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fac-[Bis(dimethylphosphino)methane]bromotricarbonylmanganese(I) and -Rhenium(I)

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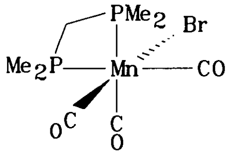
Abstract

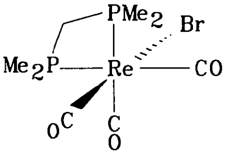
The complexes *fac*-*M*Br(CO)$_3$(dmpm) [*M* = Mn, Re; dmpm = bis(dimethylphosphino)methane, $C_5H_{14}P_2$] are isostructural and contain the metal(I) atom in distorted octahedral coordination. The primary distortion is caused by the short 'bite' of the dmpm ligand. This constraint also results in a slight opening of the OC—*M*—CO angles from the ideal value of 90°. A significant *trans* influence of the dmpm ligand on the *M*—CO distances is evident.

Comment

In a continuation of studies on the directed synthesis of heterobimetallic complexes containing 'short-bite' bridging ligands (Mague & Lin, 1992) we have begun an investigation into the use of dmpm as the bridging ligand. Initial attempts to prepare a suitable precursor, *fac*-*M*Br(CO)$_3$(η^1-dmpm)$_2$ (*M* = Mn, Re), from *fac*-*M*Br(CO)$_3$(MeCN)$_2$ (Farona & Kraus, 1970) and an excess of dmpm under mild conditions, yielded products which did not contain monodentate dmpm. The ^{1}H NMR resonances for the ligand methyl groups appeared as virtually coupled triplets, a feature generally associated with strong P–P coupling and most frequently observed when two methyl-substituted phosphine ligands are *trans* to each other, where $^2J_{\text{P—}M\text{—P}}$ is large (Shaw & Jenkins, 1966). With this suggestion of *trans* coordination of the P atoms of dmpm in these species, the possibility that they were dinuclear with bridging dmpm ligands arose. To check this, the structures of the products were determined which showed them to be monomeric *fac*-*M*Br(CO)$_3$(dmpm) [*M* = Mn (1), Re (2)] with a chelating dmpm ligand. Since the P atoms in (1) and (2) are clearly *cis* and since *cis*-disposed *monodentate* phosphine ligands generally do not exhibit $^2J_{\text{P—}M\text{—P}}$ values large enough to produce virtual coupling effects, we conclude that there must be an additional contribution to P–P coupling here. The most likely source of the apparently large overall $^2J_{\text{P–P}}$ is a 'through-the-backbone' contribution (Grim, Barth, Mitchell & Delgaudio, 1977).



(1)



(2)

The crystal structures of complexes (1) and (2) are isomorphous and while there are some differences in bond angles that are statistically significant, no chemically significant differences in conformation exist between them. The coordination about the metal atoms is distorted octahedral with the primary distortion resulting from the short bite of the dmpm ligand. As a consequence, the {*M*(CO)$_3$} moiety shows an expansion of the C—*M*—C angles from the ideal 90° values. Additionally, all the ligand atoms *cis* to the Br atom bend towards the latter. This feature is more uniform here than in the related complex *fac*-Mn(NCS)(CO)$_3$(dppm) [dppm = bis(diphenylphosphino)methane] (Carriedo, Parra Soto, Riera, Valin, Morieras & Solans, 1987).

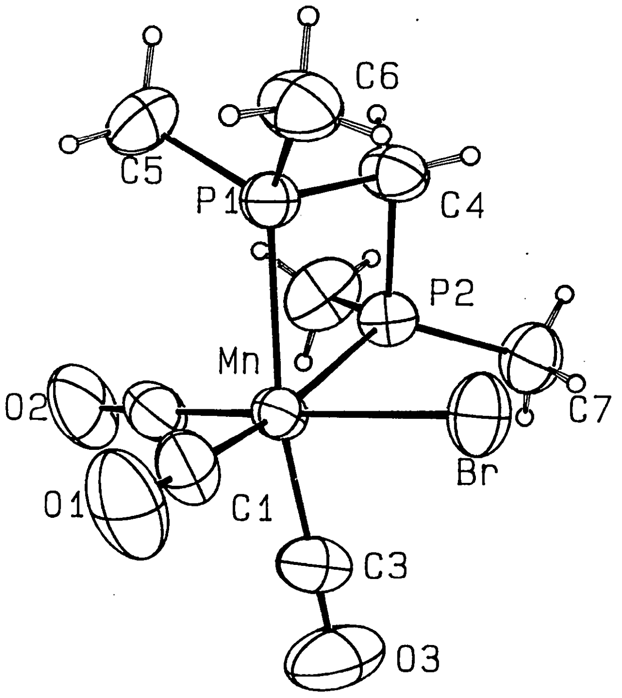


Fig. 1. A perspective view of *fac*-MnBr(CO)$_3$(dmpm), (1). Displacement ellipsoids are drawn at the 30% probability level for non-H atoms. H atoms are represented by circles of arbitrary size.

