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A crystallographic and spectroscopic investigation of the stereochemistry of $[\text{MBr}(\text{CO})_3\text{L}_2]$ ($\text{M} = \text{Mn}, \text{Re}$) complexes: crystal and molecular structures of $[\text{MBr}(\text{CO})_3\text{L}_2]$ $\{\text{M} = \text{Mn}, \text{L} = \text{P}(\text{C}_6\text{H}_4\text{Cl-4})_3, 1/2\text{dppe}, 1/2\text{dppf}; \text{M} = \text{Re}, \text{L} = \text{P}(\text{C}_6\text{H}_4\text{OMe-4})_3, 1/2\text{dppf}\}$

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Abstract

A series of $[\text{MBr}(\text{CO})_3\text{L}_2]$ complexes $\{\text{M} = \text{Mn}, \text{L} = \text{P}(\text{C}_6\text{H}_4\text{Cl-4})_3$ (**1**), $\text{P}(\text{C}_6\text{H}_4\text{OMe-4})_3$ (**2**), $\text{P}(\text{CH}_2\text{C}_6\text{H}_4)_3$ (**3**), $1/2\text{dppe}$ (**4**), $1/2\text{dppb}$ (**5**), $1/2\text{dppf}$ (**6**); $\text{M} = \text{Re}, \text{L} = \text{P}(\text{C}_6\text{H}_4\text{Cl-4})_3$ (**7**), $\text{P}(\text{C}_6\text{H}_4\text{OMe-4})_3$ (**8**), $\text{P}(\text{CH}_2\text{C}_6\text{H}_4)_3$ (**9**), $1/2\text{dppp}$ (**10**), $1/2\text{dppb}$ (**11**), $1/2\text{dppf}$ (**12**) $\}$ were synthesised and characterised by elemental analysis, m.p., IR and ³¹P-NMR spectroscopy. With the exception of **4**, all compounds are previously unreported. Five selected examples (**1**, **4**, **6**, **8**, and **12**) were characterised by single crystal X-ray diffraction studies. These studies confirmed *fac,cis* geometries for Re(I) derivatives and all complexes with bidentate ligands; the remaining Mn(I) derivatives had *mer,trans* geometries.

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Keywords: Manganese; Rhenium; Carbonyl complex; Organophosphine ligands; X-ray structure

1. Introduction

The chemistry of Group 7 metal carbonyl halide complexes derived from $[\text{MX}(\text{CO})_5]$ ($\text{M} = \text{Mn}, \text{Re}; \text{X} = \text{Cl}, \text{Br}, \text{I}$) is well documented in the literature [1,2]. We were drawn into re-examining this area as we required the preparation of a series of suitable precursor complexes, $[\text{MBr}(\text{CO})_3\text{L}_2]$ ($\text{M} = \text{Mn}, \text{Re}; \text{L} = \text{triorganophosphine}$), for the synthesis of some new Group 7

metallatetraborane derivatives [3]. Several of these complexes were previously unreported, and their synthesis and characterization form the basis of this report. The stereochemistry of $[\text{MBr}(\text{CO})_3\text{L}_2]$ ($\text{M} = \text{Mn}, \text{Re}; \text{L} = \text{triorganophosphine}$) complexes has often been assigned, in the absence of single-crystal X-ray diffraction data, by examination of their IR CO stretching regions [1,2]. However, this type of analysis may occasionally result in erroneous stereochemical assignments [4]. This manuscript reports the preparation of 11 new and one previously synthesised $[\text{MBr}(\text{CO})_3\text{L}_2]$ ($\text{M} = \text{Mn}, \text{Re}; \text{L} = \text{triorganophosphine}$) complexes and examines their IR and ³¹P-NMR spectra. Single-crystal X-ray studies

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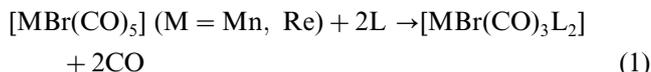
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of five of these complexes {M = Mn, L = P(C₆H₄Cl-4)₃, 1/2dpppe, 1/2dppf; M = Re; L = P(C₆H₄OMe-4)₃, 1/2dppf} are reported. The IR spectra of these complexes of known stereochemistry are then used as a benchmark to assign the stereochemistries of the other derivatives on the basis of their IR spectra.

2. Results and discussion

2.1. Synthesis and stereochemistry of [MBr(CO)₃L₂] (M = Mn, Re) derivatives

The complexes [MBr(CO)₃L₂] {M = Mn with L = P(C₆H₄Cl-4)₃ (**1**), P(C₆H₄OMe-4)₃ (**2**), P(CH₂C₆H₄)₃ (**3**), 1/2dppe (**4**), 1/2dppb (**5**), 1/2dppf (**6**); M = Re with L = P(C₆H₄Cl-4)₃ (**7**), P(C₆H₄OMe-4)₃ (**8**), P(CH₂C₆H₄)₃ (**9**), 1/2dppp (**10**), 1/2dppb (**11**), 1/2dppf (**12**)} were prepared following a literature method [5] by a stoichiometric reaction in refluxing chloroform for 8 h (Mn) or 24 h (Re) (Eq. (1)). Satisfactory elemental analysis was obtained for all compounds and characterisation data are reported in Section 3. Yields were moderate to excellent and ranged from 51 to 91% (Mn) and 49 to 85% (Re). All compounds except **4** [6–9] are previously unreported.



