

Cyanide Ion as a Four-electron Donating Bridging Ligand in a Dimanganese Compound †

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Reaction of $[\text{Mn}_2(\text{CO})_5(\text{dppm})_2]$ ($\text{dppm} = \text{Ph}_2\text{PCH}_2\text{PPh}_2$) with $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ in the presence of acetonitrile gives the complex $[\text{Mn}_2\text{H}(\text{CO})_5(\text{NCMe})(\text{dppm})_2][\text{BF}_4]$ which reacts with cyanide ion to give $[\text{Mn}_2\text{H}(\text{CN})(\text{CO})_5(\text{dppm})_2]$, shown by ^1H , ^{31}P , and ^{13}C (90% enriched ^{13}C) n.m.r. to contain a terminal cyanide ligand. Decarbonylation with $\text{Me}_3\text{NO} \cdot 2\text{H}_2\text{O}$ gives $[\text{Mn}_2\text{H}(\text{CN})(\text{CO})_4(\text{dppm})_2]$, n.m.r. spectra of which at -90°C are consistent with an asymmetrically bridging CN, probably C-bonded at one Mn atom and η^2 -bonded at the other. The ^{13}C n.m.r. signal with coupling to ^{31}P changes from a 1:4:6:4:1 quintet ($J = 10.8$ Hz) at 25°C to a 1:2:1 triplet ($J = 22.1$ Hz) at -90°C because the CN group is oscillating between the two metal atoms.

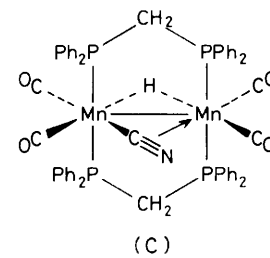
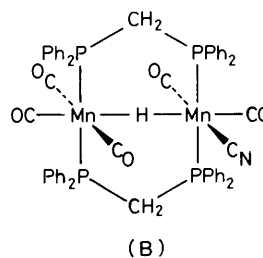
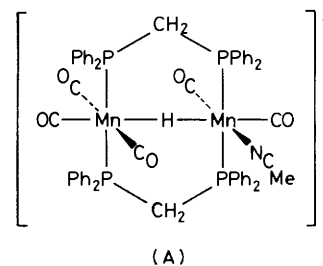
The bridging carbonyl in $[\text{Mn}_2(\text{CO})_4(\mu\text{-CO})(\text{dppm})_2]$ [$\text{dppm} = \text{bis}(\text{diphenylphosphino})\text{methane}$] is a four-electron donor.¹⁻⁴ The related compound $[\text{Mn}_2(\text{CO})_4(\mu\text{-}p\text{-MeC}_6\text{H}_4\text{NC})(\text{dppm})_2]$ similarly contains a four-electron donating isocyanide.^{5,6} These bridging ligands are bound at one manganese atom as in a normal terminal case and η^2 bound at the other. Cyanide ligands are normally terminal but are known to bridge in a linear M-C-N-M manner in polymeric metal cyanides or in binuclear compounds such as $[(\text{CN})_5\text{Co-C-N-Co}(\text{NH}_3)_5] \cdot \text{H}_2\text{O}$. Bridging through carbon only, as does CO, is unusual and while in $[\{\text{Cu}(\text{CN})(\text{NH}_3)\}_n]$ two Cu atoms are bridged by a C atom the N atom of the cyanide is further bonded to another copper atom.^{7,8} The compound $[\text{Mo}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_4(\text{CN})]^-$ seems to be the only known case of cyanide bridging asymmetrically as a four-electron donor like the $\mu\text{-CO}$ in $[\text{Mn}_2(\text{CO})_5(\text{dppm})_2]$.⁹

We now report a dinuclear cyanide complex of manganese with very similar characteristics to those of the above dimolybdenum compound.

