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Heterometallic complexes with borole ligands†‡

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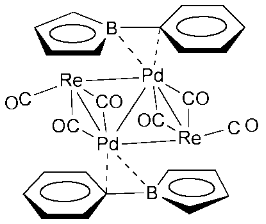
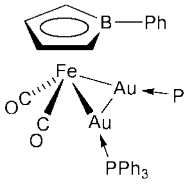
The borole-containing carbonylmetalates $[(\eta\text{-}C_4H_4BPh)Re(CO)_3]^-$ ($[Re]^-$) and $[(\eta\text{-}C_4H_4BPh)Fe(CO)_2H]^-$ ($[Fe]^-$) were used for the synthesis of heterometallic complexes with Re–Hg, Re–Cu, Re–Ag, Re–Au or Fe–Pt metal–metal bonds, respectively. The complex [Re]–Hg–[Re] **1** was characterized by X-ray diffraction and contains a linear metal chain. In the presence of $HgCl_2$, redistribution reactions were observed, leading to [Re]–Hg–Cl **2** which was independently prepared from $[Re]^-$ and an excess of $HgCl_2$. The reaction of $[Fe]^-$ with *trans*-$[PtBr_2(4\text{-Mepy})_2]$ (4-Mepy = 4-methylpyridine) afforded the trinuclear complex *trans*-$[Pt[Fe]_2(4\text{-Mepy})_2]$ **6** which was characterized by X-ray diffraction and contains two hydrido ligands which bridge the Fe–Pt bonds.

The isolobal analogy between the borole dianion $(C_4H_4BR)^{2-}$ (R = Ph) and the cyclopentadienide ion $(C_5H_5)^-$ may be used to compare the reactivity and bonding capabilities of organometallic reagents of two adjacent columns of the Periodic classification (*e.g.* $[(\eta\text{-}C_4H_4BR)Re(CO)_3]^-$ and $[(\eta\text{-}C_5H_5)W(CO)_3]^-$). This appears particularly attractive in heterometallic chemistry where tuning of the selectivity of metal–metal and metal–ligand interactions plays an essential role in synthetic chemistry and has considerable structural and catalytic consequences.[1] Recent studies in our groups with the carbonylmetalates $[(\eta\text{-}C_4H_4BPh)Re(CO)_3]^-$ and $[(\eta\text{-}C_4H_4BPh)Fe(CO)_2H]^-$ have established that these reagents are convenient precursors to incorporate a borole ligand in heterobimetallic systems. The resulting Re_2Pd_2[2] and $FeAu_2$[3] complexes, shown below, have demonstrated that the borole ligand is susceptible to bind to a single metal centre in an η^5 manner and in addition, to an adjacent metal *via* a boron–metal interaction. Considering the very limited number of heterometallic borole complexes known at the moment,[2–6] we sought to evaluate further the synthetic potential of these reagents in heterometallic chemistry.

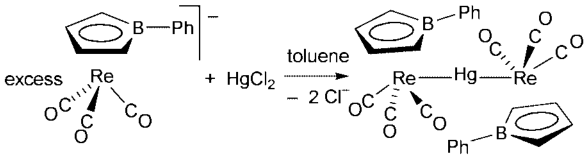




Results and discussion

A. Reactions with $[NMe_4][(\eta\text{-}C_4H_4BPh)Re(CO)_3]$ ($[NMe_4][Re]$)

The reaction of $HgCl_2$ with an excess of this rhenium metalate in toluene led to the light green trinuclear chain complex [Re]–Hg–[Re] **1** which is soluble in this solvent, in contrast to the precursors [eqn. (1)].

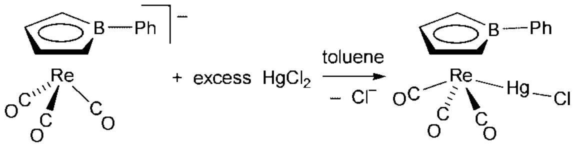


(1)

1

The shift of the $\nu(CO)$ absorptions towards higher wavenumbers in **1** compared to $[NMe_4][Re]$ is consistent with the formation of a covalent metal–metal bond. This was confirmed by an X-ray diffraction study (see below). In the ^1H NMR spectrum, the resonances for the 3,4-borole protons show shoulders owing to coupling with ^{199}Hg ($I = 1/2$, 16.9% natural abundance). A homodecoupling experiment of the 2,5-borole protons did not allow a complete resolution of the signal and its satellites and the value of the $^3J(H\text{–}Hg)$ coupling constant was estimated as 9 Hz.

Reaction of $[NMe_4][Re]$ with an excess of $HgCl_2$ in toluene afforded colourless [Re]–Hg–Cl **2** [eqn. (2)].



(2)

2

The ^1H NMR resonances of the 3,4-borole protons clearly show the ^{199}Hg satellites and decoupling of the 2,5-borole protons led to a spectral resolution which allowed to determine $^3J(H\text{–}Hg) = 22.3$ Hz, a value significantly larger than for **1**.

