussion

$MnBr(CO)_5$ reacts with tedip with evolution of carbon monoxide to give I (65%) or II (75%) as air-stable yellow-orange crystals, depending upon the reaction conditions, (Scheme 1, (i) and (iv)). The structures of these compounds are based on spectroscopic data*; significantly, the infrared spectra of



SCHEME 1. (i) Ligand/Mn 0.5/1, 90 min, refluxing hexane. (ii) ligand/Mn 0.5/1, 75 min, 45°C hexane. (iii) 60 min, refluxing hexane. (iv) ligand/Mn 1/1, 60 min, refluxing toluene. (v) ligand/Mn 1/1, 10 min, refluxing benzene. (vi) 90 min, refluxing benzene. (vii) THF, Na/Hg; H_3PO_4(aq.). (viii) THF, Na/Hg; HCl(g). (ix) excess of ligand, 30 min, refluxing hexane.

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*Key spectroscopic data for new compounds. Compound I: ν(CO) (hexane), 2070 s, 2052 s, 1987 vs, 1981 vs and 1944 vs cm^{-1}; ^1H NMR ($CDCl_3$), δ 4.44 (m, OCH_2), 1.50 (m, CH_3) ppm; $^{31}P\{^1H\}$ NMR 147.0 (s) ppm. Compound II: ν(CO) (CH_2Cl_2), 1957 s and 1888 s cm^{-1}; ^1H NMR ($CDCl_3$), δ 4.37 (m, OCH_2), 1.38 (m, CH_3) ppm; $^{31}P\{^1H\}$NMR, 162.2 (s) ppm. Compound III: ν(CO) (CH_2Cl_2), 2041 s, 1981 s and 1942 s cm^{-1}; ^1H NMR ($CDCl_3$), δ 4.28 (m, OCH_2), 1.34 (m, CH_3) ppm; $^{31}P\{^1H\}$NMR, 141.0 (s) ppm. Compound V: ν(CO) (hexane), 2064 s, 2032 s, 1985 s, 1969 s, and 1948 vs cm^{-1}; ^1H NMR ($CDCl_3$), δ 4.06 (m, OCH_2), 1.34 (m, CH_3), −15.3 (triplet, J(P—H) 28.4 Hz, MnHMn) ppm; $^{31}P\{^1H\}$NMR, 158.3 (s) ppm. Compound VI: ν(CO) (CH_2Cl_2), 1976 m, 1954 s and 1894 s cm^{-1}; ^1H NMR ($CDCl_3$), δ 3.98 (m, OCH_2), 1.26 (m, CH_3), −15.2 (quintet, J(P—H) 24.0 Hz, MnHMn); $^{31}P\{^1H\}$NMR, 168.7 (s) ppm.

I and II show, respectively, five and two strong absorptions in the ν(CO) range, as expected for the proposed local C_{2v} and D_{2h} symmetry. The structure of II has been confirmed by a single-crystal X-ray study*. It is shown in Fig. 1 together with the more significant bond distances and angles. The complex has an imposed crystallographic C_i symmetry with a non-bonding Mn. . .Mn distance (3.517 (4) Å) shorter than in the bromide bridged