The geometrical configuration about the metal centre in [MBr(CO)₃L₂] (M = Mn, Re) derivatives may be *mer,cis*-, *mer,trans*-, or *fac,cis*-. The [ReBr(CO)₃L₂] complexes generally, unless forcing conditions are employed in the synthesis, have *fac,cis*- stereochemistry [10,11], and our products are all formulated as such with the *fac* structures of **8** and **12** confirmed by a single-crystal X-ray studies. The *fac,cis*- configuration is also likely to be obtained for Mn(I) derivatives with bidentate organophosphine ligands and complexes **4–6** are assigned this configuration, with the structures of **4**, **CHCl₃** and **6** confirmed by crystallographic studies. A recent publication by Pope and Reid [9] has reported the synthesis of **4** and also describes an X-ray structure of **4** · 1/2CHCl₃. The structures of the [MnBr(CO)₃L₂] complexes with two monodentate organophosphine ligands usually have either *fac,cis*- or *mer,trans*- stereochemistry, and their relative stabilities must be very similar since Kruger et al. [12] have isolated and crystallographically characterised both isomers for [MnBr(CO)₃{P-Ph(OMe)₂}]₂. There are no literature reports of isolation of the *mer,cis*- structural type to date, although it appears that such species have been generated electrochemically [13]. It has been argued [5,14] that thermal substitution of [MnBr(CO)₅] proceeds stepwise with the *fac,cis*-[MnBr(CO)₃L₂], obtained from substitution of

the initially formed *cis*-[MnBr(CO)₄L], being thermally isomerised to *mer,trans*-[MnBr(CO)₃L₂]. Our Mn(I) complexes of monodentate ligands (**1–3**), obtained after 8 h reflux in CHCl₃, are formulated as the *mer,trans*-isomers on the basis of spectroscopic evidence and a crystallographic study of **1**.

Spectroscopic evidence for these structural assignments is based on IR and ³¹P-NMR data. The use of IR spectra for distinguishing between isomeric metal–carbonyl species based on *local* symmetry of the CO groups has been used extensively by organometallic chemists [4]. However, much early literature on these *fac,cis*- and the *mer,trans*-[MBr(CO)₃L₂] systems is confused with two bands sometimes taken (erroneously) as clear evidence for the *fac,cis*- product. Using the point group symmetry of the complexes both the *fac,cis* (C_s) and the *mer,trans* (C_{2v}) isomers, should both show 3 (2A' + A'' for *fac,cis*; 2A₁ + B₂ for *mer,trans*) carbonyl bands. Consistent with this, three bands were observed in the 1850–2050 cm⁻¹ region for all compounds **1–12** (see Section 3 for data). The relative intensities of these bands were diagnostic of their structures: **1–3** showed two intense bands with a weaker band at higher energy, whilst **4–12** showed three bands of approximately equal intensity but with the absorption at highest energy being much sharper and slightly more intense. Single-crystal diffraction studies on representative examples (**1**, **4**, **6**, **8**, and **12**) confirmed *mer,trans*- geometries for **1** (and hence **1–3**) and *fac,cis*- structures for **4**, **6**, **8**, and **12** (and hence **4–12**). These general structural assignments for **1–12** are in accord with previous literature formulations for related compounds [6–9,15–18]. ³¹P-NMR spectroscopic evidence was also supportive of the above formulations with all compounds displaying one signal, consistent with either the *mer,trans* or *fac,cis* configuration and inconsistent with the *mer,cis* configuration which would be expected to show two signals. Δδ(³¹P) values (= δ_{ligand} – δ_{complex}/ppm) for complexes **1–12** were generally negative (except **9**) demonstrating an expected high frequency ³¹P shift upon coordination to the metal. Generally larger shifts to high frequency are observed for the Mn(I) derivatives than for the Re(I) complexes, and this may be due to differences in size and electron distribution about the metal. The Δδ values for complexes **1–12** fit within the range defined by the extreme values observed for dppe and dppm complexes [17]. Δδ(³¹P) values for the related complexes [MnBr(CO)₃(PPh₃)₂] (Δδ – 59.3), and [ReBr(CO)₃(PPh₃)₂] (Δδ – 5.0) were measured and these also fit within these dppe/dppm extremes. For Mn(I) these shifts were not diagnostic of configuration: the *mer,trans*-Mn(I) complexes **1–3** and [MnBr(CO)₃(PPh₃)₂] (Δδ – 54.2 to – 62.0) were within the range observed for the *fac,cis*-Mn(I) complexes **4–6** (Δδ – 49.7 to – 82.8).