As expected, reaction of **2** with $[NMe_4][Re]$ led to **1** which, in turn, reacts with $HgCl_2$ to give **2**. The corresponding symmetrization equilibrium is slow on the ^1H NMR time-scale since it does not affect the resolution of the signals for each of these complexes present in the reaction mixture [eqn. (3)].

$$\underset{\mathbf{2}}{[Re]\text{-}Hg\text{-}Cl} \xrightleftharpoons[+\,HgCl_2,\ -\,[Re]\text{-}Hg\text{-}Cl]{+[NMe_4][Re],\ -\,[NMe_4]Cl} \underset{\mathbf{1}}{[Re]\text{-}Hg\text{-}[Re]} \qquad (3)$$

$$[NMe_4][Re] + HgCl_2 \xrightleftharpoons[+\,[NMe_4]Cl]{-\,[NMe_4]Cl} \underset{\mathbf{2}}{[Re]\text{-}Hg\text{-}Cl} \qquad (4)$$

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† Part of the PhD Thesis of M. N.

‡ Dedicated to Dr Marcel Sergent (Université de Rennes I), on the occasion of his retirement, with our warmest wishes.

Table 1 FIR Data for [Re]$^-$, [Re]–HgCl **2**, [Re]–Hg–[Re] **1** and related complexes

	ν/cm^{-1}
[Re]	326w, 193w, 119w
2	362m, 286m
1	338w, 159m
[W]-Hg-[W][7]	169s, 115m
$HgCl_2$	374s
$(C_6Cl_5)HgCl$	357s, 330m, 119m

[W] = $WCp(CO)_3$.

Table 2 Infrared ν(CO) absorptions for [Re]$^-$[10] and [Re]–ML$_n$ (M = Hg, Cu, Ag, Au)

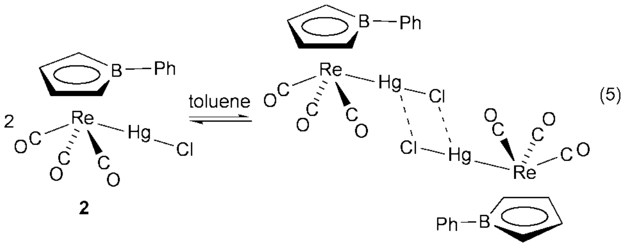
Complex	Medium	Absorptions/cm^{-1}
[Re]$^-$	CH_2Cl_2	1970s, 1867s, 1855 (sh)
[Re]–Hg–[Re] **1**	Toluene	2040s, 2020s, 1960 (sh), 1949s
	KBr	2038w, 2017s, 1961s, 1947s
[Re]–Hg–Cl **2**	Toluene	2050s, 1985 (sh), 1971s
	KBr	2050s, 1975s, 1946s
[Re]–Cu(PPh_3)$_2$ **3**	Toluene	1997s, 1919s, 1890s
[Re]–Ag(PPh_3) **4**	Toluene	1996s, 1919s, 1894s
[Re]–Au(PPh_3) **5**	Toluene	2007s, 1935s, 1914s

In contrast, the equilibrium shown in eqn. (4) is significantly faster and induces broadening of the borole ^{1}H NMR resonances in CH_2Cl_2 at room temperature.

The far-IR absorptions of **1** and **2** are compared in Table 1 with those of related molecules.

By comparison with the ν_{asym}(Hg–W) absorption at 169 cm^{-1} in [Hg{W(CO)$_3$Cp}$_2$][7] and with the value of 152 cm^{-1} for the ν_{asym}(Au–W) vibration in the isoelectronic complex [Au{W(CO)$_3$Cp}$_2$]$^-$,[8] we assign the absorption at 159 cm^{-1} in **1** to the metal–metal vibration ν_{asym}(Hg–Re). In view of the similarity between the atomic masses of W and Re, and between their ligands, the difference of 10 cm^{-1} between the values for ν_{asym}(Hg–W) and ν_{asym}(Hg–Re) appears indicative of a weaker force constant for the metal–metal bond in **1**.

