Heterobimetallic Methylenebis(diphenylphosphine) Complexes.
Synthesis, Structure and Reactions of a Mixed Palladium–Manganese System

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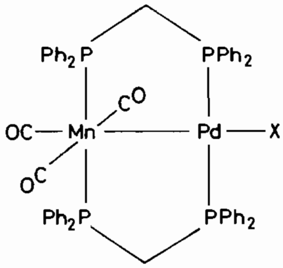
The preference of methylenebis(diphenylphosphine) (dppm) for coordinating to metal centres by bridging rather than chelating, has led to an extensive chemistry based on the bimetallic core, $M_2(\mu\text{-dppm})_2$ (M = Pd, Pt, Rh, Ir, Mn or Re) [1]. As a bridging ligand, dppm shows considerable flexibility in accepting a range of metal–metal distances suggesting that a wide variety of metal centres could participate in such structures [2]. Of particular note is that a number of these systems add small molecules, often reversibly, and exhibit catalytic activity in solution towards such reactions as the water-gas shift and reduction of carbon dioxide [3]. In attempts to extend the catalytic utility of dppm-based systems we have examined possible synthetic routes to complexes containing different but interactive metal centres [4]. Here, we wish to report the synthesis and some reactions of complexes based on the $MnPd(\mu\text{-dppm})_2$ core.

Reaction of the zerovalent, $Pd_2(dppm)_3$, with an equivalent of $MnBr(CO)_5$ in refluxing toluene affords, on cooling, air-stable, red crystals analysing as $[MnPd(\mu\text{-dppm})_2(CO)_3Br]$ in 35% yield. This may be increased to 85–90% by adding instead an intimate mixture of Pd(dibenzylideneacetone)$_2$, $MnX(CO)_5$ and dppm (1:1:2 mol ratio), to refluxing toluene, affording $[MnPd(\mu\text{-dppm})_2(CO)_3X]$ [X = Cl(*1*), Br(*2*), I(*3*)].**

Infra-red and NMR spectral data (Table 1) of the diamagnetic (*1*)–(*3*) indicate a structure,



X = Cl(*1*), Br(*2*), I(*3*),
N_3(*4*), NCO(*5*),
NCS(*6*), $SnCl_3$(*7*)

Formation of these complexes represents a formal insertion of a Pd(0) unit into a Mn–halogen bond, possibly affording a Pd(I)–Mn(0) metal–metal bonded unit. Complexes (*1*)–(*3*) are thermally stable (decomp. > 200 °C), showing no sign of disproportionation into the known symmetrical dimers [PdX-dppm]$_2$ (*8*) or $[Mn(CO)_3dppm]_2$. Their syntheses are analogous to reports of Pd(0) insertion into dppm Pd(II)– or Pt(II)–halide complexes to afford (*8*) or its mixed PdPt analogue [4a]. Compound (*1*) has also recently been isolated in low yield by a complex reaction of either (*8*) with $[Mn(CO)_5]^-$ or $[Pd[Mn(CO)_5]_2(NCPh)_2]$ with dppm [5].

The molecular structure of (*2*) has been established by X-ray diffraction of crystals grown from CH_2Cl_2/Et_2O at −5 °C: $C_{53}H_{44}BrMnP_4PdO_3$; *M* 1094.1, monoclinic, a = 18.317(2) Å, b = 13.412(2) Å, c = 21.013(4) Å, β = 117.5(1)°, V = 4795 Å^3, D_m = 1.510(1) Mg m^{-3}, Z = 4, D_c = 1.515 Mg m^{-3},