The Mn—Br distance in (1) is identical to that found in *fac*-MnBr(CO)$_2${P(OPh)$_3$}(dppm) [2.527 (1) Å; Connelly, Hassard, Dunne, Orpen, Raven, Carriedo & Riera, 1988] while the *M*—P distances are slightly shorter than that *trans* to CO in the same complex and those in *fac*-$Mn(NCS)(CO)_2$(dppm). The Mn—C(1) and Mn—C(3) distances are slightly different but comparable to those found in the thiocyanate complex. By contrast, the Mn—C(2) distance is considerably shorter, reflecting a significantly smaller structural *trans* influence of Br compared with P. The Re—Br distance in (2) compares favorably with those found in *fac*-$ReBr(CO)_3\{\overline{P(Ph)N(Ph)N{=}C(Ph)}CHPh\}_2$, [2.622 (1) Å; Baccolini, Busetto, Roncarol, Albano & Demartin, 1987] and $(Me_3P)(CO)_4OsReBr(CO)_4$ [2.635 (2) Å; Einstein, Jennings, Krentz, Pomeroy, Rushman & Willis, 1987]. Similarly, the Re—C(2) distance is essentially the same as that *trans* to Br in the former complex but the difference between this and the other two Re—C distances is larger here suggesting a greater *trans* influence of the dmpm ligand compared with the diazaphosphole ligand. The Re—P distances are equal and virtually the same as those found in $Re_2(CO)_7(C_2Ph)(\mu\text{-}H)(\mu\text{-dmpm})$ [2.440 (2) and 2.429 (1) Å; Lee, Pennington, Cordes & Brown, 1985].

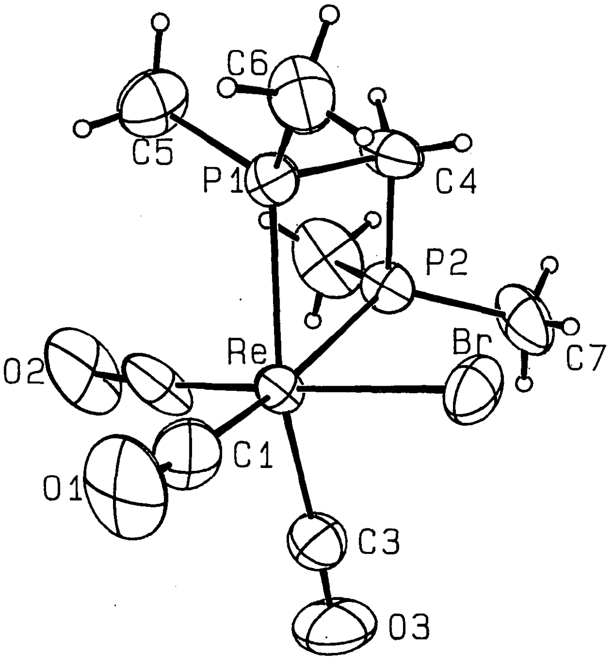


Fig. 2. A perspective view of *fac*-$ReBr(CO)_3$(dmpm), (2). Displacement ellipsoids are drawn at the 30% probability level for non-H atoms. H atoms are represented by circles of arbitrary size.

