A New Carbonyl Bridging Mode: *X*-Ray Structure and Infrared Spectrum of the Metal Carbonyl Derivative $[Mn_2(CO)_5(Ph_2PCH_2PPh_2)_2]$

By RAY COLTON, CHRISTOPHER J. COMMONS, and BERNARD F. HOSKINS
(*Department of Inorganic Chemistry, University of Melbourne, Parkville, Victoria* 3052, *Australia*)

Summary The i.r. spectrum of the dimeric manganese(0) carbonyl complex $[Mn_2(CO)_5(Ph_2PCH_2PPh_2)_2]$ exhibits an unusually low carbonyl stretching frequency which a crystal structure determination has revealed to be caused by a carbonyl ligand bonded in a novel bridging manner.

REACTION of $[Mn_2(CO)_{10}]$ with $Ph_2PCH_2PPh_2$ (mdpp) (2 mol. equiv.) in n-decane under nitrogen yields the red diamagnetic complex $[Mn_2(CO)_5(mdpp)_2]$. Its solid-state i.r. spectrum contains four strong bands between 2000 and 1800 cm^{-1} (1942, 1903, 1860, and 1835 cm^{-1}) together with a strong band at 1645 cm^{-1}. The former absorptions were readily assigned to terminal carbonyl stretching vibrations, but the origin of the band at 1645 cm^{-1} was not obvious since it is lower than normal terminal or bridging carbonyl modes.[1] This anomaly has been resolved by a single-crystal *X*-ray diffraction study revealing a binuclear arrangement (shown in Figure 1) with one of the carbonyl ligands involved in an unusual bridging mode which is shown in Figure 2.

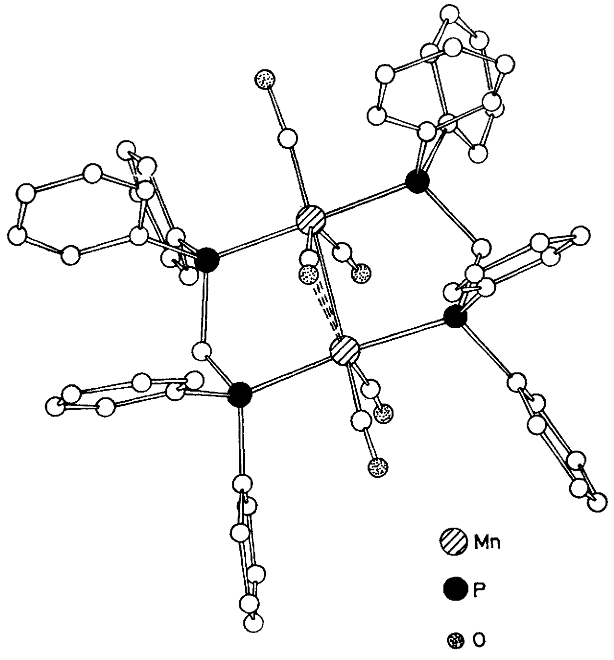

FIGURE 1. The atomic arrangement in $[Mn_2(CO)_5(mdpp)_2]$.

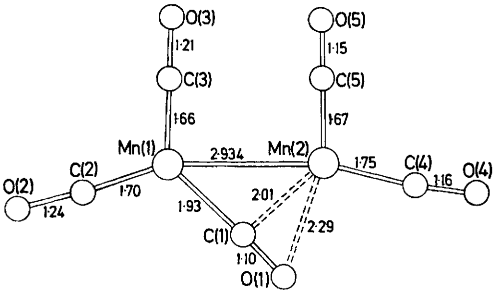

FIGURE 2. The manganese–carbonyl system. Bond lengths are given in Å and the average estimated standard deviations for the Mn–Mn, Mn–C, Mn–O, and C–O interatomic distances are 0·006, 0·03, 0·02, and 0·04 Å respectively. Important angles are: C(1)–Mn(1)–C(2) 120; C(2)–Mn(1)–C(3) 108; C(1)–Mn(1)–Mn(2) 43; C(3)–Mn(1)–Mn(2) 89; C(4)–Mn(2)–C(5) 99; Mn(1)–Mn(2)–C(5) 94; O(1)–Mn(2)–C(4) 98; C(1)–Mn(2)–C(4) 126; Mn(1)–Mn(2)–C(1) 41°. The estimated standard deviation for each bond angle is *ca.* 1°.

