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Preliminary communication

PHOTOCHEMICAL DECARBONYLATION OF $Mn_2(\mu\text{-}PPh_2)_2(CO)_8$ TO FORM $Mn_2(\mu\text{-}PPh_2)_2(\mu\text{-}CO)(CO)_6$ WITH A SEMI-BRIDGING CARBONYL

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Summary

The facile preparation of $Mn_2(\mu\text{-}PPh_2)_2(\mu\text{-}CO)(CO)_6$ by photochemical decarbonylation of $Mn_2(\mu\text{-}PPh_2)_2(CO)_8$ with visible light is reported. The product has a Mn—Mn single bond (281.2(2) pm) and a semi-bridging carbonyl group. The product reverts easily to the starting complex upon exposure to carbon monoxide gas.

During ESR studies of ion radicals derived from $M_2(\mu\text{-}EPh_2)_2(CO)_8$ (M = Mn, V; E = As, P) [1], a halocarbon solution of $Mn_2(\mu\text{-}PPh_2)_2(CO)_8$ (1) was inadvertently exposed to sunlight. Upon this exposure, the colour of the dimanganese complex solution changed from pale yellow to deep red within a few minutes. Although the physicochemical properties of this class of complexes have been explored extensively [2,3], their photochemical behaviour is scarcely known. Thus we decided to examine the photochemistry of 1. We report here our preliminary results: 1 is photochemically decarbonylated to form $Mn_2(\mu\text{-}PPh_2)_2(\mu\text{-}CO)(CO)_6$ (2) and the decarbonylation is accompanied by an increase of the metal—metal bond order and semi-bridging of a carbonyl.

When a yellow solution of 1 [4] (440 mg) in CH_2Cl_2 (250 ml), cooled in an ice-water bath, was irradiated internally with visible light from a 150 W halogen lamp with rather vigorous Ar-bubbling, a dark red solution was obtained. The irradiation was continued until the absorbance ratio of $\{A(337\ \text{nm}) - A(308\ \text{nm})\}/A(337\ \text{nm})$ of the reaction solution exceeded 0.29; it took about 7 h. After the solution was passed through a short column of Florisil under Ar, the solvent was evaporated under vacuum and the residual products were recrystallized from a

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CH_2Cl_2/n-C_6H_{14} mixture under an inert atmosphere to give shiny purple-red crystals (170 mg). The crystalline product is practically stable in air for more than a month. A single crystal of the product was subjected to an X-ray diffraction study.

Crystal data: $C_{31}H_{20}Mn_2O_7P_2$, M = 676.3, monoclinic, space group $P2_1$, a 1249.1(3), b 1006.6(2), c 1246.1(3) pm, β 109.28(2)°, U 1478.9(7) × 10^6 pm^3, D_C 1.519 gm l^{-1}, Z = 2, graphite monochromatized Cu-K_α radiation, μ(Cu-K_α) 87.38 cm^{-1}. Intensity data were collected with a RIGAKU AFC-5 automated diffractometer (ω—2θ scan, θ_{max} = 60°). The structure was solved by the heavy-atom method and was refined by least-squares techniques, the final R-value being 5.5% for 2149 reflections for which $F_o \geqslant 3\sigma(F_o)$*.

The crystallographic analysis showed the product to be $Mn_2(\mu\text{-}PPh_2)_2(\mu\text{-}CO)(CO)_6$ with the structure illustrated in Fig. 1.

The fact that the distance between Mn(1) and C(7) is shorter than the sum of the Van der Waals radii, and the bond angles around C(7) indicate the C(7)O(7) carbonyl to be classified as the semi-bridging one [5,6]. The phosphido bridges