Experimental

Compound (1)

Crystal data

[$MnBr(CO)_3(C_5H_{14}P_2)$]
$M_r = 354.99$
Orthorhombic
$P2_12_12_1$
$a = 10.3329$ (7) Å
$b = 11.199$ (2) Å
$c = 12.372$ (1) Å
$V = 1431.7$ (5) Å^3
$Z = 4$
$D_x = 1.65$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 11.77\text{–}16.66°$
$\mu = 3.86$ mm^{-1}
$T = 293$ K
Block
0.40 × 0.33 × 0.26 mm
Orange
Crystal source: $CH_2Cl_2/C_6H_5CH_3/C_6H_{14}$

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical
$T_{min} = 0.821$, $T_{max} = 0.998$
1637 measured reflections
1637 independent reflections

1295 observed reflections [$I \geq 3\sigma(I)$]
$\theta_{max} = 26.0°$
$h = 0 \rightarrow 12$
$k = 0 \rightarrow 13$
$l = 0 \rightarrow 15$
3 standard reflections
frequency: 120 min
intensity variation: ±1%

Refinement

Refinement on F
$R = 0.027$
$wR = 0.037$
$S = 1.204$
1295 reflections
136 parameters
H-atom parameters not refined

$w = 4F/[\sigma^2(I) + (0.04F^2)^2]$
$(\Delta/\sigma)_{max} = 0.02$
$\Delta\rho_{max} = 0.771$ e Å^{-3}
$\Delta\rho_{min} = -0.651$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Compound (2)

Crystal data

[$ReBr(CO)_3(C_5H_{14}P_2)$]
$M_r = 486.26$
Orthorhombic
$P2_12_12_1$
$a = 10.365$ (1) Å
$b = 11.375$ (3) Å
$c = 12.518$ (3) Å
$V = 1475.8$ (8) Å^3
$Z = 4$
$D_x = 2.19$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 11.60\text{–}16.47°$
$\mu = 11.2$ mm^{-1}
$T = 293$ K
Block
0.33 × 0.33 × 0.26 mm
Colorless
Crystal source: $CH_2Cl_2/C_6H_5CH_3/C_6H_{14}$

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical (*DIFABS*; Walker & Stuart, 1983)
$T_{min} = 0.814$, $T_{max} = 1.538$
1681 measured reflections
1681 independent reflections

1392 observed reflections [$I \geq 2.0\sigma(I)$]
$\theta_{max} = 26.0°$
$h = 0 \rightarrow 12$
$k = 0 \rightarrow 13$
$l = 0 \rightarrow 15$
3 standard reflections
frequency: 120 min
intensity variation: ±1%

Refinement

Refinement on F
$R = 0.036$

$w = 4F/[\sigma^2(I) + (0.04F^2)^2]$
$(\Delta/\sigma)_{max} = 0.07$

$wR = 0.047$
$S = 1.498$
1392 reflections
136 parameters
H-atom parameters not refined

$\Delta\rho_{\max} = 0.94$ e Å^{-3}
$\Delta\rho_{\min} = -1.47$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$B_{\rm eq} = (8\pi^2/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$
(1)				
Br	0.92419 (6)	0.93454 (6)	0.90643 (5)	4.37 (1)
Mn	0.73287 (7)	0.87972 (7)	0.78910 (6)	2.99 (1)
P(1)	0.8763 (1)	0.7666 (1)	0.6872 (1)	3.36 (3)
P(2)	0.7448 (1)	0.6903 (1)	0.8638 (1)	3.28 (2)
O(1)	0.7681 (6)	1.1097 (4)	0.6745 (4)	7.4 (1)
O(2)	0.5137 (5)	0.8074 (5)	0.6560 (4)	7.4 (1)
O(3)	0.5604 (5)	0.9852 (5)	0.9524 (4)	7.9 (1)
C(1)	0.7541 (6)	1.0212 (5)	0.7178 (5)	4.4 (1)
C(2)	0.5991 (6)	0.8388 (5)	0.7072 (5)	4.7 (1)
C(3)	0.6283 (6)	0.9455 (6)	0.8893 (5)	4.7 (1)
C(4)	0.8899 (6)	0.6479 (5)	0.7889 (4)	4.1 (1)
C(5)	0.8180 (8)	0.6967 (7)	0.5641 (5)	5.8 (2)
C(6)	1.0378 (6)	0.8089 (6)	0.6502 (5)	5.2 (1)
C(7)	0.7738 (7)	0.6615 (6)	1.0062 (5)	4.9 (1)
C(8)	0.6237 (7)	0.5803 (6)	0.8284 (5)	5.6 (1)
(2)				
Re	0.26807 (5)	0.11514 (5)	0.21129 (4)	2.606 (8)
Br	0.0655 (2)	0.0654 (2)	0.0932 (1)	4.22 (3)
P(1)	0.2526 (4)	0.3125 (3)	0.1355 (3)	3.02 (7)
P(2)	0.1214 (4)	0.2388 (4)	0.3149 (3)	3.08 (8)
O(1)	0.443 (2)	−0.003 (1)	0.042 (1)	7.7 (4)
O(2)	0.497 (1)	0.191 (1)	0.347 (1)	8.5 (4)
O(3)	0.232 (2)	−0.118 (1)	0.334 (1)	6.8 (3)
C(1)	0.378 (2)	0.035 (1)	0.103 (1)	4.7 (4)
C(2)	0.408 (2)	0.155 (2)	0.298 (1)	5.0 (4)
C(3)	0.242 (2)	−0.033 (1)	0.294 (1)	4.2 (3)
C(4)	0.107 (1)	0.353 (1)	0.213 (1)	3.7 (3)
C(5)	0.376 (2)	0.420 (2)	0.170 (2)	5.0 (4)
C(6)	0.217 (2)	0.345 (2)	−0.002 (1)	4.7 (4)
C(7)	−0.043 (2)	0.196 (2)	0.350 (2)	5.4 (4)
C(8)	0.181 (2)	0.314 (2)	0.433 (1)	6.1 (5)