2.2. Solid state crystal and molecular structures of $1 \cdot \text{CHCl}_3$, $4 \cdot \text{CHCl}_3$, 6 , 8 , and 12

Crystallographic studies of selected $[\text{MBr}(\text{CO})_3\text{L}_2]$ ($\text{M} = \text{Mn}$, Re , $\text{L} = \text{organophosphine}$) species were undertaken to establish unequivocally their stereochemistries, and to establish trends in bond-lengths and bond-angles. Single crystals suitable for X-ray diffraction analysis were grown by diffusion of hexane into solutions of the complexes in CHCl_3 . Thermal ellipsoid plots of the molecular structures of **1**, **4**, **6**, **8**, and **12** can be found in Figs. 1–5, respectively. Selected bond lengths and bond angles for each structure can be found in the legends to the figures. The structures of all the compounds can be seen as octahedral or distorted octahedral with *fac,cis* geometries for **4**, **6**, **8**, and **12**, and a *mer,trans* geometry for **1**. The molecular structure reported here for **4**, as its solvate $4 \cdot \text{CHCl}_3$, is very

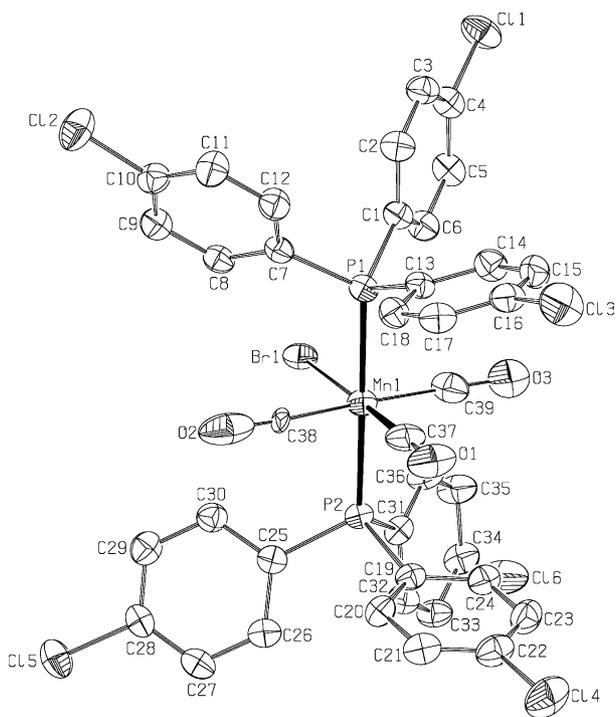


Fig. 1. Molecular structure of *mer,trans*- $[\text{MnBr}(\text{CO})_3\{\text{P}(\text{C}_6\text{H}_4\text{Cl}-4)_3\}]$ (**1**) as found in $1 \cdot \text{CHCl}_3$ showing atomic numbering scheme. Selected interatomic distances (Å) and angles ($^\circ$) with esds in parenthesis: C37–Mn1 1.7986(8); C38–Mn1 1.7086(7); C39–Mn1 1.804(4); P1–Mn1 2.3260(11); P2–Mn1 2.3275(10); Mn1–Br1 2.5458(7); C37–Mn1–C38 171.03(8); C37–Mn1–C39 85.58(17); C38–Mn1–C39 85.66(17); C37–Mn1–P1 88.41(12); C38–Mn1–P1 89.82(12); C39–Mn1–P1 91.27(13); C37–Mn1–P2 91.48(12); C38–Mn1–P2 90.59(11); C39–Mn1–P2 90.71(13); P1–Mn1–P2 178.01(4); C37–Mn1–Br1 94.76(8); C38–Mn1–Br1 94.03(7); C39–Mn1–Br1 178.87(12); P1–Mn1–Br1 89.82(3); P2–Mn1–Br1 88.21(3).

similar to that previously reported [9] for $4 \cdot 1/2\text{CHCl}_3$ but unit cell parameters and Z values are very different. Bond lengths and bond angles may be appropriately compared to previously structurally characterised bromotricarbonyl Mn(I) and Re(I) P-donor ligand derivatives: $4 \cdot 1/2\text{CHCl}_3$ [9], *fac,cis*- $[\text{MBr}(\text{CO})_3\text{L}_2]$ $\{\text{M} = \text{Mn}$, $\text{L} = \text{PPhH}_2$, $\text{PPh}(\text{OMe})_2$ [9,12] $\text{M} = \text{Re}$, $\text{L} = \text{PPh}_2(\text{OEt})$, $1/2\eta^2\text{-CH}_3\text{C}(\text{CH}_2\text{PPh}_2)_3$, $1/2\text{C}_6\text{H}_4\text{P}(\text{CH}_2\text{OH})_2$ [19–21] $\}$ and *mer,trans*- $[\text{MnBr}(\text{CO})_3\{\text{PPh}(\text{OMe})_2\}_2]$ [12]. The chloro compounds $[\text{MnCl}(\text{CO})_3(\text{dppf})]$ and $[\text{ReCl}(\text{CO})_3(\text{dppf})]$, which are closely related to **6** and **12** have also been characterized crystallographically [22,23].