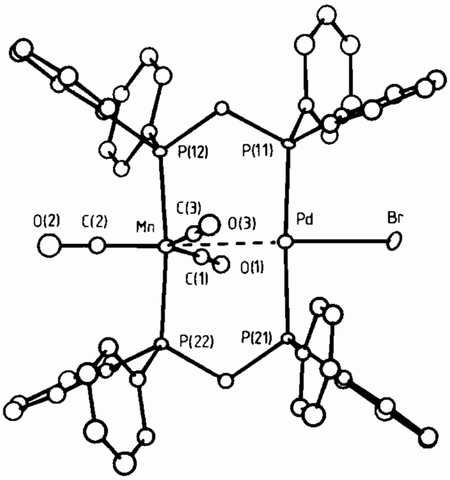


Fig. 1. Molecular structure of $MnPd(CO)_3(dpm)_2Br$ (*2*). Selected bond lengths (Å) and angles are: Pd···Mn 2.810(2), Pd–Br 2.547(2), Pd–P(11) 2.299(4), Pd–P(21) 2.290(4), Mn–P(12) 2.254(3), Mn–P(22) 2.276(3), Mn–C(1) 1.96(1), Pd···C(1) 2.44(1), Pd···O(1) 3.00(1), Mn–C(2) 1.63(2), Mn–C(3) 1.78(1), Pd···C(3) 2.95(1), Mn–C(1)–O(1) 174(1)°, Mn–C(3)–O(3) 175(1)°.

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**Satisfactory elemental analyses were obtained for all new compounds.

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TABLE I. Infra-red and ^{31}P NMR Spectral Data.

Compound			ν(CO) cm^{-1} [a]	δP (PdP)[b]	δP (MnP)[b]	JPP's (Mz)[c]
$MnPd(CO)_3(dppm)_2X$	X = Cl	(*1*)	1932(m), 1860(s)[d]	22.2(dd)	75.4(dd)	63.7, 56.2
	X = Br	(*2*)	1933(m), 1860(s)	20.0(dd)	75.5(dd)	63.0, 55.5
	X = I	(*3*)	1932(m), 1860(s)	16.6(dd)	74.2(dd)	61.0, 53.7
	X = N_3	(*4*)	1939(m), 1856(s)[e]	22.1(dd)	76.5(t)	63.9, 56.7
	X = NCO	(*5*)	1929(m), 1853(s)[f]	22.7(dd)	76.5(t)	65.3, 58.0
	X = NCS	(*6*)	1934(m), 1856(s)[g]	23.1(dd)	74.2(t)	61.0, 54.9
	X = $SnCl_3$	(*7*)	1948(m), 1872(s)[h]	18.6(t)	69.5(t)	54
$[MnPd(CO)_3(dppm)_2Br][BF_4]$		(*10*)	2062(m), 1961(s), 1938(s)	2.5(t)	54.5(br,s)	21.4
$[MnPd(CO)_3(dppm)_2(NCMe)][BF_4]$		(*11*)	1958(vs), 1930(m)	18.5(dd)	67.9(t)	63.5, 55.0

[a] In CH_2Cl_2. [b] $^{31}P-\{^1H\}$ spectra in ppm downfield from 85% H_3PO_4. [c] J_{AX} and $J_{AX'}$ in an AA'XX' spectrum. [d] ν(Pd–Cl) = 264 cm^{-1} (Nujol). [e] $\nu(N_3)$ = 2022(s) cm^{-1} (CH_2Cl_2). [f] ν(NCO) = 2194(s) cm^{-1} (CH_2Cl). [g] ν(NCS) = 2098(s) cm^{-1} (CH_2Cl_2). [h] ν(Sn–Cl) = 310 cm^{-1} (Nujol).

F(000) = 2208, space group Cc (No. 9), MoK_α radiation, (λ = 0.71069 Å, graphite monochromator), μ = 1.66 mm^{-1}. Intensity data were collected on an Enraf-Nonius CAD-4 diffractometer. Data were corrected for Lorentz, polarization and adsorption effects, yielding 7286 independent observed reflections [$I \geqslant 3\sigma(I)$]. The structure was solved by Patterson and Fourier methods*. Refinement by a least-squares procedure (unit weights) converged with R = 0.060.

