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Synthesis and characterisation of a series of Group 7 metal 2,2,2,2-dicarbonylbis(triorganophosphine)-*arachno*-2-metallatetraboranes, $[M(CO)_2L_2(B_3H_8)]$ (M = Re, Mn); crystal and molecular structures of $[Re(CO)_2(dppf)(B_3H_8)]$ and $[Mn(CO)_2(dppe)(B_3H_8)]$

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Abstract

Arachno-2-metallatetraboranes, $[M(CO)_2L_2(B_3H_8)]$ (M = Re, L = PPh_3, $P(C_6H_4Cl\text{-}4)_3$, $P(C_6H_4OMe\text{-}4)_3$, $P(CH_2Ph)_3$; M = Mn and Re, L = 1/2dppm, 1/2dppp, 1/2dppb, 1/2dppf; M = Mn, L = 1/2dppe), have been synthesised from reactions of $[NBu_4][B_3H_8]$ with *fac,cis*-$[MBr(CO)_3L_2]$ under photolytic conditions. These compounds were characterised by NMR (^1H, ^{11}B, ^{31}P) and IR spectroscopy. $[Mn(CO)_2(dppe)(B_3H_8)]$ and $[Re(CO)_2(dppf)(B_3H_8)]$ were further characterised by single-crystal X-ray diffraction studies. These studies confirmed molecular *Cs* symmetry and a *trans* dicarbonyl arrangement. Similar reactions with the bis(monodentate) organophosphine complexes, *mer,trans*-$[MnBr(CO)_3L_2]$, did not yield isolatable *arachno*-2-metallatetraboranes.

Keywords: Boron; Carbonyl complexes; Manganese; Octahydrotriborate(2−); Organophosphine ligands; Rhenium; X-ray structures

1. Introduction

The first *arachno*-2-metallatetraboranes were reported in 1967 [1,2], and since then interest in this class of compounds has continued with examples documented for metals from most Groups of the Periodic Table [3,4]. The Group 7 *arachno*-2-metallatetraboranes were first reported by Gaines and co-workers [5–9] in the 1970s but this Group of the Periodic Table has received little attention since [10]. Gaines and co-workers [5–9] described the synthesis of *arachno*-$[M(CO)_4(B_3H_8)]$ (M = Mn, Re) from $[M_2(CO)_{10}]$, and the synthesis of *arachno*-$[Mn(CO)_3(PPh_3)(B_3H_8)]$ and $[Mn(CO)_2(dppe)(B_3H_8)]$, from *cis*-$[MnBr(PPh_3)(CO)_4]$ and *fac*-$[MnBr(dppe)(CO)_3]$, respectively. Subsequent halogenation of *arachno*-$[Mn(CO)_4(B_3H_8)]$ yielded *arachno*-$[Mn(CO)_4(B_3H_7X)]$ (X = Cl, Br, I), whilst decarbonylation afforded *nido*-$[Mn(CO)_3(B_3H_8)]$ which when reacted with Lewis bases gave *arachno*-$[Mn(CO)_3L(B_3H_8)]$ (L = CO, NH_3, PF_3) derivatives. The closely relates dimetallic species, $[Mn_2(CO)_6(\mu\text{-}Br)(B_3H_8)]$ was reported in 1980 [11]. Comparative structural data down Groups and across Periods of the Periodic Table for particular polyhedral structural classes are limited, and it is of considerable interest to examine such trends. This publication describes the systematic synthesis of a number of Group 7 metallatetraboranes, and includes the crystal and molecular structures of $[Mn(CO)_2(dppe)(B_3H_8)]$ and $[Re(CO)_2(dppf)(B_3H_8)]$.

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2. Results and discussion

2.1. Synthesis of Mn and Re *arachno*-2-metallatetraboranes

The *arachno*-2-metallatetraboranes $[M(CO)_2L_2(B_3H_8)]$ {M = Mn with L = 1/2dppe (**1**), 1/2dppm (**2**), 1/2dppp (**3**), 1/2dppb (**4**), 1/2dppf (**5**); M = Re with L = PPh_3 (**6**), $P(C_6H_4Cl\text{-}4)_3$ (**7**), $P(C_6H_4OMe\text{-}4)_3$ (**8**), $P(CH_2C_6H_4)_3$ (**9**), 1/2dppm (**10**), 1/2dppp (**11**), 1/2dppb (**12**), 1/2dppf (**13**)} were prepared by sealed tube photolytic reactions in CH_2Cl_2 solutions in poor to moderate yields, according to Eq. (1). Reaction times were ~20 h with yields ranging from 17 to 59%.