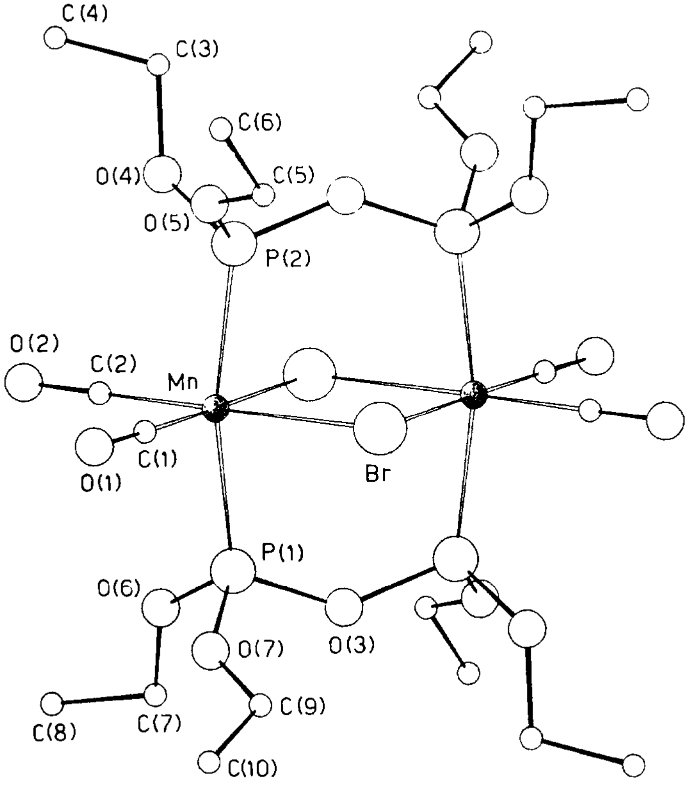

Fig. 1. A view of the complex [$Mn_2Br_2(CO)_4(tedip)_2$] (II). Important bond distances (Å) and angles (°): Mn—Br 2.525(3), Mn′—Br 2.522(4), Mn—P(1) 2.241(6), Mn—P(2) 2.238(6); Mn—Br—Mn′ 88.4(1), P(1)—Mn—P(2) 167.6(2).

***Crystal data:* Compound II, $C_{20}H_{40}Br_2Mn_2O_{10}P_4$, M = 834.11, orthorhombic, space group *Pbca*, a 15.378(4), b 16.327(5), c 14.453(4) Å, U 3629(2) Å^3, $Z = 4$, D_c 1.527 g cm^{-3}, $F(000) = 1680$, μ(Mo-K_α) 30.64 cm^{-1}. The intensities of 2845 independent reflections were collected on a Philips PW-1100 diffractometer (with θ in the range 3—24°); graphite-monochromated Mo-K_α 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 1164 observed reflections (having $I \geqslant 3\sigma(I)$) to an R value of 6.5%.

Compound VI: $C_{20}H_{41}BrMn_2O_{10}P_4$, M = 755.21, orthorhombic, space group *Pbca*, a 33.066(22), b 14.435(7), c 14.806(7) Å, U 7067(7) Å^3, $Z = 8$, D_c 1.420 g cm^{-3}, $F(000) = 3088$, μ(Mo-K_α) 20.25 cm^{-1}. The intensities of 5589 independent reflections were collected on a Siemens AED diffractometer (with θ in the range 3—24°); Nb-filtered Mo-K_α 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 2406 observed reflections (having $I \geqslant 2\sigma(I)$) to an R value of 8.0%. The atomic coordinates for II and VI are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW.

$Mn_2(\mu\text{-}Br)_2(CO)_8$ [7] (3.743 (8) Å)). It seems that tedip shows special ability to behave as bridging ligand, since analogous reactions with $Ph_2PCH_2PPh_2$ (dppm), gave mononuclear substituted complexes $MnBr(CO)_{5-2n}(dppm)_n$ (n = 1, 2) [8] or $MnBr(CO)_2(dppm)_2$ [9] in which the diphosphine is acting as chelate or/and monodentate ligand.

Periodical monitoring of the reactions by infrared spectroscopy allows the detection of transitory carbonyl species, and some of them can be identified when the temperature and reaction times are carefully controlled. Thus, heating a solution of equimolar amounts of $MnBr(CO)_5$ and tedip in benzene under reflux for 10 min (Scheme 1 (v)) gives an unseparable mixture, in which III is the major component. When hexane is used instead of benzene, other minor carbonyl species can be detected but these have not yet been characterized. Nevertheless, compound III can be isolated (50%) as yellow crystals by refluxing a mixture of $Mn_2(\mu\text{-}Br)_2(CO)_8$ and an excess of tedip in hexane, then evaporating off some of the solvent and keeping the residual solution at 0°C. Similarly, reaction (ii) (Scheme 1) gives mainly IV, which was isolated as yellow-orange crystals (40%) by cooling; ν(CO) 2105 m, 2044 s, 2024 vs,