Structural features of the *fac,cis*-Mn(I) (**4** and **6**) and *fac,cis*-Re(I) (**8** and **12**) complexes will be described first. The Mn–Br distances in compounds **4** and **6** ranged from 2.5068(8)–2.5198(10) Å, and were significantly larger than those found for the *mer,trans* derivative **1** (2.5458(7) Å). These distances for $4 \cdot \text{CHCl}_3$ and **6** were within error of those observed for these distances in $4 \cdot 1/2\text{CHCl}_3$ [9] and *fac,cis*- $[\text{MnBr}(\text{CO})_3(\text{PPhH}_2)_2]$ [9]. The Re–Br distances in compounds **8** and **12**, were as expected longer, and ranged from 2.586(3) to 2.6308(6) Å and comparable to those observed in previous Re–Br derivatives [19–21]. Likewise, the Mn–P distances $\{2.3206(17)\text{--}2.4000(11)\text{Å}\}$ were shorter than analogous distances $\{2.5180(18)\text{--}2.5520(16)\text{Å}\}$ found in the Re derivatives.

The M–C bondlength ranges overlapped for the Mn $\{1.818(7)\text{--}1.953(9)\text{Å}\}$ and Re $\{1.855(19)\text{--}1.950(4)\text{Å}\}$ derivatives although the average Mn–C distance (1.86 Å) was shorter than the average Re–C distance (1.92 Å). The inter-ligand angles about Mn(I) in $4 \cdot \text{CHCl}_3$ $\{172.58\text{--}178.69$, av. 176.27° , and $84.74(6)\text{--}93.96(17)$, av. $89.97^\circ\}$ and **6** $\{169.25(12)\text{--}174.17(12)$, av. 172.26° , and $81.56(12)\text{--}96.85(3)$, av. $89.93^\circ\}$ and Re(I) in **8** $\{168.79(11)\text{--}177.98(10)$, av. 172.22° , and $83.82(10)\text{--}105.89(3)$, av. $90.05^\circ\}$, and **12** $\{169.6(2)\text{--}175.4(5)$, av. 172.59° , and $84.6(4)\text{--}99.79(6)$, av. $90.1^\circ\}$ indicate slightly distorted octahedral environment about the d^6 -metal centres. The P–Re–P angles in **8** and **12** were always the largest of the ‘*cis*’-angles within these complexes, at $105.89(3)$ and $99.79(6)^\circ$, respectively. Similarly, the P–Mn–P angle of the Mn/dppf complex (**6**) was large at $94.88(4)^\circ$ whereas $4 \cdot \text{CHCl}_3$ (with the dppe ligand) had a more normal ‘bite-size’ angle of $84.74(6)^\circ$. The ‘bite-size’ angle in $[\text{ReCl}(\text{CO})_3(\text{dppf})]$ is $93.58(4)^\circ$ [22] and that of $[\text{MnCl}(\text{CO})_3(\text{dppf})]$ $94.95(5)^\circ$ [23].

Of the five compounds crystallographically characterised, $1 \cdot \text{CHCl}_3$ has the unique *mer,trans* geometry, with CO ligands *mer* and the organophosphines *trans*. The inter-ligand angles about Mn(I) range from $85.58(17)$ to $94.76(8)^\circ$ (av. 90.0°), and $171.03(8)\text{--}178.87^\circ$ (av. 175.97°) are indicative of a slightly distorted octahedral environment about the d^6 -Mn(I) centre. The

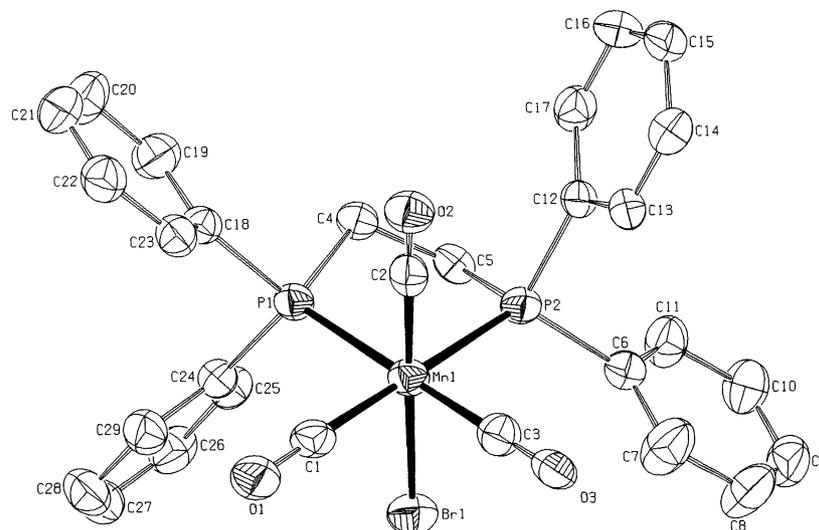


Fig. 2. Molecular structure of *fac,cis*-[MnBr(CO)₃(dppe)] (**4**) as found in 4·CHCl₃ showing atomic numbering scheme. Selected interatomic distances (Å) and angles (°) with esds in parenthesis: Mn1–C1 1.827(6); Mn1–C2 1.818(7); Mn1–C3 1.953(9); Mn1–Br1 2.5198(10); Mn1–P1 2.3206(17); Mn1–P2 2.3325(17); Br1–Mn1–C2 177.56(17); P1–Mn–C3 178.69(17); P2–Mn1–C1 172.58(19); P1–Mn1–P2 84.74(6); P1–Mn1–C1 90.56(18); P1–Mn1–C2 90.06(17); P1–Mn1–Br1 89.05(5); P2–Mn1–C2 92.72(17); P2–Mn1–Br1 84.94(5); P2–Mn1–C3 93.96(17); Br1–Mn1–C1 89.26(18); Br1–Mn–C3 90.70(16); C1–Mn1–C2 93.0(2); C1–Mn–C3 90.7(2); C3–Mn–C2 90.1(2).