$$\begin{aligned} &fac,cis\text{-}[MBr(CO)_3L_2](M = Mn,\ Re) + [NBu_4][B_3H_8] \\ &\quad \rightarrow [M(CO)_2L_2(B_3H_8)] + [NBu_4]Br + CO \qquad (1) \end{aligned}$$

Compound **1** has been previously prepared by Gaines and Hildebrandt and our spectroscopic and physical data were in accord with their literature values [7]. Compounds **2**–**13** are previously unreported. All compounds gave satisfactory elemental analysis data, and their spectroscopic and analytical data indicated that they were isomerically pure and that they should all be formulated as isostructural with **1**, i.e. *arachno*-2-metallatetraboranes with axial *trans* dicarbonyls, equatorial *cis* triorganophosphines, and overall C_s molecular symmetry. The bis(monodentate) organophosphine complexes with the Re(I) metal centre, *fac,cis*-$[ReBr(CO)_3L_2]$ {L = PPh_3, $P(C_6H_4Cl\text{-}4)_3$, $P(C_6H_4OMe\text{-}4)_3$, $P(CH_2Ph)_3$}, also yielded isomerically pure compounds **6**–**9** with spectroscopic properties consistent with the other rhenatetraboranes and therefore we have formulated them with the same stereochemistry. We were unable, under similar conditions, to isolate *arachno*-2-manganatetraborane products from the bis(monodentate) organophosphines complexes, *mer,trans*-$[MnBr(CO)_3L_2]$ {L = PPh_3, $P(C_6H_4Cl\text{-}4)_3$, $P(C_6H_4OMe\text{-}4)_3$, $P(CH_2Ph)_3$}, presumably as a result of the reluctance of these bulky organophosphines to adopt the required *cis* geometry about the smaller Mn(I) centre, as was found for all other isolated products.

The spectroscopic evidence for formulating compounds **2**–**13** as derivatives of **1** is based upon NMR (^{11}B, ^{31}P, ^{1}H) and IR data. Single-crystal X-ray diffraction studies of **1** and **13** were also undertaken and the former confirmed Gaines and Hildebrandt's [7] initial structural formulation. The $^{11}B-\{^1H\}$ spectra of compounds **1**–**13** (at 80.25 MHz) all showed sharp low frequency singlet resonances at ~−41 ppm and broader resonances at ~0 ppm. The exact chemical shifts of these higher frequency resonances were hard to determine due to their broadness. Analysis of spectra was further hindered by a baseline 'hump' in this central spectral region downfield region of the spectra due to boron in the NMR probe, and accurate integration of the signals was not possible. Qualitatively, the higher frequency resonance always appeared with an intensity of approximately half that of the lower frequency signal. To confirm this, a 128 MHz $^{11}B-\{^1H\}$ spectrum of **1**, obtained on a low boron content probe, clearly showed the two signals at −40.6 (2B) and +3.0 ppm (1B) in accord with literature data [7]. The $^{11}B-\{^1H\}$ MAS NMR spectrum of **5** and **10** both showed two signals of relative intensity 2:1 at δ −41.4 and −3.4, and −44.4 and −3.9 ppm, respectively, consistent with their solution NMR data and indicating the boron centres are non-equivalent at room temperature on the NMR timescale. There has been one other reported solid-state $^{11}B-\{^1H\}$ MAS NMR study [12] of 2-*arachno*-metallatetraboranes and this demonstrated a solid-state fluxionality of the B atoms in Group 11 metal derivatives, $[M(PR_3)_2(B_3H_8)]$ (M = Ag, Cu) and 'static' structures for Group 6 metal derivatives, $[NMe_4][M(CO)_4(B_3H_8)]$ (M = Cr, W). The $\nu_{1/2}$ values of the lower frequency resonances of **5** and **10** were ~800 Hz whilst the higher frequency resonances were ~2000 Hz. These signals were considerably sharper than the those observed for the Group 6 derivatives [12], with $\nu_{1/2}$ of ~1500 and 2750 Hz, for the analogous low and high frequency resonances.