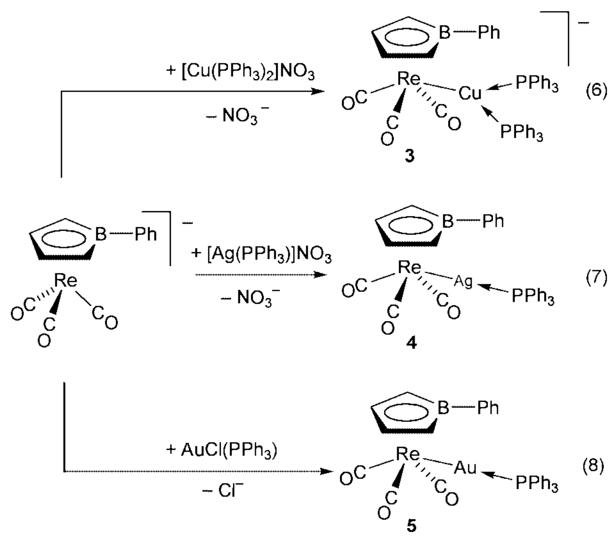
The absorption at 362 cm^{-1} in **2** may be confidently assigned to ν(Hg–Cl) by comparison with those we found at 374 and 357 cm^{-1} for [$HgCl_2$] and [HgCl(C_6Cl_5)], respectively. An absorption observed at 286 cm^{-1} could tentatively be due to dimer formation in the solid-state, generating bridging chlorides, as also observed with the related complex [Cp(OC)$_3$Mo–HgCl][9] [eqn. (5)].



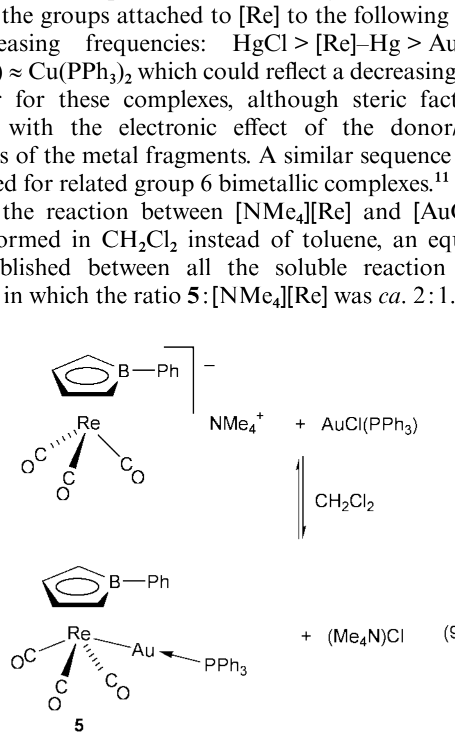
This would also be consistent with the observation that the ν(CO) absorptions of **2** appear at slightly lower wavenumbers in KBr than in solution, whereas those of **1** remain unaffected (Table 2).

Synthesis of Re–M complexes (M = Cu, Ag, Au). The complexes [Re]–Cu(PPh_3)$_2$ **3**, [Re]–Ag(PPh_3) **4** and [Re]–Au(PPh_3) **5** were prepared in benzene or toluene in which they are soluble, in contrast to [NMe_4][Re] and [NMe_4]Cl [eqn. (6)–(8)]. Only **5** was isolated in the solid state while **3** and **4** were spectroscopically characterized *in situ*.

The IR ν(CO) data for these colourless complexes are given in Table 2. A comparison of the average ν(CO) frequencies leads for the groups attached to [Re] to the following sequence of decreasing frequencies: HgCl > [Re]–Hg > Au(PPh_3) > Ag(PPh_3) ≈ Cu(PPh_3)$_2$ which could reflect a decreasing covalent character for these complexes, although steric factors may interfere with the electronic effect of the donor/acceptor properties of the metal fragments. A similar sequence has been established for related group 6 bimetallic complexes.[11]



When the reaction between [NMe_4][Re] and [AuCl(PPh_3)] was performed in CH_2Cl_2 instead of toluene, an equilibrium was established between all the soluble reaction partners [eqn. (9)] in which the ratio **5**:[NMe_4][Re] was *ca.* 2:1.



Whereas the IR absorptions of both [NMe_4][Re] and **5** are clearly present in the spectrum of the reaction mixture, the ^{1}H NMR resonances of the 2,5-borole protons are broad at room temperature and indicate chemical exchange. Owing to the smaller $\Delta\nu$ separation between the individual signals of the 3,4-borole protons of these complexes, they are already in the fast exchange regime in the mixture at room temperature.

Crystal structure of [Re]–Hg–[Re] 1. A view is shown in Fig. 1 and selected bond distances and angles are reported in Table 3.

The mercury atom occupies an inversion centre in the molecule and the Re–Hg distance of 2.748(1) Å compares with the values found in the literature for this bond, which range from 2.621 to 2.790 Å.[13]

It is interesting to compare the structure of **1** with that of its isoelectronic and isolobal analogue [Hg{W(CO)$_3$Cp}] which contains a C_2-axis passing through the Hg atom.[14] The W–Hg distance of 2.7513(3) Å is similar to the Hg–Re distance in **1**. A comparison of the geometries around the Re and W centres in these molecules is shown in Fig. 2.