Mn–P distances {av. 2.3267(10) Å} are somewhat longer than that found in *mer,trans*-[MnBr(CO)₃{P-Ph(OMe)₂}]₂ {av. 2.264(8) Å} [12] but this may be attributed to the weaker π-acceptor nature of the P(C₆H₄Cl-4)₃ ligands. The three Mn–C bonds in 1·CHCl₃ varied from 1.7086(7) to 1.804(4) Å but such variations were not as would be expected from the *trans* influence, indicating that other factors such as crystal packing were dominant.

3. Experimental

3.1. General

Reactions were carried out under N₂ in dried solvents. IR spectra were recorded on a Perkin–Elmer FT-IR spectrometer as KBr discs or as thin-films between NaCl plates. ³¹P-NMR were recorded on a Bruker AC250 CP/MAS NMR spectrometer operating at 101.25 MHz and

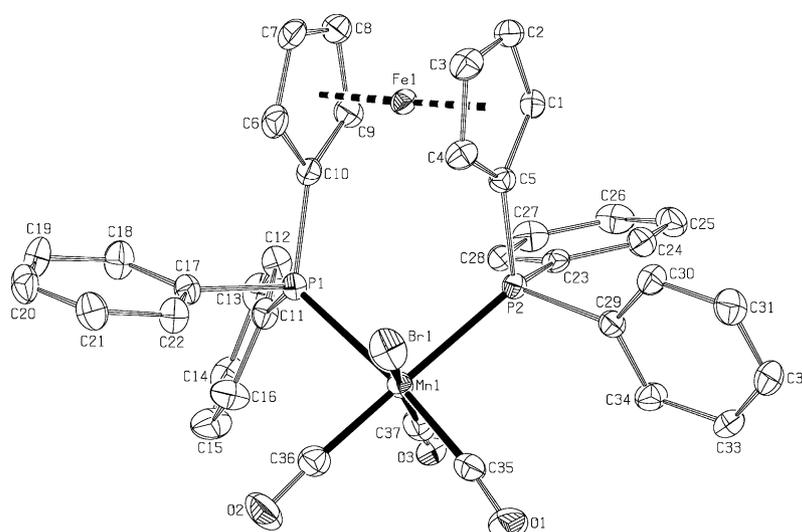


Fig. 3. Molecular structure of *fac,cis*-[MnBr(CO)₃(dppf)] (**6**) showing atomic numbering scheme. Selected interatomic distances (Å) and angles (°) with esds in parenthesis: Mn1–Br1 2.5068(8); Mn1–C35 1.821(4); Mn1–C36 1.824(4); Mn1–C37 1.938(5); Mn1–P1 2.4000(11); Mn1–P2 2.3769(11); Br1–Mn1–P1 96.85(3); Br1–Mn1–P2 87.58(3); Br1–Mn1–C35 81.56(12); Br1–Mn1–C36 86.90(12); Br1–Mn–C37 169.25(12); P1–Mn1–P2 94.88(4); C35–Mn1–C36 85.85(16); C35–Mn1–C37 87.71(17); C36–Mn1–C37 91.62(15); C35–Mn1–P2 91.50(11); C36–Mn1–P2 174.17(12); C37–Mn1–P2 93.46(10); C35–Mn1–P1 173.36(11); C36–Mn1–P1 87.62(11); C37–Mn1–P1 93.72(12).