The separation of the Mn atoms [2·934(6) Å] is comparable with that of $[Mn_2(CO)_{10}]$ (ref. 2) indicating the presence of a metal–metal bond and the pair of metal atoms are bridged by two mdpp ligands in the manner shown in Figure 1. The two manganese and four phosphorus atoms are almost coplanar. The carbonyl groups also lie approximately in a plane which passes through the metal atoms and is nearly at right angles to the Mn_2P_4 plane. There are four terminal carbonyl ligands and one which is simultaneously bonded to the two manganese atoms in a manner different to the normal symmetrical bridging mode (Figure 2). The Mn(2)–C(1) and Mn(2)–O(1) distances of 2·01(3) and 2·29(2) Å respectively indicate strong interaction between this metal and the carbonyl group. We believe this bond is similar to that observed in many metal-olefin complexes, *e.g.*, Zeise's salt. This carbonyl is also bonded to the Mn(1) atom, but as would be expected the Mn(1)–C(1) distance [1·93(3) Å] is significantly larger than other Mn–C bond lengths. The arrangement of carbonyl ligands is consistent with the i.r. spectrum of the complex, and we assign the band at 1645 cm^{-1} to the stretching vibration of the bridging carbonyl. The diamagnetism of the complex is readily interpreted in terms of a metal–metal bond and by regarding the unique carbonyl as a four-electron donor with two electrons going to each Mn atom.

The stereochemistry of the manganese atoms is best regarded as being derived from trigonal bipyramidal geometry with the addition of a metal–metal bond through one edge of the trigonal planes. For both metals, phosphorus atoms occupy the axial positions and two terminal carbonyl ligands lie in the equatorial plane. In the case of Mn(1) the remaining trigonal position is occupied by C(1), whereas for Mn(2) this is occupied by the C(1)–O(1) bond.

The C–O distances range from 1·10(4) to 1·24 (4) Å, but unfortunately no definite conclusions can be drawn from the variation of carbonyl bond lengths because of the relatively high e.s.d.s associated with the structure analysis. The geometry and dimensions of the diphosphine ligands conform to expected values.

The crystal used for the *X*-ray work contained discrete molecules of $[Mn_2(CO)_5(mdpp)_2]$ together with molecules of n-hexane and dichloromethane incorporated in the lattice as solvent of crystallization.

Crystal data: $[Mn_2(CO)_5(mdpp)_2],CH_2Cl_2,C_6H_{14}$, $M =$ 1189·9, monoclinic, $a = 19{\cdot}65$, $b = 16{\cdot}90$, $c = 22{\cdot}25$ Å, $\beta = 130{\cdot}85°$, $U = 5589$ Å^3, space group *Cc*, $D_m =$ *ca.* 1·4, $D_c = 1{\cdot}42$ g cm^{-3}, $Z = 4$, Cu-K_α radiation (Ni-filtered), absorption corrections applied, Siemens automatic diffractometer. Heavy atoms were located using a three-dimensional sharpened Patterson map and the lighter atoms were found from successive electron-density maps. With all atoms, isotropic refinement has converged at a conventional *R*-factor of 0·105. Because of the relatively high thermal motion and somewhat unstable nature of the solvated crystals few reflections were observed beyond a Bragg angle of 40°. The number of independent, statistically significant reflections, on a 2σ criterion, was 1893. Crystals were mounted in a Lindemann glass capillary in the presence of mother liquor.

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[1] F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' 3rd edn , Interscience, New York, 1972, p. 692.

[2] L. F. Dahl and R. E. Rundle, *Acta Cryst.*, 1963, **16**, 419.