metal-organic compounds

μ-Bis(diphenylphosphino)methane-P:P′-octacarbonyldimanganese(Mn–Mn) and its toluene hemisolvate

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The Mn—Mn bonds in the two independent molecules of the unsolvated title compound, $[Mn_2(C_{25}H_{22}P_2)(CO)_8]$, (I), are 2.9714 (7) and 2.9746 (7) Å. This bond is distinctly shortened in the toluene hemisolvate, $[Mn_2(C_{25}H_{22}P_2)(CO)_8] \cdot 0.5C_7H_8$, (II), to 2.9338 (14) Å and this shortening is accompanied by an increase in magnitude of the P—Mn—Mn—P torsion angle [26.93 (3) and 28.44 (3)° in (I), and 33.25 (7)° in (II)], while the P···P 'bite' is much less affected [3.092 (2) and 3.099 (2) Å in (I), and 3.091 (3) Å in (II)]. The toluene solvate molecule in (II) lies on a twofold axis.

Comment

The argument is often made that changing the 'bite distance' of a bridging ligand in a binuclear compound will change the metal–metal distance. For example, the Rh—Rh bond lengths in $[Rh_2(\mu\text{-}L\text{-}L)_2(CO)_2(\mu\text{-}2,5\text{-dimethylpyrazolatate})]PF_6$ are 3.060 (3) and 3.220 (2) Å when L–L is dppm and dpam, respectively [dppm is 1,2-bis(diphenylphosphino)methane and dpam is 1,2-bis(diphenylarsino)methane; Janke *et al.*, 1986]. The difference in the bond lengths was proposed to be largely attributable to the difference in the L–L bite distances. The bite distance is certainly important, but the L—M—M—L dihedral angle is an often overlooked parameter that can affect the metal–metal distance.

The crystal structures reported here for $Mn_2(dppm)(CO)_8$, (I), and $Mn_2(dppm)(CO)_8 \cdot 0.5(toluene)$, (II), illustrate this point. The increase in the P—Mn—Mn—P torsion angle from (I) to (II) (see *Abstract*, and Tables 1 and 2) is accompanied by a shortening of the Mn—Mn bond, but the P···P bite distance is almost unchanged. Simple mechanical considerations require that an increase in the dihedral angle for a given bite distance must be accompanied by a decrease in the Mn—Mn bond length. There are no other significant differences in bond lengths, or in the Mn—Mn—P, Mn—P—C, and P—C—P bond

angles. Equivalently, $Mn_2(dpam)(CO)_8$ has essentially the same Mn—Mn bond length [2.962 (3) Å] as (I), but the significantly greater bite distance of dpam [3.242 (2) Å] leads to a greater dihedral angle [30.5 (8)°; Hoskins & Steen, 1983].
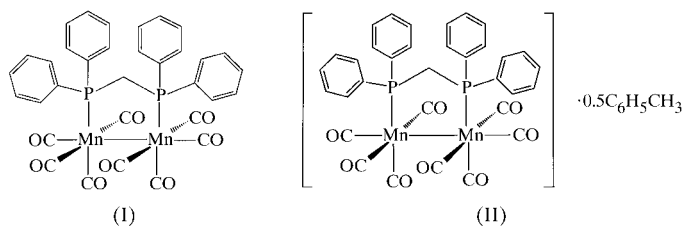
The origin of the structural differences between (I) and (II) is not evident. The energy surface for the molecule is apparently very flat with respect to bond distance and dihedral angle, and crystal-packing forces are presumably important in
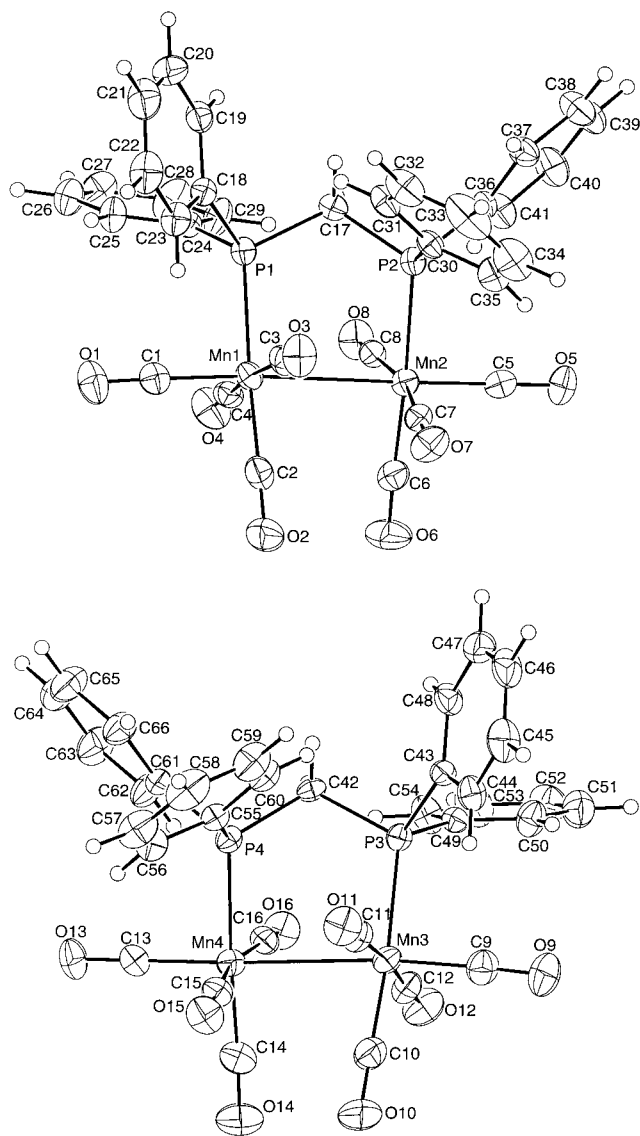