The ^1H NMR spectra of compounds **1**–**13** all showed, in addition to resonances associated with the *P*-organyl ligands, resonances associated with the B–*H*–B region (~ −0.5 ppm) and the M–*H*–B region (−8.5 to −12.9 ppm) in ranges in accord with other reported 2-metallatetraboranes, and in particular to **1**, $[M(CO)_4(B_3H_8)]$ (M = Mn, Re) [7], and $[ReCp^*H_3(B_3H_8)]$ [10]. Both bridging B–*H*–B and M–*H*–B signals were invariably broad with $\nu_{1/2}$ values of 50–100 Hz. There were clearly defined ranges for Re–*H*–B proton (−8.5 to −9.4 ppm) and Mn–*H*–B proton (−12.7 to −12.9 ppm) chemical shifts, with the exception of **5** (Mn–*H*–B = −9.8 ppm) The Re–*H*–B δ values for **6**–**13** are in the low frequency region of the wide range (−8.0 to −14.1 ppm) reported [7,10,13–16] for rhenaboranes with Re–*H*–B bridges, whilst the Mn–*H*–B δ values for **1**–**5** slightly extend to high frequency the previously reported range (−9.55 to −12.6 ppm) [7,16] for such environments.

The $^{31}P-\{^1H\}$ spectra of compounds **1**–**13** were singlets consistent with the *cis* phosphine and *trans* carbonyl structure proposed by Gaines and Hildebrant for **1**. The effect of replacing {CO and Br^-} ligands with $[B_3H_8]^-$ in *fac*-$[MBr(CO)_3(PR_3)_2]$ complexes generally resulted in $\delta(^{31}P)$ shifts to higher frequency. These shifts were larger for Mn (~35 ppm) than for Re (~20 ppm). Exceptions to these generalities were the low frequency shifts for dppf/Mn (22.5 ppm) and dppb/Re (2.8 ppm). The dppf/Re derivatives showed the smallest high frequency shift (2.7 ppm) of all the Re derivatives.

These shifts to higher frequency may be indicative of the weak π-acceptor nature of the $[B_3H_8]^-$ ligand.

IR spectra generally show two strong bands appropriate for a *trans* geometry and molecular mirror plane symmetry at 1945–1971 and 1882–1912 cm^{-1}. However, Gaines and Hildebrant reported a single strong band at 1922 cm^{-1} for **1**, and we were able to confirm this result and explain it as a result of coincidental overlap of two bands.

*2.2. Solid-state crystal and molecular structures of **1** and **13***

Single-crystals suitable for X-ray diffraction analysis of **1** and **13** were grown by diffusion of hexane into solutions of the metallatetraboranes in $CHCl_3$. Thermal ellipsoid plots of the molecular structures of **1** and **13** are shown in Figs. 1 and 2, respectively, with selected interatomic distances and angles given in the legends to these figures. The co-ordination complexes **1** and **13** have similar gross structures, based upon octahedral geometries about the d^6-Mn(I) (**1**) or d^6-Re(I) (**13**) metal centre with the bidentate organophosphine ligands *trans* to two *cis* metal–hydrogen bridge bonds to boron, and mutually *cis* to two *trans* CO ligands. The $[B_3H_8]^-$ ligand co-ordinates to the metal centres *via* two boron hydrogen bridges and the $\{MB_3\}$ moiety adopts the familiar 'butterfly' structure of *arachno*-B_4H_{10}. The compounds are thus described as 'wing-tip' isomers or *arachno*-2-metallatetraboranes with a d^6-ML_4 fragment replacing a BH_2 'wing-tip' moiety of B_4H_{10}. The spectroscopic data for **1** and **13** described above are in full agreement with their solid-state structures. The $\{MB_3\}$ moieties in **1** and **13** are very similar to other previously structurally characterised *arachno*-2-metallatetraborane derivatives including $[NMe_4][Cr(CO)_4(B_3H_8)]$ [17], $[Mn(CO)_4(B_3H_7Br)]$ [9], $[Cu(PPh_3)_2(B_3H_8)]$ [18], $[NbCp_2(B_3H_8)]$ [19], $[RuH(CO)(PPh_3)_2(B_3H_8)]$ [20], $[Ru(C_6Me_6)Cl(B_3H_8)]$ [21], $[Ru(PPh_3)(HBpz_3)(B_3H_8)]$ [22], $[OsH(CO)(PPh_3)_2(B_3H_8)]$ [23], $[ReCp^*H_3(B_3H_8)]$ [10] and $[WH_3(PMe_3)_3(B_3H_8)]$ [24]. In particular, the Mn1–B1 and Mn1–B3 distances in **1** are similar, but slightly shorter than corresponding lengths of 2.356(9) Å reported for $[Mn(CO)_4(B_3H_7Br)]$ [9], consistent with the