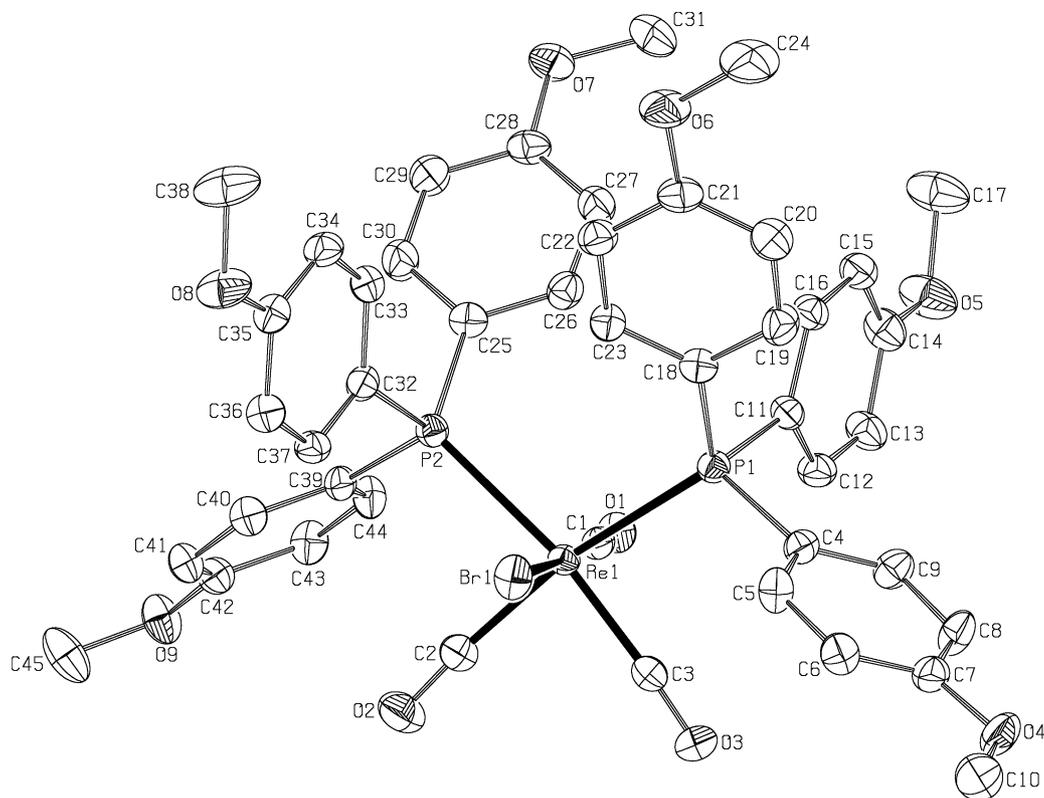


Fig. 4. Molecular structure of *fac,cis*-[ReBr(CO)₃{P(C₆H₄OMe-4)₃}₂] (**8**) showing atomic numbering scheme. Selected interatomic distances (Å) and angles (°) with esds in parenthesis: Re1–Br1 2.6308(6); Re1–P1 2.5279(9); Re1–P2 2.5467(10); Re1–C1 1.926(4); Re1–C2 1.950(4); Re1–C3 1.941(4); C1–Re1–C3 91.21(15); C1–Re1–C2 92.88 (15); C3–Re1–C2 86.48(15); C1–Re1–P1 92.91(10); C3–Re1–P1 83.82(10); C2–Re1–P1 168.79(11); C1–Re1–P2 85.66(10); C2–Re1–P2 84.11(11); C3–Re1–P2 169.91(10); P1–Re1–P2 105.89(3); C1–Re1–Br1 177.98(10); C2–Re1–Br1 87.36(11); C3–Re1–Br1 90.80(11); P1–Re1–Br1 87.19(2); P2–Re1–Br1 92.37(2).

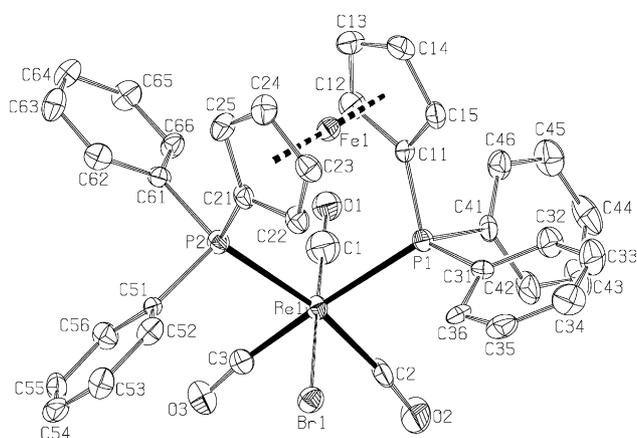


Fig. 5. Molecular structure of molecule **I** in *fac,cis*-[ReBr(CO)₃(dppf)] (**12**) showing atomic numbering scheme. There are three independent molecules within the asymmetric unit cell. Selected interatomic distances (Å) and angles (°) with esds in parenthesis: Re1–C1 1.855(19); Re1–C2 1.930(7); Re1–C3 1.943(8); Re1–P1 2.5180(18); Re1–P2 2.5520(16); Re1–Br1 2.586(3); C1–Re1–C2 90.6(5); C1–Re1–C3 91.0(5); C2–Re1–C3 87.6(3); C1–Re1–P1 84.6(4); C2–Re1–P1 87.7(2); C3–Re1–P1 172.76(19); C1–Re1–P2 97.4(4); C2–Re1–P2 169.6(2); C3–Re1–P2 86.42(19); P1–Re1–P2 99.79(6); C1–Re1–Br1 175.4(5); C2–Re1–Br1 85.4(2); C3–Re1–Br1 86.7(2); P1–Re1–Br1 97.33(6); P2–Re1–Br1 86.41(6).

chemical shifts are given in ppm with positive values towards high frequency of 85% H₃PO₄. Elemental analysis (C, H, N) were obtained on a Carlo-Erba EA-1108 Elemental Analyzer instrument using helium as a carrier gas. Single-crystals, suitable for X-ray diffraction of **1**·CHCl₃, **4**·CHCl₃, **6**, **8**, and **12** were grown by slow diffusion of hexane into CHCl₃ solutions of the complexes at 6 °C.