Results and Discussion

Treatment of $[\text{Mn}_2(\text{CO})_5(\text{dppm})_2]$ with $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ in the presence of MeCN gives $[\text{Mn}_2\text{H}(\text{CO})_5(\text{NCMe})(\text{dppm})_2][\text{BF}_4]$ which, although difficult to crystallise, can be obtained as orange crystals. The ^1H n.m.r. spectrum contains a quintet ($\delta -23.87$) consistent with there being a Mn-H-Mn bridge (see Experimental section for spectroscopic data for all compounds). The $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectrum is a singlet, but probably due to accidental coincidence since closely related compounds such as the MeNC analogue show AA'BB' patterns. The Mn atoms are in different environments with a terminal MeCN at one of these. Furthermore, the non-equivalence of the CH_2 protons of dppm requires the MeCN to be *cis* to the hydride bridge and so the compound has the structure (A).

This acetonitrile compound is a very useful material from which to prepare various hydrido-bridged dimanganese compounds which will be described elsewhere. Here we describe just one example. The replacement of MeCN by cyanide ion gives the corresponding neutral compound $[\text{Mn}_2\text{H}(\text{CN})(\text{CO})_5(\text{dppm})_2]$, having structure (B) based on spectroscopic evidence. The ^1H n.m.r. (CH_2) signals show two well separated multiplets (δ 3.83 and 4.36) which give an AB quartet ($J_{\text{HH}} = 13.9$ Hz) with ^{31}P decoupling, while each multiplet when decoupled from the other shows a poorly resolved quintet ($J_{\text{PH}} = 6$ Hz) resulting from virtual coupling



to all four ^{31}P nuclei. The $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectrum is an AA'BB' system, while further coupling is observed in just one branch for the 90%-enriched compound $[\text{Mn}_2\text{H}(^{13}\text{CN})(\text{CO})_5(\text{dppm})_2]$ consistent with the cyanide bonding to just one Mn atom (Figure 1). The ^{13}C n.m.r. spectrum for this enriched sample shows a clear, well resolved 1:2:1 triplet for the ^{13}C group (δ 160.5, $^2J_{\text{PC}} = 23.8$ Hz) (Figure 2). We have briefly indicated previously that these pentacarbonyl complexes may be formed.¹⁰

Treatment of the terminal cyanide complex with $\text{Me}_3\text{NO} \cdot 2\text{H}_2\text{O}$ in a refluxing dichloromethane-methanol mixture (visible irradiation increases the rate and the yield of product) gives the decarbonylation product $[\text{Mn}_2\text{H}(\text{CN})(\text{CO})_4(\text{dppm})_2]$ referred to in the title of this paper. We believe that the cyanide ligand is bridging, acting as a four-electron donor to compensate for the loss of the CO ligand. There is just one reported example of such cyanide bridging.⁹ The X-ray single-crystal structure of $[\text{Mo}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_4(\text{CN})]^-$ shows an asymmetric CN bridge, although there is a complication with the cyanide disordered between the two possible asymmetrically bridging orientations. Even so, it was possible to interpret the structure in terms of a linear Mo-C-N arrangement at one Mo atom of a normal type and a η^2 -CN contact with the other metal atom. Coalescence behaviour of the C_5H_5 n.m.r. resonances indicates a low barrier ($\Delta G^\ddagger = 10.4 \pm 0.4$ kcal mol⁻¹) for cyanide oscillation. We believe that the

† Non-S.I. unit employed: 1 cal = 4.184 J.