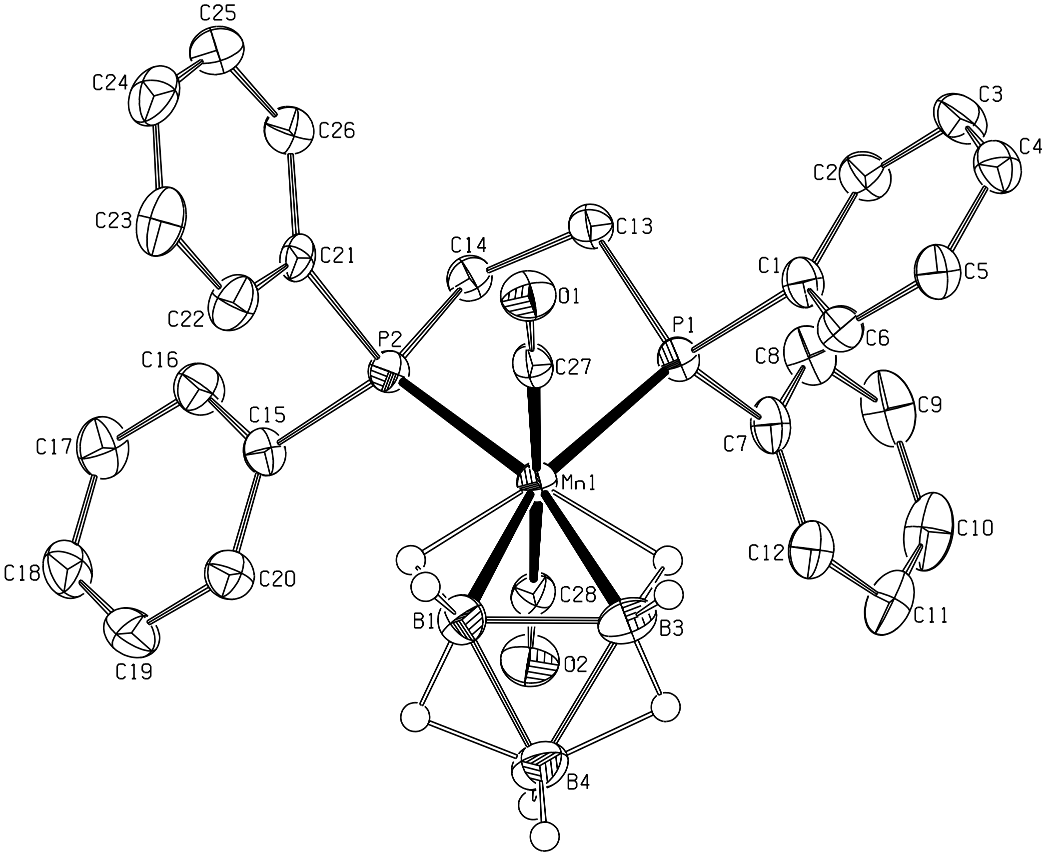

Fig. 1. Molecular structure of $[Mn(CO)_2(dppe)(B_3H_8)]$ (**1**) showing atomic numbering scheme. Selected interatomic distances (Å) and angles (°) with esd's in parenthesis: Mn1–C28 1.835(3); Mn1–C27 1.844(3); Mn1–P1 2.2480(8); Mn1–P2 2.2495(7); Mn1–B1 2.330(3); Mn1–B3 2.336(3); B1–B3 1.756(4); B1–B4 1.788(4); B3–B4 1.815(5); C28–Mn1–C27 176.96(10); C28–Mn1–P1 91.99(7); C27–Mn1–P1 88.55(7); C28–Mn1–P2 87.10(7); C27–Mn1–P2 89.95(7); P1–Mn1–P2 86.34(3); C28–Mn1–B1 96.76(11); C27–Mn1–B1 83.86(11); P1–Mn1–B1 156.69(8); P2–Mn1–B1 115.57(8); C28–Mn1–B3 95.84(11); C27–Mn1–B3 86.69(11); P1–Mn1–B3 113.50(8); P2–Mn1–B3 159.75(8); B1–Mn1–B3 44.22(11); B2–B1–B4 61.59(18); B3–B1–Mn1 68.08(14); B4–B1–Mn1 104.78(17); B1–B3–B4 60.07(17); B1–B3–Mn1 67.70(14); B4–B3–Mn1 103.64(18); B1–B4–B3 58.34(17). O1–C27–Mn1 178.3(2); O2–C28–Mn1 177.3(2). The dihedral angle between planes B1, Mn1, B3 and B1, B3, B4 is 122.06(13)°.