Figure 1
The two independent molecules in the unsolvated compound, (I), with 30% probability displacement ellipsoids and the atom-numbering scheme. H atoms are drawn as small spheres of arbitrary radii.

determining the details of the molecular structure. The differences cannot be directly attributed to the presence of toluene solvate molecules in (II), as there are no significantly short complex–complex or complex–solvent contacts in either compound.
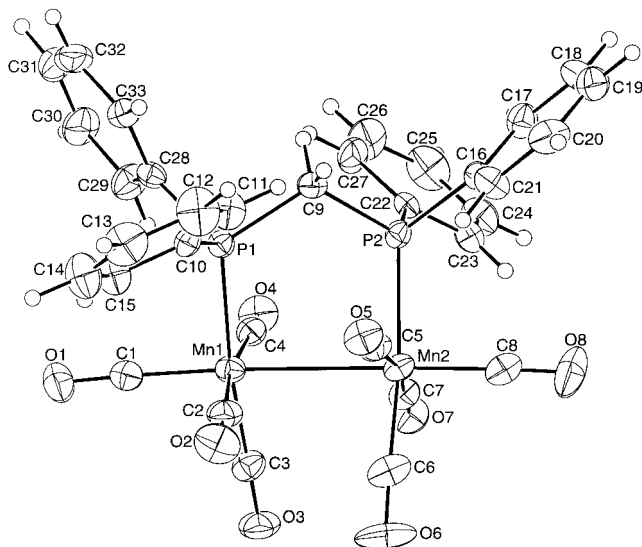

Figure 2
The [Mn$_2$(CO)$_8$(dppm)] molecule in the toluene hemisolvate, (II), with 30% probability displacement ellipsoids and the atom-numbering scheme. H atoms are drawn as small spheres of arbitrary radii.

Experimental

The title compounds were prepared according to the method of Colton & Commons (1975). Compound (I) was recrystallized from ethanol and (II) was recrystallized from toluene by evaporation under N$_2$. Axial photographs of (II) confirmed that the Laue symmetry is 4/mmm.

Compound (I)

Crystal data

[Mn$_2$(C$_{25}$H$_{22}$P$_2$)(CO)$_8$]	$Z = 4$
$M_r = 718.36$	$D_x = 1.493$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 12.6428$ (13) Å	Cell parameters from 25
$b = 15.351$ (4) Å	reflections
$c = 17.868$ (8) Å	$\theta = 12.6$–13.9°
$\alpha = 111.91$ (3)°	$\mu = 0.94$ mm^{-1}
$\beta = 94.05$ (3)°	$T = 296$ K
$\gamma = 90.48$ (2)°	Plate, yellow
$V = 3207$ (2) Å^3	0.40 × 0.20 × 0.05 mm

Data collection

Enraf–Nonius CAD-4	$R_{int} = 0.021$
diffractometer	$\theta_{max} = 25°$
$\omega/2\theta$ scans	$h = 0 \rightarrow 15$
Absorption correction: analytical	$k = -18 \rightarrow 18$
(de Meulenaer & Tompa, 1965)	$l = -21 \rightarrow 21$
$T_{min} = 0.763$, $T_{max} = 0.958$	3 standard reflections
11 815 measured reflections	frequency: 60 min
11 243 independent reflections	intensity decay: 4.5%
8260 reflections with $I > \sigma(I)$	

Refinement

Refinement on F^2	H-atom parameters constrained
$R(F) = 0.041$	$w = 4F_o{}^2/[\sigma^2(I) + (0.02I)^2]$
$wR(F^2) = 0.044$	$(\Delta/\sigma)_{max} = 0.025$
$S = 1.60$	$\Delta\rho_{max} = 0.47$ e Å^{-3}
11 243 reflections	$\Delta\rho_{min} = -0.46$ e Å^{-3}
811 parameters	

Table 1
Selected geometric parameters (Å, °) for (I).