Table 2. *Selected geometric parameters* (Å, °) *for* (1) (*M* = Mn) *and* (2) (*M* = Re)

	(1)	(2)
M—Br	2.528 (1)	2.629 (2)
M—P(1)	2.322 (2)	2.443 (4)
M—P(2)	2.317 (2)	2.443 (4)
M—C(1)	1.827 (6)	1.99 (2)
M—C(2)	1.774 (7)	1.87 (2)
M—C(3)	1.802 (7)	1.99 (2)
Br—*M*—P(1)	86.86 (5)	85.8 (1)
Br—*M*—P(2)	87.22 (5)	85.7 (1)
Br—*M*—C(1)	88.4 (2)	88.7 (6)
Br—*M*—C(2)	179.1 (2)	177.7 (5)
Br—*M*—C(3)	88.5 (2)	90.1 (5)
P(1)—*M*—P(2)	71.52 (5)	68.7 (1)
P(1)—*M*—C(1)	97.7 (2)	101.2 (7)
P(1)—*M*—C(2)	92.7 (2)	93.0 (7)
P(1)—*M*—C(3)	168.3 (2)	165.6 (5)
P(2)—*M*—C(1)	168.6 (2)	168.7 (7)
P(2)—*M*—C(2)	91.9 (2)	92.0 (6)
P(2)—*M*—C(3)	97.6 (2)	97.2 (5)
C(1)—*M*—C(2)	92.4 (3)	93.4 (8)
C(1)—*M*—C(3)	92.9 (3)	92.6 (8)
C(2)—*M*—C(3)	91.8 (3)	90.6 (8)
M—C(1)—O(1)	179.1 (6)	176 (2)
M—C(2)—O(2)	177.0 (6)	173 (2)
M—C(3)—O(3)	178.6 (7)	175 (2)

For compound (1), an absorption correction based on ψ scans for four reflections having χ near 90° was applied to the data. The Br atom was located from an origin-removed Patterson map and the remainder of the structure developed from $\Delta\rho$ maps following intervening cycles of full-matrix least-squares refinement. Following refinement of all non-H atoms with anisotropic displacement parameters, reasonable positions were found in a $\Delta\rho$ map for the H atoms. These were placed in idealized positions (C—H = 0.95 Å) with isotropic displacement parameters 20% larger than those of the attached C atoms and updated periodically. Following convergence of this model, the opposite enantiomer was refined to convergence resulting in significantly lower (> 95% confidence level) values for R and wR. Hence, the latter enantiomer is the correct choice.

For compound (2), an empirical absorption correction (Walker & Stuart, 1983) was applied to the data following refinement of the model with isotropic displacement parameters. Based on the apparent isomorphism of (2) and (1), the final positional parameters obtained for (1) were used as a starting point and full-matrix least-squares refinement rapidly converged. At this point, with all non-H atoms having anisotropic displacement parameters, the opposite enantiomer was refined to convergence resulting in significantly (> 95% confidence level) lower values of R and wR. Hence, the latter enantiomer is the correct one. Treatment of the H atoms was the same as for (1).