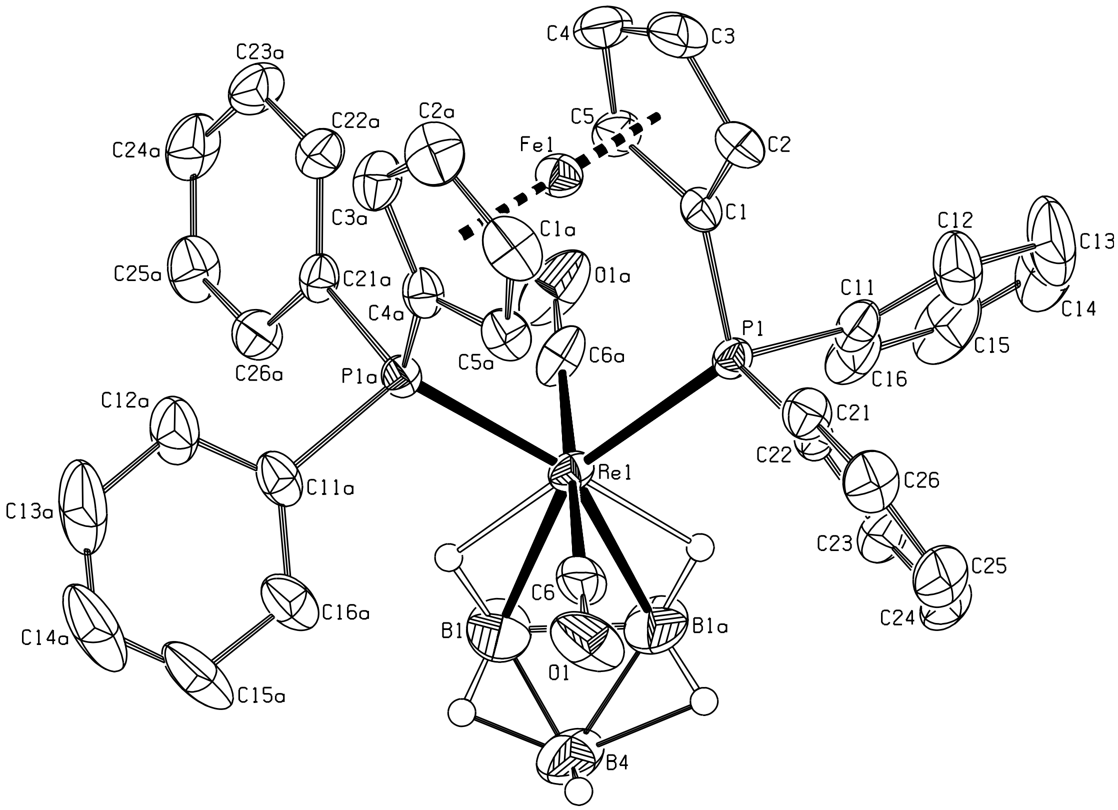

Fig. 2. Molecular structure of $[Re(CO)_2(dppf)(B_3H_8)]$ (**13**) showing atomic numbering scheme and with only one component of the crystallographic disorder shown. Selected interatomic distances (Å) and angles (°) with esd's in parenthesis: Re1–C6 and Re1–C6A 1.968(4); Re1–P1 and Re1–P1A 2.3911(7); Re1–B1 and Re1–B1A 2.432(4); Re1–H(B1) and Re1–H(B1A) 1.83(3); B1–B4 1.653(11); B1–B1A 1.754(10); B4–H1C 1.307(5), B4–H4A 1.247(1), B4–H4B 1.258(1); B1–H1C, 1.098(5), B1–H1A 1.062(5), B1–H1B 1.214(3). P1–Re1–P1A 101.34(3); C6–Re1–C6A 177.17(17); B1–Re1–B1A 42.3(2); C6–Re1–P1A and C6A–Re1–P1 89.64(10); C6–Re1–P1 and C6A–Re1–P1A 88.57(9); C6–Re1–B1 and C6A–Re1–B1A 92.19(17); C6–Re1–B1A and C6A–Re1–B1 90.45(17); P1–Re1–B1 and P1A–Re1–B1A 150.46(12); P1–Re1–B1A and P1A–Re1–B1 108.20(12); H1B–Re1–C6A 89.42(10), H1B–Re1–C6 92.40(10), H1B–Re1–P1A 79.26(10), H1B–Re1–P1 178.87(10), H1B–Re1–B1A 71.22(10), H1B–Re1–B1 28.94(10). The dihedral angle between planes B1, Re1, B1A and B1, B1A, B4 is 127.01(14)°.

trans influence. The dihedral angle for the Mn1–B1–B3/B4–B1–B3 planes of 122.06(13)° for **1** is in the usual range of values (120°–128°) reported for *arachno*-2-metallatetraboranes [9,10,17–24], but significantly smaller than that of 127° reported for $[Mn(CO)_4(B_3H_7Br)]$ [9].