The borole ring approaches the Hg centre more than the Cp

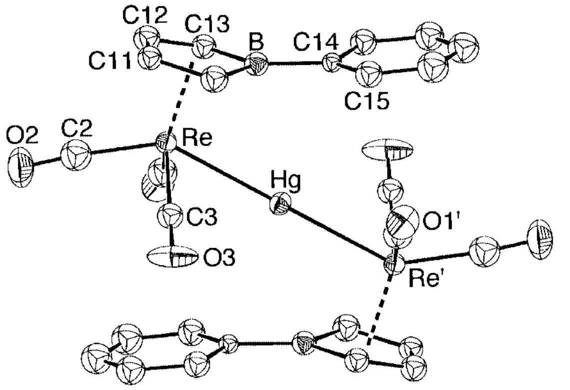


Fig. 1 Molecular structure of **1** in the crystal (PLATON[12]). Displacement ellipsoids and spheres are drawn at 30% probability. Primed atoms are related to unprimed ones by inversion.

Table 3 Selected interatomic distances (Å) and angles (°) for [Re]–Hg–[Re] **1**

Hg–Re	2.748(1)	B–C10	1.53(3)
Re–C1	1.97(3)	C10–C11	1.44(3)
C1–O1	1.12(3)	C11–C12	1.40(3)
Re–C2	1.89(3)	C12–C13	1.37(3)
C2–O2	1.18(3)	C13–B	1.58(3)
Re–C3	1.90(3)	B–C14	1.58(3)
C3–O3	1.16(2)	Hg–B	3.09(3)
Re–B	2.52(3)	Re–C12	2.20(2)
Re–C10	2.29(2)	Re–C13	2.26(2)
Re–C11	2.22(2)		
Re–Hg–Re′	180.0	Hg–Re–B	71.8(6)
C1–Re–C2	86(1)	B–C10–C11	108(2)
C1–Re–C3	108.0(9)	C10–C11–C12	108(2)
C2–Re–C3	86(1)	C11–C12–C13	113(2)
Re–C1–O1	174(2)	C12–C13–B	107(2)
Re–C2–O2	175(2)	C13–B–C10	101(2)
Re–C3–O3	174(2)		

ligand in the tungsten–mercury complex. It shows a 13° folding along the C(13)–C(10) axis (the boron atom is situated 0.22 Å out of the mean plane containing the four borole carbon atoms, away from the Re). The fact that this deviation is not accompanied by an unusual slip distortion (this amounts to only 0.08 Å) indicates that it does not result from a tendency for the borole ligand to change its coordination from η^5 to η^4 but merely reflects the steric interactions between the phenyl groups and the carbonyl ligands of the other rhenium unit. Finally, one should note that the resulting B–Hg separation of 3.09(3) Å is probably too long to represent a significant bonding interaction. For comparison, a B–Pd distance of 2.59(2) Å has been observed recently in the tetranuclear, centrosymmetric cluster {[Re]Pd}$_2$.[2]

B. Reactions with [NBu$_4$][(η-C$_4$H$_4$BPh)Fe(CO)$_2$H] ([NBu$_4$][Fe])

The reaction of two equivalents of [(η-C$_4$H$_4$BPh)Fe(CO)$_2$H]$^-$ ([Fe]$^-$) with *trans*-[PtBr$_2$(4-Mepy)$_2$] (4-Mepy = 4-methylpyridine) led to the trinuclear complex *trans*-[Fe]–Pt(4-Mepy)$_2$–[Fe] **6** [eqn. (10)].

In solution this complex (like its pyridine analogue prepared similarly) is very air- and moisture-sensitive. The detailed arrangement of the ligands, including the presence of bridging hydrides, was ascertained by an X-ray diffraction study on dark ruby-red single crystals obtained from CH$_2$Cl$_2$–toluene.

Crystal structure of 6. A view of the molecule is shown in Fig. 3 and selected bond distances and angles are given in Table 4.

The Pt atom occupies a centre of inversion in the molecule and the Pt–Fe distance of 2.774(3) Å is consistent with the presence of metal–metal bonds.[15] The two CO ligands on each Fe moiety are almost orthogonal to each other [95.2(4)°]. The hydride ligands could be located by a difference Fourier synthesis. They occupy a bridging position, resulting in a three center–two electron (3c–2e) bonding for the Fe(μ-H)Pt unit. The 4-Mepy ligand is almost perpendicular to the Pt(μ-H)Fe plane.