The molecular geometry of (*2*) shown in Fig. 1 consists of a bimetallic PdMn unit spanned by two bridging, mutually *trans*-dppm ligands. With the inclusion of the Mn atom, the coordination geometry around the Pd centre is essentially square planar. However the Mn geometry is not octahedral as expected, but instead appears to be a distorted trigonal bipyramid, with the three carbonyl groups forming a well defined trigonal plane and the Pd atom being sterically undemanding. At least one of the carbonyl groups between the Mn and Pd atoms appears to be semibridging [Pd–C(1) = 2.44(1) Å, Pd–C(3) = 2.95(1) Å]. Similar semi-bridging carbonyl ligands have been reported in $[(Et_3P)_2(OC)Rh-Co(CO)_4]$ in which a relatively undistorted tetrahedral $Co(CO)_4$ moiety is bonded to a Rh(I) centre [6]. The Pd–Mn distance of 2.810(2) Å suggests a Pd–Mn bond which is somewhat longer than those observed for the dppm or CO bridged Pd–Mn bonds in $[Pd_2Mn_2(CO)_9(dppm)_2]$ (*9*) [2.580(1) and 2.698(1) Å], but similar to the unbridged Pd–Mn bond [28.21(2) Å] in (*9*) [5]. At this stage it is not clear whether there is a direct Pd–Mn bond in (*2*) or whether spin-pairing occurs between the d^7-Mn(0) and d^9-Pd(I) centres by some other mechanism, such as through the semibridging carbonyl ligands.

The halide ligands in (*1*)–(*3*) readily undergo metathesis with a variety of alkali metal salts in acetone, allowing for the formation of new complexes where X = N_3 (*4*), NCO (*5*), NCS (*6*) (Table). Insertion of $SnCl_2$ into the Pd–Cl bond of (*1*) in CH_2Cl_2 solution results in a purple, crystalline heterotrimetallic complex, $[MnPd(\mu\text{-dppm})_2(CO)_3(SnCl_3)]$ (*7*). The latter reaction is solvent dependent and readily reversible; dissolution of (*7*) in methanol results in the reformation of (*1*). Mild oxidising agents such as Br_2 or $PhN_2^+BF_4^-$ react with (*2*), affording a cationic complex $[MnPd(\mu\text{-dppm})_2(CO)_3Br]$-[X], isolated as yellow air-stable crystals (X = BF_4) (*10*). This paramagnetic complex (μ_{eff} = 1.4 B.M.) exhibits a six-line e.s.r. spectrum (g = 2.015; A_{iso} (^{55}Mn) = 97 G in CH_2Cl_2 glass at 77 K), and an NMR (see Table I and p. L69) spectrum in which the ^{31}P resonance associated with the phosphine ligands attached to the Mn atom is preferentially broadened. Reaction between $AgBF_4$ and (*2*) in non-coordinating solvents (*e.g.* CH_2Cl_2) is complex, presumably owing to competing oxidation and halogen abstraction reactions. However, in acetonitrile the halide ligand is cleanly replaced, resulting in the labile, purple, cationic, $[MnPd(\mu\text{-dppm})_2(CO)_3(NCMe)][BF_4]$ (*11*).

Preliminary data on the homogeneous catalytic activity of the Pd–Mn system, using (*2*) as a precursor, indicate an ability to produce ethyl formate (at a rate of 7 mol/mol *2*/hr) from a CO_2/H_2 mixture (1:1, 1.2 MPa) in the presence of ethanol and triethylamine at 130 °C. Similarly methanol

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*Although the overall molecular geometry and space group are noncentrosymmetric the dppm framework possesses an almost precise centre of symmetry at the mid-point of the Mn–Pd vector. This allows for both enantiomers to coexist without any apparent alteration to the crystal packing, which accounts for a degree of disorder (approx. 25%) observed in this analysis.

reacts with CO/H_2 (1:1, 1.4 MPa) at 130 °C in the presence of (*3*) and aqueous HI to afford a mixture of Me_2O (25% molar selectivity), MeCOOH (1%), MeOOCMe (19%) and $MeCH(OMe)_2$ (55%) at a rate of 23 mol of MeOH converted/mol (*3*)/hr. The catalytically active species in these reactions are presently under study.

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