The molecular structure of another *arachno*-2-rhenatetraborane, $[ReCp^*H_3(B_3H_8)]$, was published [10] during the preparation of this manuscript and the interatomic angles and distances adopted by $\{ReB_3\}$ moiety of **13** are generally very similar. The Re–B distances of the Re–H–B bridge bonds are 2.432(4) Å. These data may be compared with corresponding M–B distances of 2.420(8) and 2.453(9) Å for $[ReCp^*H_3(B_3H_8)]$ [10], 2.441(8) and 2.437(10) Å for $[OsH(CO)(PPh_3)_2(B_3H_8)]$ [23], and 2.491(8) and 2.520(7) Å for $[WH_3(PMe_3)_3(B_3H_8)]$ [24]. This distance is within the wide range {2.16(3)–2.52(7) Å} of the corresponding distance in other reported structurally characterised rhenaboranes with Re–H–B bridges: $[ReCp^*H_3(B_3H_8)]$ [10], $Cp^*_2Re_2B_7H_{11}$ [15], $(PMe_2Ph)_3H$-ReB_9H_{13} [13], $(PMe_2Ph)_2ClHReB_9H_{12}(PMe_2Ph)$ [13], and $(PMe_2Ph)_3H_2ReB_8H_{11}$ [14]. The Re–H distances of the Re–H–B bridge bonds at 1.83(3) Å are not significantly different from 1.79(3) and 1.65(4) Å found in the bridge bonds of $(PMe_2Ph)_3HReB_9H_{13}$ [13]. The dihedral angle for the Re1–B1–B1A/B4–B1–B1A planes of 127.01(14)° for **13** is in the usual range of values (120°–128°) reported for 2-metallatetraboranes [9,10,17–24], including 123.5° and 127° reported [23,24] for $[WH_3(PMe_3)_3(B_3H_8)]$ and $[OsH(CO)(PPh_3)_2(B_3H_8)]$.

3. Experimental

3.1. General

Reactions were carried out under N_2 in dried solvents. IR spectra were recorded on a Perkin–Elmer FT-IR spectrometer as KBr discs or as thin-films between NaCl ^{1}H, ^{11}B and ^{31}P NMR were recorded on a Bruker AC250 CP/MAS NMR spectrometer operating at 250.1, 80.2 and 101.25 MHz respectively. Chemical shifts are given in ppm with positive values towards high frequency of $SiMe_4$ (^{1}H), $BF_3 \cdot OEt_2$ (^{11}B), and 85% H_3PO_4 (^{31}P). Elemental analysis (C,H,N) were obtained on a

Carlo-Erba MOD-1106 instrument using helium as a carrier gas. The *fac,cis*-[MBr(CO)$_3$L$_2$] complexes were all prepared by known literature methods and their synthesis and characterisation are reported elsewhere [25].

3.2. Synthesis

The [M(CO)$_2$L$_2$(B$_3$H$_8$)] complexes **1**–**13** were all prepared following a similar method to that adopted by Gaines and Hildebrant [7] as described below for **1**. Elemental analysis data, reaction yields, m.p., and selected IR and NMR data for compounds **1**–**13** are listed below.

3.2.1. [Mn(CO)$_2$(dppe)(B$_3$H$_8$)] (1)

To a Carius tube containing dried and degassed CH$_2$Cl$_2$ (20 cm^3) was added *fac,cis*-[MnBr(CO)$_3$(dppe)] (351 mg, 0.5 mmol) and [^{n}Bu$_4$N][B$_3$H$_8$] 90.5 mmol, 141 mg). The tube was cooled to −196 °C, evacuated and sealed. The sealed tube was irradiated at room temperature for 20 h by a medium power Hg UV lamp. After this time the tube was opened, and the solvent removed. The solid residue was purified by column chromatography using CH$_2$Cl$_2$/hexane (1:4) on Florisil to yield the product as a pink/brown solid. Yield 160 mg, 59%. M.p. = 243 °C. ν(CO) cm^{-1}: 1922(s) (lit. [7] 1915(s)). δ(^{11}B) ppm: −40.6 (2B), +3.0 (1B) (lit. [7] −40.6, +3.8). δ(^{1}H) ppm: −0.8 (BHB); −12.9 (MnHB). δ(^{31}P) ppm: +100.1. (Required for C$_{28}$H$_{32}$B$_3$MnO$_2$P$_2$: C, 61.2: H 5.9. Found: 60.9; H 6.0%).