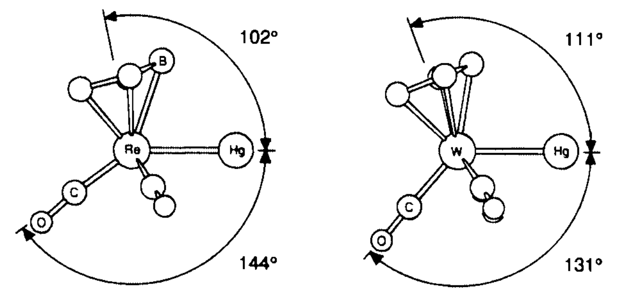
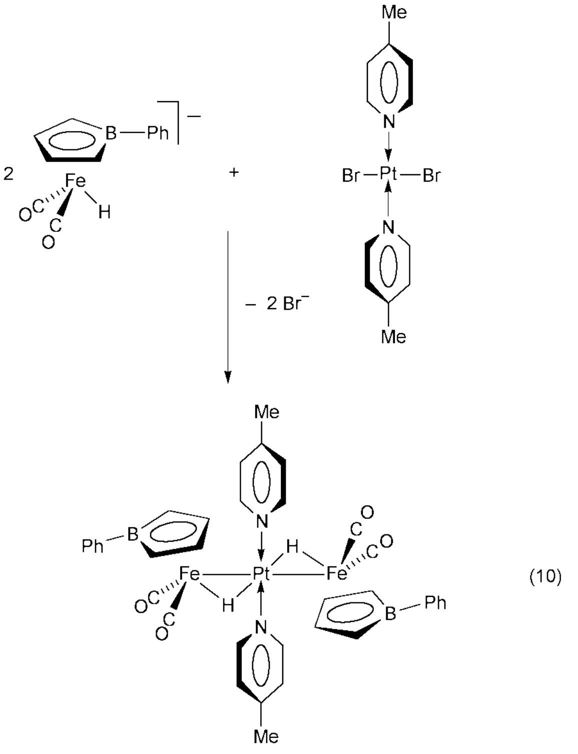


Fig. 2 Comparison of the structural arrangements in [Re]–Hg–[Re] **1** and in [W]–Hg–[W] (Hg–M–CO$_{trans}$ are always in the projection plane).



6

(10)

Relevant distances in platinum bridging hydride complexes are compared in Table 5. The range of Pt(μ-H) distances is large (1.40–2.21 Å) and this is also reflected in the values found for ^1J [Pt(μ-H)] coupling constants in ^{1}H NMR spectroscopy (Table 6). Complex **6** is isoelectronic with the Mn–Pt–Mn complex *trans*-[{Cp′(OC)$_2$Mn(μ-H)}$_2$Pt(3-Mepy)$_2$][14] [(η-C$_4$H$_4$-BPh)Fe$\leftarrow\sigma\rightarrow$Cp′Mn]. In these complexes, the iron and manganese centres have similar ligand arrangements. Both the ^{1}H NMR chemical shift for the μ-H ligand and the ^1J(Pt–H) values are very similar in these complexes. In the other complexes which contain phosphine ligands, the coupling constants are smaller.

Reaction of [NBu$_4$][Fe] with *cis*-[PtCl$_2$(PR$_3$)]$_2$. When [Fe]$^-$ was reacted with *cis*-[PtCl$_2$(PR$_3$)$_2$] in a manner similar to that used to prepare **6**, only *trans*-[Pt(H)Cl(PR$_3$)$_2$] was characterized. It is likely that the hydride transfer reaction that leads to this product occurs *via* a bimetallic complex containing a bridging hydride ligand [eqn. (11)].

It is interesting that the reaction of [HCr(CO)$_5$]$^-$ with [PtCl$_2$(dppm-*P*,*P*)] [dppm = bis(diphenylphosphino)methane]

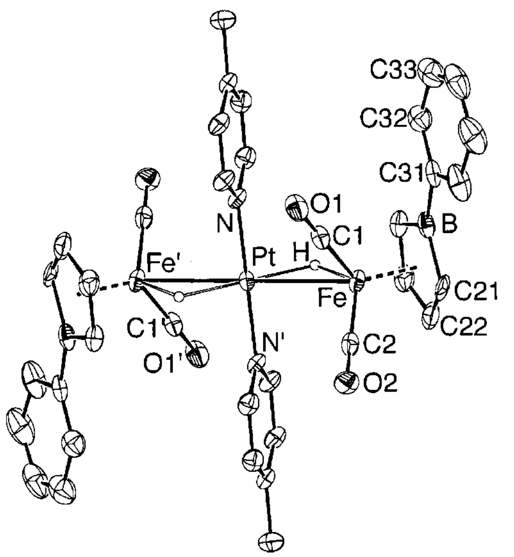
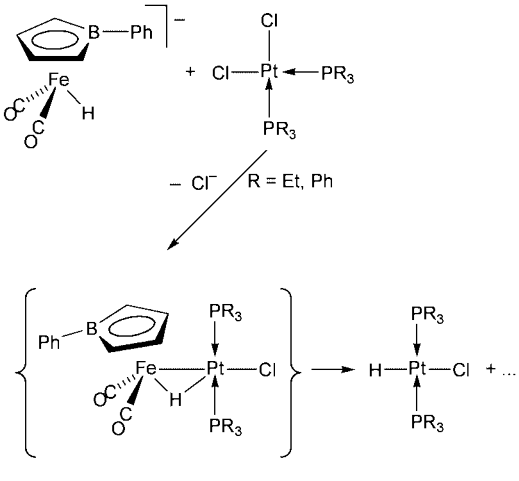


Fig. 3 Molecular structure of **6** in the crystal (PLATON[12]). Displacement ellipsoids and spheres are drawn at 30% probability. Primed atoms are related to unprimed ones by inversion.