All calculations were performed on a VAXstation 3100. Crystal orientation, unit-cell determination and refinement and data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Data reduction, structure solution and refinement: *MolEN* (Fair, 1990). Graphics: *ORTEP*II (Johnson, 1976).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CR1086). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Tetrasodium Bis(μ-L-tartrato)-1κ^2O^1,O^2:2κ^2O^3,O^4-bis[oxovanadate(IV)] Hexahydrate

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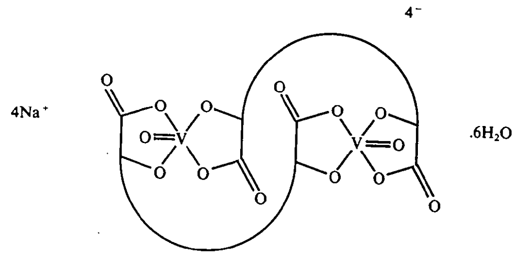
Abstract

The structure of the title compound, Na$_4$[(VO)(L-C$_4$H$_2$O$_6$)]$_2$.6H$_2$O, is described. The crystal structure comprises an arrangement of dimeric tetranegative [(VO)(L-C$_4$H$_2$O$_6$)]$_2^{4-}$ anions, Na cations and water molecules. The vanadyl ions are coordinated by two L-tartrate ligands in a *cis* position. These ions exhibit a V···V′ intradimeric distance of 4.2929 (5) Å and are nearly colinear, showing an O=V···V′ angle of 177.30 (9)°. In the crystal structure, the Na$^+$ cations and the water molecules form layers which alternate with layers of the dimeric anions along the *c* axis.

Comment

There is a growing interest in alkaline earth vanadium oxides because of the proposed relationship between spin $\frac{1}{2}$ antiferromagnets and superconductivity. Heterobimetallic complexes of alkaline earth ions and vanadium(IV) are of potential value in this context because they contain well defined V^{IV}:M^{II} ratios and can result in mixed oxides after adequate thermal treatment (García-Jaca, Insausti, Larramendi, Arriortua, Rojo & Hernandez, 1993; García-Jaca, Insausti, Pizarro, Cortes, Arriortua & Rojo, 1994). The title compound (I) has been used as a precursor for the preparation of alkaline earth vanadyl L-tartrates.



(I)

The crystal structure of the title compound consists of dimeric tetranegative [(VO)(L-C$_4$H$_2$O$_6$)]$_2^{4-}$ anions and a complex arrangement of Na$^+$ ions and water molecules. The dimeric anions are formed by two VO^{2+} ions [V···V^i 4.2929 (5) Å; symmetry code: (i) y, x, $-z$] bonded by two L-tartrate tetranegative ligands forming a geometry with C_2 but close to D_2 symmetry, as shown in Fig. 1. The vanadyl groups in each dimer are nearly parallel with an O=V···V^i angle of 177.30 (9)°. Each VO^{2+} group is coordinated by the O atoms of two hydroxyl groups [O(3) and O(4)] and by one O atom of each of two carboxyl groups [O(2) and O(5)] from the tartrate ligands; the four coordinating O atoms deviate significantly from coplanarity. The two V—O(hydroxyl) bond lengths [V—O(3) and V—O(4)] are slightly shorter than the two V—O(carboxyl) bond lengths

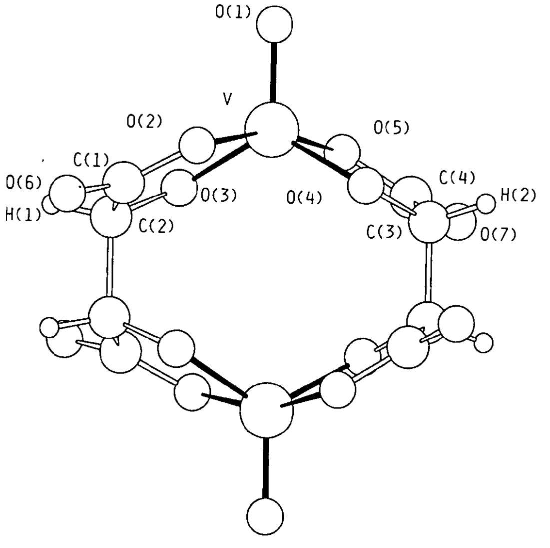


Fig. 1. A view of the [(VO)(L-C$_4$H$_2$O$_6$)]$_2^{4-}$ dimer, showing the atomic numbering.