3.2.2. [Mn(CO)$_2$(dppm)(B$_3$H$_8$)] (2)

Yield = 28%. M.p. = 187 °C. ν(CO) cm^{-1}: 1961(s), 1901(s). δ(^{11}B) ppm: −40.1, +1.0. δ(^{1}H) ppm: −0.9 (BHB); −12.7 (MnHB). δ(^{31}P) ppm: +49.6. (Required for C$_{27}$H$_{30}$B$_3$MnO$_2$P$_2$: C, 60.5: H 5.6. Found: 60.2; H 5.4%).

3.2.3. [Mn(CO)$_2$(dppp)(B$_3$H$_8$)] (3)

Yield = 17%. M.p. = 85 °C. ν(CO) cm^{-1}: 1960(s), 1907(s). δ(^{11}B) ppm: −40.1, 0.0. δ(^{1}H) ppm: −0.2 (BHB); −12.7 (MnHB). δ(^{31}P) ppm: +63.4. (Required for C$_{29}$H$_{34}$B$_3$MnO$_2$P$_2$: C, 61.8: H 6.1. Found: 61.7; H 6.4%).

3.2.4. [Mn(CO)$_2$(dppb)(B$_3$H$_8$)] (4)

Yield = 24%. M.p. = 157 °C. ν(CO) cm^{-1}: 1960(s), 1907(s). δ(^{11}B) ppm: −40.1, +1.0. δ(^{1}H) ppm: −0.7 (BHB); −12.9 (MnHB). δ(^{31}P) ppm: +68.9. (Required for C$_{30}$H$_{36}$B$_3$MnO$_2$P$_2$: C, 62.4: H 6.3. Found: 62.6; H 6.0%).

3.2.5. [Mn(CO)$_2$(dppf)B$_3$H$_8$)] (5)

Yield = 36%. M.p. = 138 °C. ν(CO) cm^{-1}: 1959(s), 1882(s). δ(^{11}B) ppm: −40.6, +1.0. δ(^{1}H) ppm: −0.2 (BHB); −9.8 (MnHB). δ(^{31}P) ppm: +14.6. (Required for C$_{36}$H$_{36}$B$_3$FeMnO$_2$P$_2$: C, 61.3: H 5.1. Found: 61.3; H 5.4%).

3.2.6. [Re(CO)$_2$(PPh$_3$)$_2$(B$_3$H$_8$)] (6)

Yield = 20%. M.p. = 175 °C. ν(CO) cm^{-1}: 1945(s), 1915(s). δ(^{11}B) ppm: −40.9, 0.0. δ(^{1}H) ppm: −1.1 (BHB); −8.5 (ReHB). δ(^{31}P) ppm: +31.8. (Required for C$_{38}$H$_{38}$B$_3$O$_2$P$_2$Re: C, 56.5: H 4.7. Found: 56.1; H 4.7%).

3.2.7. [Re(CO)$_2${P(C$_6$H$_4$Cl-4)$_3$}$_2$(B$_3$H$_8$)] (7)

Yield = 36%. M.p. = 129 °C. ν(CO) cm^{-1}: 1971(s), 1913(s). δ(^{11}B) ppm: −40.2, 0.0. δ(^{1}H) ppm: −1.1 (BHB); −9.0 (ReHB). δ(^{31}P) ppm: +16.6. (Required for C$_{38}$H$_{32}$B$_3$Cl$_6$O$_2$P$_2$Re: C, 45.0: H 3.2. Found: 44.9; H 3.0%).

3.2.8. [Re(CO)$_2${P(C$_6$H$_4$OMe-4)$_3$}(B$_3$H$_8$)] (8)

Yield = 31%. M.p. = 109 °C. ν(CO) cm^{-1}: 1972(s), 1920. δ(^{11}B) ppm: −41.6, +1.0. δ(^{1}H) ppm: −0.4 (BHB); −9.0 (ReHB). δ(^{31}P) ppm: +11.5. (Required for C$_{44}$H$_{50}$B$_3$O$_8$P$_2$Re: C, 53.5: H 5.1. Found: 53.4; H 5.4%).

3.2.9. [Re(CO)$_2${P(CH$_2$C$_6$H$_5$)$_3$}$_2$(B$_3$H$_8$)] (9)

Yield = 17%. M.p. = 210 °C. ν(CO) cm^{-1}: 1948(s), 1901(s). δ(^{11}B) ppm: −41.9, +1.0 δ(^{1}H) ppm: −0.2 (BHB); −8.8 (ReHB). δ(^{31}P) ppm: +7.9. (Required for C$_{44}$H$_{50}$B$_3$O$_2$P$_2$Re: C, 59.3: H 5.7. Found: 59.5; H 5.4%).