(11)

also led to hydride transfer with the high yield formation of $[Pt_2(\mu\text{-}H)(H)_2(\mu\text{-}dppm)_2]^+$.[26]

In conclusion, we have found that borole-containing carbonylmetalates are suitable precursors for the synthesis of heterometallic, metal–metal bonded complexes which provide interesting opportunities for the study of the interactions of a borole ligand with one or more metal centres.[2,3] These complexes allow useful comparisons between molecules prepared from isolobal metalates.

Experimental

Reactions were performed under purified nitrogen, using standard Schlenk-type techniques. Solvents were distilled under nitrogen and traces of water removed by usual methods. Infrared spectra were recorded on FT-IR Perkin-Elmer 1720 X and FT-IR Bruker IFS 66/113 spectrometers. NMR spectra were recorded on Varian VXR 500 (^1H, 500 MHz, relative to TMS, ^{13}C, 125.70 MHz, relative to TMS, ^{31}P, 202.33 MHz, relative to H_3PO_4), Bruker SY 200 (^1H, 200 MHz, relative to TMS), and Bruker WP 80 SY (^1H, 80 MHz, relative to TMS) spectrometers. Elemental analyses were performed by the Analytisches Labor Pascher, Remagen (Germany).

Syntheses

The complexes $[NBu_4][(\eta\text{-}C_4H_4BPh)Fe(CO)_2H]$ and $[NMe_4]$-$[(\eta\text{-}C_4H_4BPh)Re(CO)_3]$ were prepared as described in the literature.[6a,10]

Table 4 Selected bond distances (Å) and angles (°) for *trans*-[Fe]–Pt(4-Mepy)$_2$–[Fe] **6**

Pt–Fe	2.774(3)	B–C21	1.54(2)
Pt–H	1.70(7)	C21–C22	1.37(2)
Fe–H	1.63(9)	C22–C23	1.42(2)
Fe–C1	1.713(9)	C23–C24	1.42(2)
C1–O1	1.17(1)	C24–B	1.55(2)
Fe–C2	1.84(1)	B–C31	1.58(1)
C2–O2	1.18(1)	Pt–N	2.022(7)
Fe–B	2.14(1)	Fe–C23	2.050(9)
Fe–C21	2.08(2)	Fe–C24	2.04(1)
Fe–C22	2.09(1)		
Fe–Pt–H	33(3)	Pt–Fe–B	140.2(3)
H–Fe–Pt	34(3)	B–C21–C22	110(1)
Pt–H–Fe	113(5)	C21–C22–C23	110(1)
Fe–Pt–N	87.9(2)	C22–C23–C24	110.2(9)
H–Pt–N	86(3)	C23–C24–B	107.8(9)
Pt–N–C11	120.2(5)	C21–B–C24	101.4(8)
Pt–N–C15	122.7(7)	Fe–C2–O2	175.9(9)
Pt–Fe–C1	73.8(3)		
Pt–Fe–C2	96.0(3)		
C1–Fe–C2	95.2(4)		
Fe–C1–O1	178.4(9)		

[Re]–Hg–[Re] 1 and [Re]–Hg–Cl 2. A suspension of $[NMe_4][Re]$ (164 mg, 0.34 mmol) and $HgCl_2$ (27 mg, 0.1 mmol) in toluene (10 mL) was stirred for 2 h. The yellow–green solution was filtered, evaporated to dryness and the resulting solid recrystallized from CH_2Cl_2–hexane, affording **1** as yellow–green crystals. Yield: 63 mg (0.062 mmol, 36% based on $[Re]^-$) (Found: C, 30.39; H, 1.80. $C_{26}H_{18}B_2HgO_6Re_2$ ($M = 1021.06$) requires C, 30.58; H, 1.78%). NMR: ^1H (300 MHz, $CDCl_3$), δ 7.59, 7.34 (m, 10 H, phenyl), 5.11 (m, 4 H, $N = 6.3$ Hz, $^3J_{H\text{-}Hg} = 9$ Hz, 3,4-borole), 3.58 (m, 4 H, $N = 6.3$ Hz, 2,5-borole); (500 MHz, $CDCl_3$), δ 7.57, 7.31 (m, 10 H, phenyl), 5.09 (m, 4 H, $N = 6.4$ Hz, 3,4-borole), 3.56 (m, 4 H, $N = 6.4$ Hz, 2,5-borole); $^{13}C\text{-}\{^1H\}$ (126 MHz, $CDCl_3$), δ 191.32 (s, 6 C, CO), 136.26 (s, 4 C, *ortho*-phenyl), 128.92 (s, 2 C, *para*-phenyl), 128.29 (s, 4 C, *meta*-phenyl), 85.36 (s, 4 C, 3,4-borole), 73.97 (br s, 4 C, 2,5-borole). IR (toluene): 2040s, 2020s, 1960 (sh), 1949s cm^{-1}; (KBr): 2038w, 2017s, 1961s, 1947vs cm^{-1}; far-IR (polyethylene): 338w, 159m cm^{-1}. Mass spectrum ($SIMS^+$, NBA): *m*/*z* 1023 (MH^+, 6.5%), 411 ($[Re]^+$, 100%), 383 ($[Re]^+ - CO$, 21%), 327 ($[Re]^+ - 3\,CO$, 5.5%).