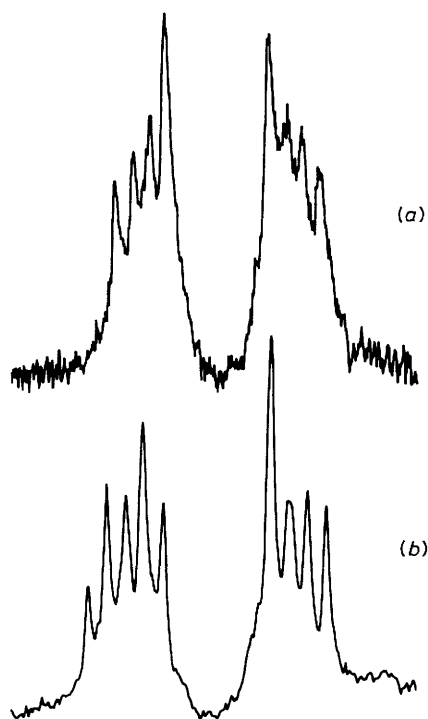


Figure 1. $^{31}\text{P}\{-^1\text{H}\}$ N.m.r. spectra (32 MHz) for (a) $[\text{Mn}_2\text{H}(\text{CN})(\text{CO})_5(\text{dppm})_2]$ in CDCl_3 at -40°C and (b) the same compound having 90% enriched ^{13}C N

cyanide ligand in $[\text{Mn}_2\text{H}(\text{CN})(\text{CO})_4(\text{dppm})_2]$ is similarly bound, the complex adopting structure (C), and similarly undergoes a rapid oscillation. Figures 2 and 3 illustrate the changes in the ^{13}C and ^{31}P n.m.r. spectra with temperature. The most striking feature is that the ^{13}C N signal is only a 1 : 2 : 1 triplet below -80°C . Between -80°C and -50°C this signal changes from a 1 : 2 : 1 triplet to a 1 : 4 : 6 : 4 : 1 quintet. The $\mu\text{-CN}$ ligand in the compound of structure (C) shows coupling to only two ^{31}P nuclei through the Mn atom to which it is linearly bonded ($^2J_{\text{PC}} = 22.1$ Hz) with unobservably small coupling to the other two ^{31}P nuclei. At -50°C when the oscillation is rapid, a time-averaged coupling to all four ^{31}P nuclei ($J_{\text{obs.}} = 10.8$ Hz) is observed. Since the time-averaged coupling constant is almost exactly half the real value of J_{PH} (22.1 Hz) the coupling of ^{13}C N to ^{31}P through the η^2 bond must be very close to zero. This coupling cannot be seen in the spectrum at -90°C . Associated coalescence of the ^{31}P signals is as expected (Figure 3), although the AA'BB' spectrum never resolves its fine-structure very well. This is probably because below -100°C the ^{31}P (162 MHz) spectrum reversibly broadens further and two new broad and weak signals between the original signals appear at -110°C . More than one species is present in solution. A possible explanation is that the M_2PCP rings have envelope conformations with the CH_2 group folded out of the plane of the other atoms but under normal conditions flipping of these rings is extremely rapid. At these lowest temperatures non-equivalent conformations with the CH_2 groups folded on the same or opposite sides are probably being frozen out. An X-ray crystal structure determination of the $\mu\text{-CN}$ complex is planned to establish the geometric details of the cyanide bridge and the conformations of the dppm bridges. The structure of $[\text{Mo}_2(\text{C}_3\text{H}_5)_2(\text{CO})_4(\text{CN})]^-$ is not sufficiently well defined to give accurate bond lengths for the bridging cyanide.