3.2.10. [Re(CO)$_2$(dppm)(B$_3$H$_8$)] (10)

Yield = 28%. M.p. = 164 °C. ν(CO) cm^{-1}: 1966(s), 1902(s). δ(^{11}B) ppm: −40.9, 0.0. δ(^{1}H) ppm: −0.2 (BHB); −8.5 (ReHB). δ(^{31}P) ppm: −21.2. (Required for C$_{27}$H$_{30}$B$_3$O$_2$P$_2$Re: C, 48.6: H 4.5. Found: 48.9; H 4.7%).

3.2.11. [Re(CO)$_2$(dppp)(B$_3$H$_8$)] (11)

Yield = 32%. M.p. = 77 °C. ν(CO) cm^{-1}: 1967(s), 1912(s). δ(^{11}B) ppm: −41.0, 0.0. δ(^{1}H) ppm: −0.5 (BHB); −9.2 (ReHB). δ(^{31}P) ppm: +0.1. (Required for C$_{29}$H$_{34}$B$_3$O$_2$P$_2$Re: C, 50.1: H 4.9. Found: 50.5; H 5.1%).

3.2.12. [Re(CO)$_2$(dppb)(B$_3$H$_8$)] (12)

Yield = 39%. M.p. = 183 °C. ν(CO) cm^{-1}: 1965(s), 1900(s). δ(^{11}B) ppm: −41.3, 0.0 δ(^{1}H) ppm: −0.1 (BHB); −9.0 (ReHB). δ(^{31}P) ppm: −6.8. (Required for C$_{30}$H$_{36}$B$_3$O$_3$P$_2$Re: C, 50.8: H 5.1. Found: 50.9; H 5.0%).

3.2.13. [Re(CO)$_2$(dppf)(B$_3$H$_8$)] (13)

Yield = 46%. M.p. = 193 °C. ν(CO) cm^{-1}: 1964(s), 1912(s). δ(^{11}B) ppm: −40.6, 1.0. δ(^{1}H) ppm: −0.3 (BHB); −9.4 (ReHB). δ(^{31}P) ppm: +2.0. (Required for C$_{36}$H$_{36}$B$_3$FeO$_2$P$_2$Re: C, 51.7: H 4.3. Found: 51.5; H 4.3%).

Table 1
Crystal data and structure refinement parameters

	1	**13**
Empirical formula	$C_{28}H_{32}B_3MnO_2P_2$	$C_{36}H_{36}B_3FeO_2P_2Re$
Formula weight	549.85	837.07
Temperature (K)	150	150
Crystal system	orthorhombic	monoclinic
Space group	*Pbca*	*C*2/*c*
a (Å)	17.123(3)	13.201(3)
b (Å)	12.328(2)	15.811(4)
c (Å)	26.170(5)	16.082(3)
α (°)	90.0	90.0
β (°)	90.0	91.056(10)
γ (°)	90.0	90.0
V (Å^3)	5524.3(17)	3356.05(13)
Z	8	4
D_{Calc} (Mg m^{-3})	1.322	1.657
Absorption coefficient (mm^{-1})	0.618	4.163
Crystal size (mm)	0.2 × 0.15 × 0.02	0.25 × 0.1 × 0.1
θ max (°)	27.34	26.02
Reflections collected, unique	37761, 6296	12891, 3274
R_{int}	0.0810	0.0361
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0429$, $wR_2 = 0.0940$	$R_1 = 0.0228$, $wR_2 = 0.0528$
R indices (all data)	$R_1 = 0.0773$, $wR_2 = 0.1062$	$R_1 = 0.0249$, $wR_2 = 0.0528$
ρ_{max}, ρ_{min} (e Å^{-3})	0.434, −0.391	1.693, −0.980

3.3. X-ray structures of **1** and **13**

Data were collected on a Bruker–Nonius KappaCCD area detector diffractometer using Mo kα radiation (λ = 0.71073Å) (Table 1). All structures were solved and refined using the SHELXL suite of programs [26]. All non hydrogen atoms were refined anisotropically, whilst hydrogen atoms for compound **1** were placed in idealised positions and refined using the riding model, those for compound **13** were located from Fourier difference maps and refined isotropically. Data were corrected for absorption effects by means of comparison of symmetry equivalent reflections using the program SORTAV [27]. Figures of the molecular structures determined are plotted using the software package PLATON [28]. The structure of compound **13** contains half a molecule in the asymmetric unit, with the complete molecule being formed by the symmetry of the space group which gives rise to two half occupied orientations of the borane moiety.

4. Supplementary material

Crystallographic data for the structure analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 1 (CCDC194145) and **13** (CCDC194146). Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ [Fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk].

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