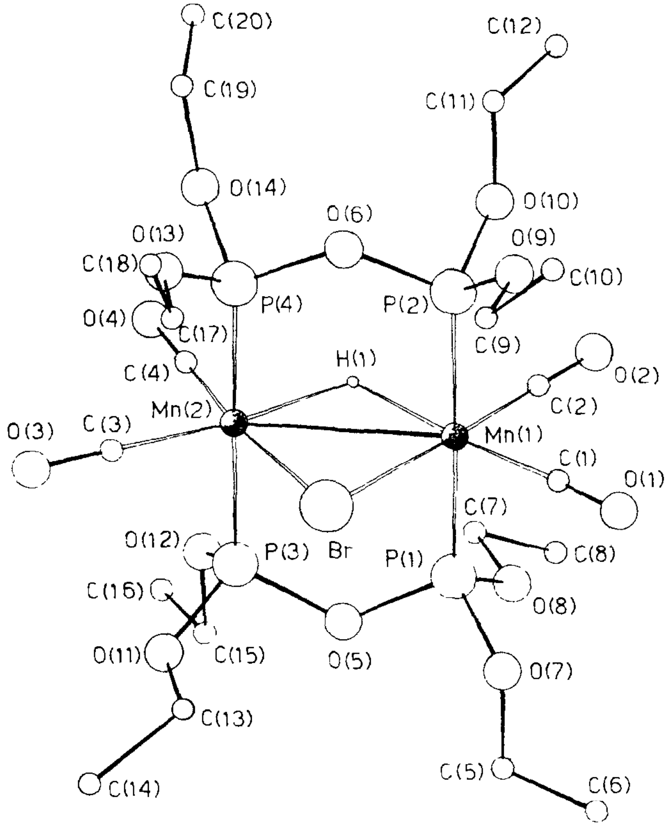

Fig. 2. A view of the complex $[Mn_2(\mu\text{-}H)(\mu\text{-}Br)(CO)_4(tedip)_2]$ (VI). Important bond distances (Å) and angles (°): Mn(1)—Br 2.477(4), Mn(2)—Br 2.484(4), Mn(1)—P(1) 2.211(5), Mn(1)—P(2) 2.209(5), Mn(2)—P(3) 2.212(5), Mn(2)—P(4) 2.216(5); Mn(1)—Br—Mn(2) 72.6(1), P(1)—Mn(1)—P(2) 176.1(2), P(3)—Mn(2)—P(4) 178.9(2).

1970 s, 1988 s cm^{-1} (hexane). Compounds III and IV undergo decarbonylation upon prolonged heating (Scheme 1, (vi) and (iii)), to give II and I, respectively, a process which leads to formation of the doubly bromide-bridged species, and which is similar to that well known for the preparation of $Mn_2(\mu\text{-Br})_2(CO)_8$ from $MnBr(CO)_5$ [10].

Treatment of tetrahydrofuran solutions of I and II with a large excess of sodium amalgam after 30 min gives highly air-sensitive red coloured solutions. Their infrared spectra show new $\nu(CO)$ absorptions shifted to lower energies, suggesting the formation of carbonyl anionic species probably with a single bromide bridge of the type $[\overline{\mathrm{Mn}(\mu\text{-Br})\mathrm{Mn}}]^-$. When these filtered solutions are treated with acids, the doubly (hydride and bromide) bridged complexes V (84%) and VI (80%) (Scheme 1) can be isolated as red air-stable crystals. The structures are in accordance with the spectroscopic data and that of VI was confirmed by a single-crystal X-ray analysis. It is depicted in Fig. 2 the caption to which lists the more important bond distances and angles. Because of the presence of the hydride bridge, the Mn—Mn distance is much shorter (2.936 (3) Å) than in II and is consistent with a single metal—metal bond (compared to the Mn—Mn bond distance in $Mn_2(CO)_{10}$ [11] (2.9038 (6) Å)). Attempts to obtain doubly hydride bridged species by treatment of I, II, V or VI with several reducing agents were unsuccessful.

Other aspects of the reactions of the carbonyl anionic precursors of V and VI and synthetic routes to dihydride species are now under further investigation.

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