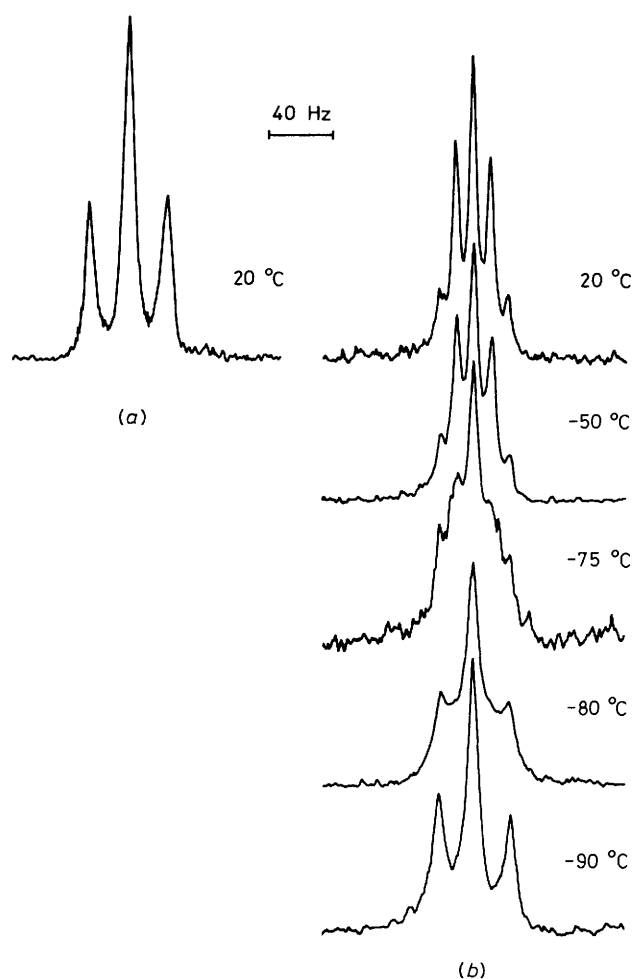


Figure 2. $^{13}\text{C}\{-^1\text{H}\}$ N.m.r. spectra (50.3 MHz) for the ^{13}C N group (90% isotopic enrichment) of (a) $[\text{Mn}_2\text{H}(\text{CN})(\text{CO})_5(\text{dppm})_2]$ in CDCl_3 and (b) $[\text{Mn}_2\text{H}(\text{CN})(\text{CO})_4(\text{dppm})_2]$ in CD_2Cl_2

Experimental

$[\text{Mn}_2(\text{CO})_5(\text{dppm})_2]$ was synthesised as reported previously.¹ Potassium cyanide (90% ^{13}C enriched) was purchased from Merck, Sharp and Dohme (Canada) Ltd. N.m.r. spectra were recorded on Varian XL-200 or Bruker WH-400 (Queen Mary College, London) spectrometers. Phosphorus-31 chemical shifts are referred to external H_3PO_4 (80%), with downfield shifts positive.

Preparation of $[\text{Mn}_2\text{H}(\text{CO})_5(\text{NCMe})(\text{dppm})_2][\text{BF}_4]$.— $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ (0.120 cm^3) was added to a stirred suspension of $[\text{Mn}_2(\text{CO})_5(\text{dppm})_2]$ (0.206 g) in acetonitrile (20 cm^3) and dichloromethane (20 cm^3) at room temperature. After 30 min a clear yellow-orange solution had formed and solid sodium bicarbonate was added to neutralise the excess of acid. The solvent was removed *in vacuo* from the solution, which had been filtered through Celite, to give an orange oil which crystallised on dissolving in chloroform (3 cm^3) and diethyl ether (3 cm^3) and cooling at -20°C , although this procedure did not always give crystals. The product was obtained as orange prisms (0.113 g, 49%) (Found: C, 57.65; H, 4.25; N, 1.1; P, 6.3. $\text{C}_{57}\text{H}_{48}\text{BF}_4\text{Mn}_2\text{NO}_5\text{P}_2$ requires C, 59.65; H, 4.2; N, 1.2; P, 10.8%). I.r.: $\nu(\text{CO})$ (CH_2Cl_2) 2 037w, 1 960vs, 1 940 (sh), and 1 893m cm^{-1} ; (Nujol) 2 031w, 1 957s, 1 945s (sh), 1 927s (sh), and 1 878m cm^{-1} . ^1H N.m.r. (CDCl_3):