Mn1—Mn2	2.9746 (7)	Mn3—Mn4	2.9714 (7)
Mn1—P1	2.3033 (9)	Mn3—P3	2.3039 (9)
Mn1—C1	1.788 (4)	Mn3—C9	1.784 (4)
Mn1—C2	1.832 (4)	Mn3—C10	1.815 (4)
Mn1—C3	1.844 (4)	Mn3—C11	1.844 (4)
Mn1—C4	1.840 (4)	Mn3—C12	1.836 (4)
Mn2—P2	2.3020 (9)	Mn4—P4	2.3028 (9)
Mn2—C5	1.788 (4)	Mn4—C13	1.781 (4)
Mn2—C6	1.814 (4)	Mn4—C14	1.820 (4)
Mn2—C7	1.842 (4)	Mn4—C15	1.854 (4)
Mn2—C8	1.827 (4)	Mn4—C16	1.827 (4)
Mn2—Mn1—P1	92.17 (3)	Mn4—Mn3—P3	91.58 (3)
Mn2—Mn1—C1	175.32 (11)	Mn4—Mn3—C9	173.93 (12)
Mn2—Mn1—C2	84.37 (11)	Mn4—Mn3—C10	83.89 (13)
Mn2—Mn1—C3	88.25 (10)	Mn4—Mn3—C11	90.51 (11)
Mn2—Mn1—C4	84.58 (10)	Mn4—Mn3—C12	83.80 (12)
P1—Mn1—C1	91.25 (12)	P3—Mn3—C9	92.57 (12)
P1—Mn1—C2	176.48 (11)	P3—Mn3—C10	175.30 (13)
P1—Mn1—C3	91.39 (11)	P3—Mn3—C11	91.51 (11)
P1—Mn1—C4	90.70 (11)	P3—Mn3—C12	90.80 (11)
C1—Mn1—C2	92.24 (16)	C9—Mn3—C10	92.04 (17)
C1—Mn1—C3	94.87 (14)	C9—Mn3—C11	93.81 (16)
C1—Mn1—C4	92.18 (15)	C9—Mn3—C12	91.71 (17)
C2—Mn1—C3	87.89 (16)	C10—Mn3—C11	87.27 (17)
C2—Mn1—C4	89.60 (16)	C10—Mn3—C12	89.98 (17)
C3—Mn1—C4	172.60 (15)	C11—Mn3—C12	173.92 (16)
Mn1—Mn2—P2	86.17 (3)	Mn3—Mn4—P4	86.09 (3)
Mn1—Mn2—C5	176.71 (11)	Mn3—Mn4—C13	175.71 (11)
Mn1—Mn2—C6	90.71 (12)	Mn3—Mn4—C14	91.53 (12)
Mn1—Mn2—C7	82.06 (10)	Mn3—Mn4—C15	81.11 (11)
Mn1—Mn2—C8	86.63 (10)	Mn3—Mn4—C16	87.43 (10)
P2—Mn2—C5	91.40 (11)	P4—Mn4—C13	90.75 (11)
P2—Mn2—C6	176.38 (12)	P4—Mn4—C14	176.67 (12)
P2—Mn2—C7	93.32 (11)	P4—Mn4—C15	93.21 (10)
P2—Mn2—C8	90.46 (10)	P4—Mn4—C16	90.28 (10)
C5—Mn2—C6	91.79 (16)	C13—Mn4—C14	91.75 (16)
C5—Mn2—C7	95.89 (14)	C13—Mn4—C15	96.19 (15)
C5—Mn2—C8	95.61 (14)	C13—Mn4—C16	95.49 (15)
C6—Mn2—C7	88.07 (16)	C14—Mn4—C15	88.71 (15)
C6—Mn2—C8	87.52 (16)	C14—Mn4—C16	87.29 (15)
C7—Mn2—C8	167.80 (14)	C15—Mn4—C16	167.76 (15)
P1—Mn1—Mn2—P2	26.93 (3)	P3—Mn3—Mn4—P4	−28.44 (3)

Compound (II)