Treatment of **1** (35 mg, 0.34 mmol) with a large excess of $HgCl_2$ (*ca.* 200 mg) and extraction with 5×10 mL toluene afforded a solution which was taken to dryness. The residue was recrystallized from CH_2Cl_2–hexane to give [Re]–Hg–Cl **2** as colourless crystals. Yield: 62 mg (0.096 mmol, 28% based on $[Re]^-$) (Found: C, 24.37; H, 1.47. $C_{13}H_9BClHgO_3Re$ ($M = 646.27$) requires C, 24.16; H, 1.40%). NMR: ^1H (300 MHz, CD_2Cl_2), δ 7.84, 7.42 (m, 5 H, phenyl), 5.50 (m, 2 H, $N = 6.5$ Hz, 3,4-borole), 4.07 (m, 2 H, $N = 6.5$ Hz, 2,5-borole); (300 MHz, $CDCl_3$), δ 7.77, 7.42 (m, 5 H, phenyl), 5.45 (m, 2 H, $N = 6.3$ Hz, $^3J_{H\text{-}Hg} = 22.3$ Hz, 3,4-borole), 4.04 (m, 2 H, $N = 6.4$ Hz, 2,5-borole); (500 MHz, $CDCl_3$), δ 7.75, 7.40 (m, 5 H, phenyl), 5.44 (m, 2 H, $N = 6.4$ Hz, Hg satellites not resolved, 3,4-borole), 4.03 (m, 2 H, $N = 6.7$ Hz, 2,5-borole); $^{13}C\text{-}\{^1H\}$ (126 MHz, $CDCl_3$), δ 188.36, 187.69 (s, 3 C, CO), 135.29 (s, 2 C, *ortho*-phenyl), 131.28 (s, 1 C, *para*-phenyl), 129.05 (s, 2 C, *meta*-phenyl), 86.34 (s, 2 C, 3,4-borole), 71.92 (br s, 2 C, 2,5-borole). IR (toluene): 2050s, 1985 (sh), 1971s cm^{-1}; (KBr): 2050s, 1975s, 1946s cm^{-1}; far IR (polyethylene) 362m, 286m cm^{-1}. Mass spectrum (EI, 140 °C): *m*/*z* 646 (M^+, 3%), 446 ($M^+ - Hg$, 3%), 411 ($M^+ - HgCl$, 100%), 383 ($M^+ - HgCl - CO$, 48%), 362 ($M^+ - Hg - 3\,CO$, 52%), 327 ($M^+ - HgCl - 3\,CO$, 84%), 202 (Hg^+, 30%).

[Re]–Cu(PPh$_3$)$_2$ 3. A mixture of $[NMe_4][Re]$ (14 mg, 0.03 mmol) and $[Cu(PPh_3)_2]NO_3$ (19 mg, 0.03 mmol) was stirred in toluene-d_8 (0.3 mL) for a few minutes. The filtered solution was studied by NMR. Since the complex was not isolated, yields

Table 5 Interatomic distances (Å) in hydrido-bridged di- and tri-metallic complexes[a]

Complex	M	*d*(M–Pt)	*d*(M–H)	*d*(Pt–H)	Ref.
[Fe]–Pt(4-Mepy)$_2$-[Fe] **6**	Fe	2.774(3)	1.63(9)	1.70(7)	This work
[{Cp′(OC)$_2$Mn(μ-H)}$_2$Pt(3-Mepy)$_2$][b]	Mn	2.804(3)	1.69(15)	2.00(15)	16
[(OC)$_4$Mn(μ-H)(μ-PPh$_2$)PtPh(PPh$_3$)]	Mn	2.864(1)	1.80(8)	1.64(8)	17
[Cp(ON)Re(μ-H)(μ-PPh$_2$)Pt(PPh$_3$)$_2$]$^+$	Re	2.8673(4)	1.57(6)	2.21(6)	18
[(dppe)Pt(μ-H)$_2$PtH(dppe)]$^+$ [c] (triclinic)[d]	Pt	2.711(1)	1.860(2), 2.049(2)	1.691(2), 1.656(2)	19
[(dppe)Pt(μ-H)$_2$PtH(dppe)]$^+$ (monoclinic)	Pt	2.728(1)	2.05, 1.78	1.71, 1.40	20
[(dppe)Pt(μ-H)(μ-CO)Pt(dppe)]$^+$	Pt	2.716(1)	1.55(4)	1.55(4)	21
H$_2$Fe(CO)$_4$[e]	Fe		1.56(2)		22

[a] Structural determination by [d] neutron diffraction, [e] electron diffraction, all others by X-ray diffraction. [b] 3-Mepy = 3-methylpyridine, Cp′ = methylcyclopentadienyl. [c] dppe = 1,2-Bis(diphenylphosphino)ethane.

