

Synthesis and Structure of Mixed Palladium–Manganese Complexes with the $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ Ligand

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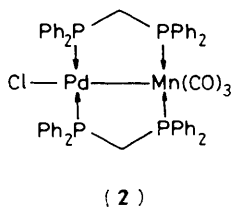
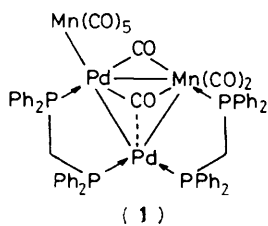
Heteronuclear palladium–manganese complexes can be prepared from reactions between $[\text{PdCl}(\text{dppm})]_2$ ($\text{dppm} = \text{Ph}_2\text{PCH}_2\text{PPh}_2$) and $\text{NaMn}(\text{CO})_5$ or between *trans*- $\text{Pd}[\text{Mn}(\text{CO})_5]_2(\text{PhCN})_2$ and dppm ; the complexes $\text{PdMnCl}(\text{CO})_3(\text{dppm})_2$ and $\text{Pd}_2\text{Mn}_2(\text{CO})_9(\text{dppm})_2$ have been obtained and the structure of the latter has been established by X-ray diffraction.

Considerable interest in the bimetallic activation and catalysis of small molecules to form useful organic products has prompted intense investigations of $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ (dppm) bimetallic complexes. The proximity in which the two metal centres are maintained by the flexible bridging dppm has given rise to a rich and unique reactivity for these complexes. This includes unusual co-ordination modes for ligands like CO, H, SO_2 , CNR, *etc.* (involving or not involving the metal–metal bond), ligand transfer, and catalytic activity in CO chemistry.^{1,2}

Considering the diverse chemistry of mixed-metal clusters³ and the original features introduced by the ligand dppm , one might expect that their combination would afford new molecules of unusual structure and reactivity. We have therefore

developed two original synthetic routes to mixed-metal clusters containing the dppm ligand. We present here our preliminary results for the preparation of palladium–manganese complexes.

In method (a), $[\text{PdCl}(\text{dppm})]_2$ was treated with $\text{NaMn}(\text{CO})_5$ (2 equiv.; tetrahydrofuran, THF; 0 °C; 4 h), to give the violet complex (1)† (23% yield) and the red complex (2)†



† Selected data: Compound (1): m.p. 170–174 °C, i.r. (KBr) $\nu(\text{CO})$ 2028(vs), 1973(s), 1927(vs), and 1899(vs) cm^{-1} ; ^1H n.m.r. (CD_2Cl_2) δ 7.68–6.8 (m, 40H, Ph), 4.45 (dt, 2H, CH_2 , $^2J_{\text{PH}}$ ca. 10 Hz, J_{PH} ca. 10 Hz), and 4.17 (t, 2H, CH_2 , $^2J_{\text{PH}}$ 10 Hz).

Typically, this dppm bridged *triangulo*-unit is characterized in its ^1H n.m.r. spectrum by two patterns for the CH_2 groups: a triplet (for coupling with 2 P atoms) assigned to the dppm bridging the two Pd atoms (by analogy with $\delta(\text{CH}_2)$ 4.17 in $[\text{PdCl}(\text{dppm})]_2$ ⁶), and a downfield doublet of triplets [for coupling with the 2 proximate P atoms and further coupling with one P atom of the $\text{Pd}_2(\text{dppm})$ unit] assigned to the dppm bridging Pd and Mn.

Compound (2): m.p. 216 °C, i.r. (KBr) $\nu(\text{CO})$ 1917(m), 1850(s), and 1815(m) cm^{-1} ; Fourier-transform i.r. (polythene) $\nu(\text{PdCl})$ 267(m) cm^{-1} ; ^1H n.m.r. (CD_2Cl_2) δ 7.35 and 7.77 (centres of two complex multiplets, 40H, Ph), and 3.89 (q, 4H, CH_2 , $^2J_{\text{PH}} + ^4J_{\text{PH}}$ 5 Hz); ^{31}P { ^1H } n.m.r. (CD_2Cl_2 , positive downfield from H_3PO_4) δ 77.0 (t) and 23.7 p.p.m. (t); A_2B_2 , J_{PP} 59 Hz.