Crystal data

[Mn$_2$(C$_{25}$H$_{22}$P$_2$)(CO)$_8$]·0.5C$_7$H$_8$	Mo $K\alpha$ radiation
$M_r = 764.43$	Cell parameters from 25
Tetragonal, $I4_1cd$	reflections
$a = 18.286$ (2) Å	$\theta = 15.5$–16.0°
$c = 41.345$ (6) Å	$\mu = 0.87$ mm^{-1}
$V = 13 824$ (3) Å^3	$T = 294$ K
$Z = 16$	Block, yellow
$D_x = 1.469$ Mg m^{-3}	0.36 × 0.32 × 0.29 mm

metal-organic compounds

Data collection

Enraf–Nonius CAD-4 diffractometer
ω scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.72$, $T_{max} = 0.77$
3084 measured reflections
3084 independent reflections

2520 reflections with $I > \sigma(I)$
$\theta_{max} = 25°$
$h = 0 \rightarrow 21$
$k = 0 \rightarrow 15$
$l = 0 \rightarrow 49$
3 standard reflections
 frequency: 60 min
 intensity decay: 1.1%

Refinement

Refinement on F^2
$R(F) = 0.045$
$wR(F^2) = 0.038$
$S = 1.31$
3084 reflections
438 parameters

H-atom parameters constrained
$w = 4F_o^2/[\sigma^2(I) + (0.02I)^2]$
$(\Delta/\sigma)_{max} = 0.005$
$\Delta\rho_{max} = 0.48$ e Å^{-3}
$\Delta\rho_{min} = -0.48$ e Å^{-3}

Table 2
Selected geometric parameters (Å, °) for (II).

Mn1—Mn2	2.9338 (14)	Mn2—P2	2.307 (2)
Mn1—P1	2.314 (2)	Mn2—C5	1.836 (9)
Mn1—C1	1.778 (8)	Mn2—C6	1.812 (8)
Mn1—C2	1.832 (9)	Mn2—C7	1.827 (7)
Mn1—C3	1.833 (8)	Mn2—C8	1.782 (9)
Mn1—C4	1.817 (8)		
Mn2—Mn1—P1	88.80 (6)	Mn1—Mn2—P2	87.74 (6)
Mn2—Mn1—C1	174.4 (2)	Mn1—Mn2—C5	89.5 (2)
Mn2—Mn1—C2	81.9 (3)	Mn1—Mn2—C6	87.2 (3)
Mn2—Mn1—C3	85.5 (3)	Mn1—Mn2—C7	80.8 (2)
Mn2—Mn1—C4	90.2 (2)	Mn1—Mn2—C8	174.8 (2)
P1—Mn1—C1	91.9 (2)	P2—Mn2—C5	89.3 (2)
P1—Mn1—C2	91.4 (2)	P2—Mn2—C6	174.5 (3)
P1—Mn1—C3	173.9 (3)	P2—Mn2—C7	93.7 (2)
P1—Mn1—C4	92.6 (2)	P2—Mn2—C8	92.6 (3)
C1—Mn1—C2	92.5 (3)	C5—Mn2—C6	88.5 (3)
C1—Mn1—C3	93.9 (3)	C5—Mn2—C7	169.8 (3)
C1—Mn1—C4	95.4 (3)	C5—Mn2—C8	95.7 (3)
C2—Mn1—C3	90.0 (3)	C6—Mn2—C7	87.5 (3)
C2—Mn1—C4	171.0 (3)	C6—Mn2—C8	92.7 (4)
C3—Mn1—C4	85.3 (3)	C7—Mn2—C8	93.9 (3)
P1—Mn1—Mn2—P2	−33.25 (7)		

Cell-reduction calculations for (I), and examination of the atomic coordinates and extended packing diagrams, failed to show any overlooked symmetry elements relating the two independent molecules. For both compounds, a *SIR*92 electron-density map (Altomare *et al.*, 1994) showed all non-H atoms, and refinement was on F^2 with net negative intensities reset to zero. H atoms [other than those of the toluene methyl group in (II)] were included at calculated positions, with C—H = 0.95 Å and $U_{iso}(H) = 1.2U_{eq}(C)$. Refinement of the structure of (II) of opposite polarity ($x, y, z \rightarrow x, \frac{1}{2} + y, -z$) converged to slightly greater residuals [$R(F) = 0.048$, $I > \sigma(I)$, and $wR(F^2) = 0.083$ and goodness-of-fit = 1.39, all data].

For both compounds, data collection: *CAD*-4-*PC Software* (Enraf–Nonius, 1993); cell refinement: *CAD*-4-*PC Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1997); program(s) used to solve structure: *TEXSAN*; program(s) used to refine structure: *TEXSAN*; software used to prepare material for publication: *TEXSAN*.

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