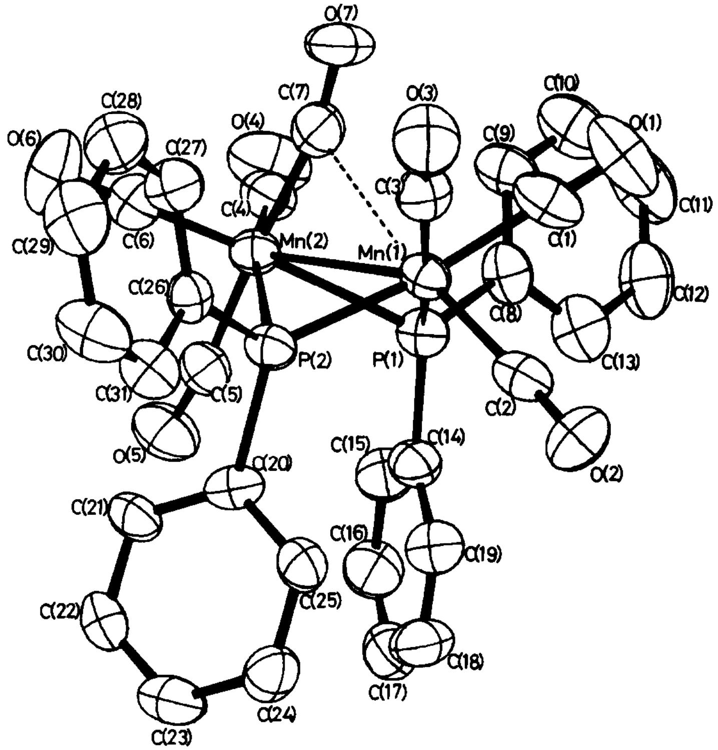

Fig. 1. Molecular structure of $Mn_2(\mu\text{-}PPh_2)_2(\mu\text{-}CO)(CO)_6$ (2). All hydrogen atoms are omitted for simplicity. Bond lengths: Mn(1)—Mn(2) 281.2(2), Mn(2)—C(7) 191.4(10), Mn(1)—C(7) 252.5(12) Mn(1)—P(1) 221.4(3), Mn(2)—P(1) 246.7(3), Mn(1)—P(2) 217.6(3), Mn(2)—P(2) 243.6(3) pm, angles: Mn(2)—C(7)—O(7) 163.0(11), Mn(1)—C(7)—O(7) 119.6(9)°, Mn(1)—P(1)—Mn(2) 73.6(1), Mn(1)—P(2)—Mn(2) 74.9(1)°.

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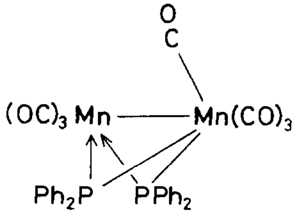
*The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

are shifted towards Mn(1) so as to compensate the semi-bridging of the carbonyl. Most of the unsymmetrically bridging carbonyls in the first-row transition metal clusters show ν(CO) below 1900 cm^{-1} [5]. However, the IR absorptions of 2 in the ν(CO) region are 2059s, 2012vs, 1995vs, 1985vs, 1954vs, 1940s, 1916s, and 1910s cm^{-1} in nujol mull, and 2075w, 2056m, 2003vs, 1975s, 1942s, and 1925s cm^{-1} in CH_2Cl_2 solution, respectively. The absence of ν(CO) below 1900 cm^{-1} for the present complex is rather abnormal. To our knowledge, only $Mn_2(CO)_6C_5H_5As(CH_3)_2$ [7] has been reported to be this type of complex.

The observed Mn—Mn distance of 281 pm indicates the existence of the Mn—Mn bond. On the basis of the 18-electron rule, a primitive expression for the bonding in this complex can be given as 3, 4, or a resonance hybrid of 3 and 4, with a formal Mn—Mn bond order of one, whereas the Mn—Mn bond order of 1 is zero [2].



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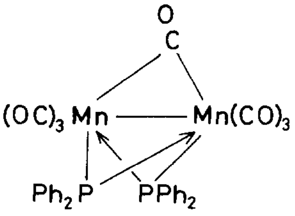

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When 2 in CH_2Cl_2 was exposed to carbon monoxide gas of atmospheric pressure at room temperature, 1 was smoothly regenerated (IR), implying that 2 can be a facile source for preparations of $Mn_2(\mu\text{-}PPh_2)_2(CO)_7L$.

$$1 \underset{CO}{\overset{h\nu\ (\lambda > 400\ \text{nm})}{\rightleftarrows}} 2$$

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