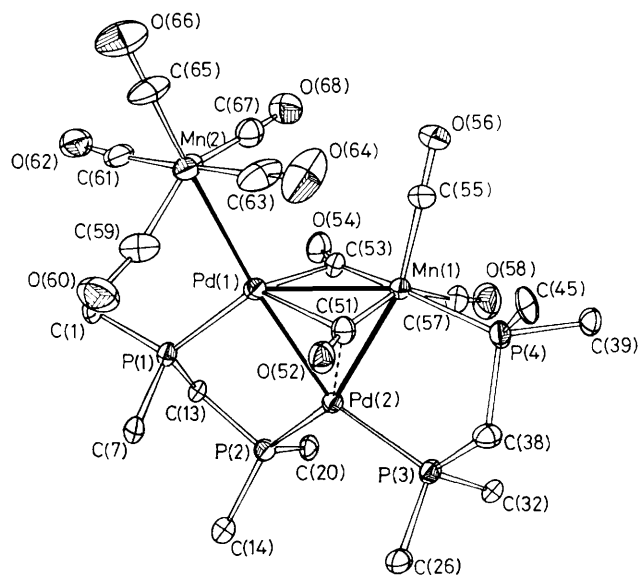


Figure 1. Molecular structure of $\text{Pd}_2\text{Mn}_2(\text{CO})_9(\text{dppm})_2$ (**1**). Principal dimensions: Pd(1)–Pd(2), 2.681(1); Pd(1)–Mn(1), 2.698(1); Pd(1)–Mn(2), 2.821(2); Pd(2)–Mn(1), 2.580(2); Pd(1)–P(1), 2.324(3); Pd(2)–P(2), 2.360(3); Pd(2)–P(3), 2.273(2); Mn(1)–P(4), 2.292(3); Mn(1)–C(51), 1.92(2); Mn(1)–C(53), 1.94(2); Mn(1)–C(55), 1.80(1); Mn(1)–C(57), 1.86(2); Pd(1)–C(51), 2.28(1); Pd(2)–C(51), 2.43(1); Pd(1)–C(53), 2.14(1); Mn(2)–C(59), 1.77(2); Mn(2)–C(61), 1.85(2); Mn(2)–C(63), 1.81(2); Mn(2)–C(65), 1.74(1); Mn(2)–C(67), 1.81(2) Å; \angle Pd(2)–Pd(1)–Mn(2), 163.39(4); Mn(1)–Pd(1)–Pd(2), 57.33(3); Pd(1)–Pd(2)–Mn(1), 61.67(4); P(1)–Pd(1)–Mn(2), 107.4(1); P(1)–Pd(1)–Pd(2), 83.21(6); P(2)–Pd(2)–P(3), 113.9(1); Pd(2)–Mn(1)–P(4), 99.5(1)°.

(18% yield). The molecular structure of (**1**) has been established by X-ray diffraction;‡ suitable crystals were obtained from PhCl–hexane at -20°C .

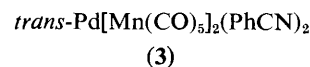
Crystal data: (**1**)–PhCl: $\text{C}_{65}\text{H}_{49}\text{ClMn}_2\text{O}_9\text{P}_4\text{Pd}_2$; $M = 1456.1$; monoclinic; space group $P2_1/c$; $a = 17.561(7)$, $b = 21.319(8)$, $c = 19.461(8)$ Å; $\beta = 113.50(2)^\circ$; $U = 6681(9)$ Å³; $D_c = 1.44$ g cm⁻³; $Z = 4$; $\mu(\text{Mo-K}\alpha) = 10.95$ cm⁻¹. Diffraction data were collected by the θ – 2θ flying step-scan technique using a Picker Facs-1 diffractometer. The structure was solved via conventional Patterson, difference-Fourier, and full-matrix least-squares methods (anisotropic thermal parameters for all non-hydrogen atoms) leading to an R value of 5.9% for 4473 independent reflections [$I > 3\sigma(I)$] with $4 < 2\theta < 60^\circ$. All non-hydrogen atoms were located, and the molecular geometry is shown in Figure 1.

The framework of this heterotetrametallic metallo-ligated cluster $\text{Pd}_2\text{Mn}_2(\text{CO})_9(\text{dppm})_2$ consists of a *triangulo*-Pd₂Mn unit of which two edges, Pd(1)–Pd(2) and Pd(2)–Mn(1), are each spanned by a dppm ligand, and an Mn(CO)₅ group connected to Pd(1). The four metal atoms and the four phosphorus are not too far from being coplanar [max. deviation, for P(3) = 0.79 Å]. Though the first complex reported to contain a Pd–Mn bond was the linear trimetallic *trans*-Pd[Mn(CO)₅]₂(py)₂ (py = pyridine),⁴ the first determination of Pd–Mn bond lengths has now been achieved

‡ Atomic co-ordinates 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.

with (**1**). Consistent with the small bite of dppm, the Pd(2)–Mn(1) bond is shorter than the Pd(1)–Mn(1) or Pd(1)–Mn(2) bonds. The Pd(1)–Pd(2) distance is similar to that found in [PdBr(dppm)]₂ [2.699(5) Å].⁵ In this 60-electron cluster, the presence of two 18-electron Mn and two 16-electron Pd atoms accounts for the four metal–metal bonds observed.

On the basis of analytical, spectroscopic,† and preliminary X-ray data, we suggest that complex (**2**) has the structure shown. In this 32-electron bimetallic complex, the Pd and Mn atoms achieve their normal 16- and 18-electron environments, respectively. The four phosphorus and the two metal atoms are probably coplanar, as the ¹H n.m.r. spectrum shows a quintet for the CH₂ protons.⁶



The synthetic method (b) involves the reaction of an appropriate heterotrimetallic palladium–manganese complex with dppm. Thus, when *trans*-Pd[Mn(CO)₅]₂(PhCN)₂ (**3**), prepared *in situ* from Pd(PhCN)₂Cl₂ + 2NaMn(CO)₅⁷ (THF; -76°C), was treated with dppm (2 equiv.; THF; -76 to 15°C ; 3 h), (**2**) was isolated (25%) after chromatography (silica gel, pentane–toluene). From this reaction, the chloride in (**2**) must originate from the NaCl present in the reaction mixture. With the linear trimetallic complexes *trans*-Pd[M(CO)₅(η^5 -C₅H₅)]₂(PhCN)₂ (M = Cr, Mo, W), analogous to (**3**) we have found that one can take advantage of the lability of the nitrile ligand to prepare the tetrametallic clusters [PdM(η^5 -C₅H₅)(CO)₃(PR₃)₂] by reaction with tertiary phosphines.⁷

Interestingly, we find that with the precursors used, both methods (a) and (b) applied to the Pd–Mn–dppm system lead to mixed-metal complexes containing dppm but with changes in the selectivity.

Whereas (**2**) is one of the few heterobimetallic complexes containing the dppm ligand,⁸ (**1**) appears to be the first example of a palladium–manganese cluster and one of the first mixed-metal dppm clusters to be structurally characterized.⁹

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