3.2. Synthesis

The [MBr(CO)₃L₂] derivatives **1**–**12** were all prepared by a standard literature method [5] and yields, elemental analyses, $\nu(\text{CO})$, $\delta(^{31}\text{P})$, and m.p.s are listed below.

3.2.1. *mer,trans*-[MnBr(CO)₃{P(C₆H₄Cl-4)₃}₂] (**1**)

Yield = 51%. M.p. = 139 °C. $\nu(\text{CO})/\text{cm}^{-1}$: 2033(w), 1951(vs), 1901(s). $\delta(^{31}\text{P})/\text{ppm}$: +52.8 ($\Delta\delta = -62.0$). (Required for C₃₉H₂₄BrCl₆MnO₃P₂: C, 49.3; H, 2.6. Found: 49.4; H, 2.4%).

3.2.2. *mer,trans*-[MnBr(CO)₃{P(C₆H₄OMe-4)₃}₂] (**2**)

Yield = 77%. M.p. = 138 °C. $\nu(\text{CO})/\text{cm}^{-1}$: 2031(w), 1946(vs), 1908(s). $\delta(^{31}\text{P})/\text{ppm}$: +44.8 ($\Delta\delta = -55.6$).

(Required for $C_{45}H_{42}BrMnO_9P_2$: C, 59.3; H, 3.3. Found: 58.7; H, 4.6%).

3.2.3. *mer,trans*-[$MnBr(CO)_3P(CH_2C_6H_4)_3\}2]$ (**3**)

Yield = 89%. M.p. = 163 °C. $\nu(CO)/cm^{-1}$: 2031(w), 1945(vs), 1912(s). $\delta(^{31}P)/ppm$: +41.8 ($\Delta\delta = -54.2$). (Required for $C_{45}H_{42}BrMnO_9P_2$: C, 65.3; H, 5.1. Found: 65.6; H, 5.1%).

3.2.4. *fac,cis*-[$MnBr(CO)_3(dppb)]$ (**5**)

Yield = 91%. M.p. = 215 °C. $\nu(CO)/cm^{-1}$: 2028(s), 1962(s), 1910(s). $\delta(^{31}P)/ppm$: +32.9 ($\Delta\delta = -49.7$). (Required for $C_{31}H_{28}BrMnO_3P_2$: C, 57.7; H, 4.4. Found: 56.9; H, 4.3%).

3.2.5. *fac,cis*-[$MnBr(CO)_3(dppf)]$ (**6**)

Yield = 60%. M.p. = 191 °C. $\nu(CO)/cm^{-1}$: 2025(s), 1959(s), 1909(s). $\delta(^{31}P)/ppm$: +37.1 ($\Delta\delta = -55.0$). (Required for $C_{37}H_{28}BrFeMnO_3P_2$: C, 57.5; H, 3.7. Found: 57.7; H, 3.8%).

3.2.6. *fac,cis*-[$ReBr(CO)_3\{P(C_6H_4Cl-4)\}_2\}$ (**7**)

Yield = 67%. M.p. = 172 °C. $\nu(CO)/cm^{-1}$: 2035(s), 1956(s), 1912(s). $\delta(^{31}P)/ppm$: -2.8 ($\Delta\delta = -6.4$). (Required for $C_{39}H_{24}BrCl_6O_3P_2Re$: C, 43.3; H, 2.2. Found: 43.1; H, 2.5%).

3.2.7. *fac,cis*-[$ReBr(CO)_3\{P(C_6H_4OMe-4)\}_2\}$ (**8**)

Yield = 70%. M.p. = 180 °C. $\nu(CO)/cm^{-1}$: 2022(s), 1954(s), 1915(s). $\delta(^{31}P)/ppm$: -4.6 ($\Delta\delta = -6.2$). (Required for $C_{45}H_{42}BrO_9P_2Re$: C, 51.1; H, 2.3. Found: 51.2; H, 2.1%).

3.2.8. *fac,cis*-[$ReBr(CO)_3\{P(CH_2C_6H_4)_3\}_2]$ (**9**)

Yield = 59%. M.p. = 179 °C. $\nu(CO)/cm^{-1}$: 2033(s), 1952(s), 1899(s). $\delta(^{31}P)/ppm$: -18.1 ($\Delta\delta = +5.7$). (Required for $C_{45}H_{42}BrO_9P_2Re$: C, 56.4; H, 4.4. Found: 55.9; H, 4.3%).

3.2.9. *fac,cis*-[$ReBr(CO)_3(dppp)]$ (**10**)

Yield = 76%. M.p. = 292 °C. $\nu(CO)/cm^{-1}$: 2034(s), 1955(s), 1904(s). $\delta(^{31}P)/ppm$: -15.9 ($\Delta\delta = -2.2$). (Required for $C_{30}H_{26}BrO_3P_2Re$: C, 47.3; H, 3.5. Found: 47.2; H, 3.4%).

3.2.10. *fac,cis*-[$ReBr(CO)_3(dppb)]$ (**11**)

Yield = 85%. M.p. = 134 °C. $\nu(CO)/cm^{-1}$: 2032(s), 1953(s), 1904(s). $\delta(^{31}P)/ppm$: -4.0 ($\Delta\delta = -12.8$). (Required for $C_{31}H_{28}BrO_3P_2Re$: C, 47.9; H, 3.6. Found: 47.9; H, 3.3%).