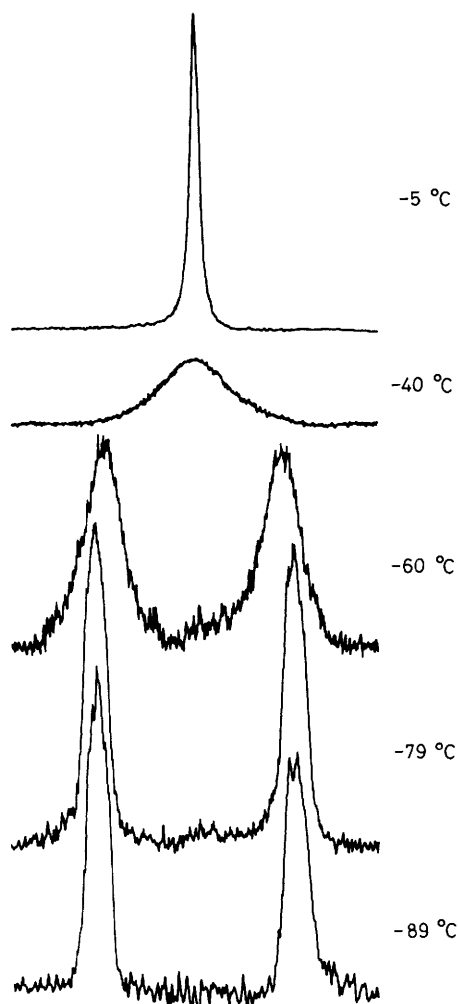


Figure 3. $^{31}\text{P}\{-^1\text{H}\}$ N.m.r. spectra (81 MHz) for $[\text{Mn}_2\text{H}(\text{CN})(\text{CO})_4(\text{dppm})_2]$ in CD_2Cl_2

δ 7.2–7.9 (m, C_6H_5), 3.96 (m) and 3.88 (m) (PCH_2P), 1.38 (s, CH_3CN), -23.87 (quintet, $J = 14.2$ Hz, MnHMn). $^{31}\text{P}\{-^1\text{H}\}$ N.m.r. (CDCl_3) (32 MHz at -40°C): δ 63.0 (s). The corresponding BPh_4^- salt also gave a singlet in the $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectrum at -40°C but an AA'BB' spectrum at 25°C : δ 64.7 (m) and 63.4 (m).

Preparation of $[\text{Mn}_2\text{H}(\text{CN})(\text{CO})_5(\text{dppm})_2]$.—The complex $[\text{Mn}_2\text{H}(\text{CO})_5(\text{NCMe})(\text{dppm})_2][\text{BF}_4]$ was synthesised as above from $[\text{Mn}_2(\text{CO})_5(\text{dppm})_2]$ (0.119 g, 0.12 mmol) but not isolated. Potassium cyanide (0.0795 g, 1.22 mmol) was added to a solution of the acetonitrile complex in methanol (15 cm^3) and the suspension stirred in the dark for 4 h. The solvent was removed *in vacuo* from the solution and an orange precipitate which had formed by this time. A chloroform (20 cm^3) extract of the residue was filtered and reduced to about 1 cm^3 and the product precipitated as orange prisms (0.0723 g, 58%) by careful addition of diethyl ether (about 2 cm^3) and cooling to -20°C . The crystals broke down to a powder *in vacuo*. Crystallisation from dichloromethane–methanol mixtures was also possible (Found: C, 63.6; H, 4.55; N, 1.3; P, 11.95. $\text{C}_{56}\text{H}_{45}\text{Mn}_2\text{NO}_5\text{P}_4$ requires C, 64.3; H, 4.35; N, 1.35; P, 11.85%). I.r. (CH_2Cl_2): $\nu(\text{CO})$ 2 037w, 1 960vs, 1 930s, and 1 873m; $\nu(\text{CN})$ 2 091w cm^{-1} . I.r. (Nujol): $\nu(\text{CO})$ 2 040m,