3.2.11. *fac,cis*-[$ReBr(CO)_3(dppf)]$ (**12**)

Yield = 60%. M.p. = 166 °C. $\nu(CO)/cm^{-1}$: 2036(s), 1958(s), 1901(s). $\delta(^{31}P)/ppm$: -0.7 ($\Delta\delta = -17.2$). (Required for $C_{37}H_{28}BrFeO_3P_2Re$: C, 49.1; H, 3.1. Found: 49.5; H, 3.3%).

3.3. X-ray structures of **1**·CHCl₃, **4**·CHCl₃, **6**, **8**, and **12**

Data were collected on a Bruker-Nonius KappaCCD area detector diffractometer using Mo-K_a radiation ($\lambda = 0.71073 \text{ \AA}$) (Table 1). All structures were solved and refined using the SHELXL suite of programs [24]. All non-hydrogen atoms were refined anisotropically, whilst hydrogens were placed in idealised positions and refined

Table 1
Crystal data and structure refinement parameters

	1	4	6	8	12
Empirical formula	$C_{40}H_{25}BrCl_9MnO_3P_2$	$C_{30}H_{25}BrCl_3MnO_3P_2$	$C_{37}H_{28}BrFeMnO_3P_2$	$C_{45}H_{42}BrO_9P_2Re$	$C_{37}H_{28}BrFeO_3P_2Re$
Formula weight	1069.44	736.64	773.23	1054.84	904.49
Temperature (K)	293	150	150	150	150
Crystal system, space group	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$	Orthorhombic, $Pbca$	Monoclinic, $P2_1/c$
<i>a</i> (Å)	15.364(3)	11.256(7)	11.515(2)	18.337(4)	9.215(1)
<i>b</i> (Å)	14.099(2)	19.584(11)	19.546(4)	20.515(4)	54.176(3)
<i>c</i> (Å)	20.536(5)	14.755(9)	14.169(3)	22.738(5)	21.767(2)
α (°)	90.0	90.0	90.0	90.0	90.0
β (°)	103.947(10)	108.075(3)	93.26(3)	90.0	111.999(3)
γ (°)	90.0	90.0	90.0	90.0	90.0
<i>V</i> (Å ³)	4317.19(15)	3092.1(3)	3183.9(11)	8554(3)	10075.9(6)
<i>Z</i> , <i>D</i> _{calc} (M g ⁻³)	4, 1.645	4, 1.582	4, 1.613	8, 1.638	12, 1.789
Absorption coefficient (mm ⁻¹)	1.901	2.113	2.245	3.905	5.353
Crystal size (mm)	0.3 × 0.2 × 0.2	0.2 × 0.05 × 0.05	0.15 × 0.125 × 0.1	0.2 × 0.2 × 0.2	0.07 × 0.07 × 0.05
θ max (°)	23.24	24.71	27.49	30.41	25.05
Reflections collected, unique	57 780, 6201	49 193, 5257	36 700, 7273	65 319, 11 208	56 559, 17 103
<i>R</i> _{int}	0.0747	0.1412	0.0652	0.0588	0.0604
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)] <i>R</i> ₁ , <i>wR</i> ₂	0.0582, 0.1643	0.0567, 0.1357	0.0494, 0.1433	0.0375, 0.0954	0.0454, 0.0928
<i>R</i> indices (all data) <i>R</i> ₁ , <i>wR</i> ₂	0.0742, 0.1513	0.1023, 0.1574	0.0663, 0.1549	0.0652, 0.1165	0.0715, 0.1007
ρ_{max} , ρ_{min} (e Å ⁻³)	1.374, -1.495	1.133, -0.531	1.049, -1.726	1.884, -2.020	1.758, -1.287

using the riding model. Data were corrected for absorption effects by means of comparison of symmetry equivalent reflections using the program SORTAV [25]. Figures of the molecular structures determined are plotted using the software package PLATON [26]. Compounds **1** and **4** both contain a molecule of CHCl_3 solvent. Complex **1** shows disorder on three of the equatorial sites where carbonyl and bromide groups share the same coordination mode with bromine sites 70, 15, 15% occupied respectively giving one bromide moiety and two carbonyls in total over the three sites. Complex **12** has three chemically equivalent but crystallographically independent molecules in the asymmetric unit. Of these molecules I (Re1) and II (Re2) have approximately the same geometry, with that of III (Re3) differing considerably. In all three molecules the axial positions of the Re coordination, occupied by Br and CO moieties was found to be disordered with the occupancy of the major components refining to 0.59, 0.56 and 0.75 respectively. An exceptionally disordered CHCl_3 solvate molecule was treated in the manner described by Sluis and Spek [27], whereby the contribution to the structure factors by this moiety is removed which essentially eliminates the solvate from the data and the model.

4. Supplementary material

Crystallographic data for the structure analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. **1**· CHCl_3 (194147), **4**· CHCl_3 (194148), **6** (194149), **8** (194150), and **12** (194151). Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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