1 963vs, 1 940vs, 1 905vs, and 1 864s; $\nu(\text{CN})$ 2 089s cm^{-1} . ^1H N.m.r. (CDCl_3): δ 7.0–7.8 (m, C_6H_5), 4.36 (m) and 3.83 (m) ($J_{\text{HH}} = 13.9$, $J_{\text{PH}} = 6$, PCH_2P), -23.87 (quintet, $J_{\text{PH}} = 18.9$ Hz, MnHMn). $^{31}\text{P}\{-^1\text{H}\}$ N.m.r. (CDCl_3) (162 MHz at -40°C): δ 65.38 (m) and 60.23 (m) (AA'BB' spectrum). The ^{13}C N compound (90% enriched) was prepared similarly. I.r. (CH_2Cl_2): $\nu(\text{CO},\text{CN})$ 2 046vw (sh), 2 037w, 1 961vs, 1 932s, and 1 874m cm^{-1} . I.r. (Nujol mull): $\nu(\text{CO},\text{CN})$ 2 047w, 2 033w, 1 960vs, 1 920vs, and 1 872s cm^{-1} . $^{13}\text{C}\{-^1\text{H}\}$ N.m.r. (CDCl_3): δ 160.5 (t, $J_{\text{PC}} = 23.8$ Hz).

Preparation of $[\text{Mn}_2\text{H}(\text{CN})(\text{CO})_4(\text{dppm})_2]$.—A stirred solution of $[\text{Mn}_2\text{H}(\text{CN})(\text{CO})_5(\text{dppm})_2]$ (0.247 g, 0.24 mmol) and $\text{Me}_3\text{NO}\cdot 2\text{H}_2\text{O}$ (0.616 g, 5.54 mmol) in CH_2Cl_2 (15 cm^3) and MeOH (30 cm^3) was heated under reflux (N_2 atmosphere) for 88 h. A considerable amount of yellow precipitate had formed and the i.r. spectrum of the solution showed a mixture of starting material and product. After removal of solvent *in vacuo*, the resultant yellow oil was extracted with dichloromethane (50 cm^3) and the extract filtered through Celite to remove most of the unreacted amine oxide. Chromatography on a silica column gave the product which was isolated as yellow needles (0.059 g, 24%) from dichloromethane–methanol at room temperature in the dark. Crystallisation from dichloromethane–pentane at -20°C was also possible. The initial decarbonylation occurs more rapidly on irradiating with tungsten lamps and yields up to 76% were obtained (Found: C, 63.3; H, 4.65; N, 1.25; P, 12.45. $\text{C}_{55}\text{H}_{45}\text{Mn}_2\text{NO}_4\text{P}_4$ requires C, 64.9; H, 4.45; N, 1.4; P, 12.15%). I.r.: $\nu(\text{CO})$ (CH_2Cl_2) 1 960w, 1 945m, 1 930vs, and 1 875s cm^{-1} ; (Nujol) 1 947m, 1 941m, 1 926vs, 1 871vs, and 1 866 (sh) cm^{-1} . ^1H N.m.r. (CDCl_3): δ 6.8–7.6 (m, C_6H_5), 3.13 (m) and 3.49 (m) (PCH_2P), -14.84 (quintet, $J_{\text{PH}} = 13.2$ Hz, MnHMn). $^{31}\text{P}\{-^1\text{H}\}$ N.m.r. (CD_2Cl_2): δ 57.99 (s) (25°C); δ 64.1 (m) and 51.9 (m) (AA'BB' spectrum) (-80°C). The ^{13}C N compound (90% enriched) was prepared similarly. I.r.: $\nu(\text{CO})$ (CH_2Cl_2) 1 964m, 1 940s, 1 923vs, 1 877vs, and 1 729m cm^{-1} . $^{13}\text{C}\{-^1\text{H}\}$ N.m.r. (CDCl_3): δ 160.7 (quintet, $J_{\text{PC}} = 10$ Hz) (25°C); spectra at low temperatures are illustrated in Figure 3.

Acknowledgements

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