Table 6 Chemical shift (ppm) and *J*(Pt–H) coupling constants (Hz) for bridging hydrides in M–Pt-complexes

Complex	δ(M–H)	J_{PtH}	Solvent	Ref.
[Fe]–Pt(4-Mepy)$_2$–[Fe] **6**	−14.74	919	CD$_2$Cl$_2$	This work
[{Cp′(OC)$_2$Mn(μ-H)}$_2$Pt(3-Mepy)$_2$]	−14.86	924.8	THF-d_8	16
[(OC)$_4$Mn(μ-H)(μ-PPh$_2$)PtPh(PPh$_3$)]	−12.6	370	CD$_2$Cl$_2$	17
[(OC)$_4$Mn(μ-PPh$_2$)(μ-H)Pt(PPh$_3$)$_2$]$^+$	−11.94	494	CD$_2$Cl$_2$	23
[Cp(OC)$_2$W(μ-PPh$_2$)(μ-H)Pt(PPh$_3$)$_2$]$^+$	−9.43	480	CD$_2$Cl$_2$	23
[(OC)$_3$Co(μ-PPh$_2$)(μ-H)Pt(PPh$_3$)$_2$]$^+$	−9.16	476	CD$_2$Cl$_2$	23
[Cp(ON)Re(μ-H)(μ-PCy$_2$)Pt(PPh$_3$)(CO)]$^+$	−5.00	506	CD$_2$Cl$_2$	18
[(Et$_3$P)$_2$(Cl$_5$C$_6$)Pt(μ-H)(AuPEt$_3$)]	−4.73	537	?	24
[(OC)$_4$Mn(μ-CO)(μ-H)Pt(PEt$_3$)$_2$]	−3.80	409	C$_6$D$_6$	25
[(dppe)Pt(μ-H)$_2$PtH(dppe)]$^+$	−2.7	503	CD$_2$Cl$_2$	20

have not been determined. NMR: ^{1}H (300 MHz, toluene-d_8), δ 7.75, 7.51, 7.23 (m, 35 H, phenyl), 5.18 (m, 2 H, $N = 6.0$ Hz, 3,4-borole), 4.21 (m, 2 H, $N = 6.2$ Hz, 2,5-borole); ^{31}P-{^{1}H} (121 MHz, toluene-d_8), δ 0.2 (br s, 2 P). IR: see Table 2.

[Re]–Ag(PPh$_3$) 4. A mixture of [NMe$_4$][Re] (15 mg, 0.03 mmol) and [Ag(PPh$_3$)]NO$_3$ (13 mg, 0.03 mmol) was stirred in benzene-d_6 (0.3 mL) for a few minutes. The filtered solution was studied by NMR. Since the complex was not isolated, yields have not been determined. NMR: ^{1}H (300 MHz, benzene-d_6), δ 7.69 (m, 2 H, *ortho*-phenyl$_{\mathrm{borole}}$), 7.17 (m, 6 H, *ortho*-phenyl$_{\mathrm{phosphine}}$), 6.97 (m, 9 H, *meta*- and *para*-phenyl$_{\mathrm{phosphine}}$), 6.85 (m, 2 H, *meta*-phenyl$_{\mathrm{borole}}$), 6.68 (m, 1 H, *para*-phenyl$_{\mathrm{borole}}$), 4.90 (m, 2 H, $N = 5.7$ Hz, 3,4-borole), 4.11 (m, 2 H, $N = 5.7$ Hz, 2,5-borole); ^{31}P-{^{1}H} (121 MHz, benzene-d_6), δ 15.8 (s, 1P, $\Delta\nu_{1/2} = 70$ Hz). IR: see Table 2.

[Re]–Au(PPh$_3$) 5. A mixture of [NMe$_4$][Re] (18 mg, 0.04 mmol) and [AuCl(PPh$_3$)] (18 mg, 0.04 mmol) was stirred in toluene-d_8 (0.3 mL) for a few minutes. The filtered solution was studied by NMR. Complex **5** was obtained from toluene–hexane as small, white cystals. Yield: 28 mg (82%) (Found: C, 42.57; H, 2.58. C$_{31}$H$_{24}$AuBO$_3$PRe ($M = 869.49$) requires C, 42.82; H, 2.78%). NMR: ^{1}H (300 MHz, toluene-d_8), δ 7.90, 7.39, 7.17, 7.06 (m, 20 H, phenyl), 5.01 (m, 2 H, $N = 6.2$ Hz, 3,4-borole), 4.20 (m, 2 H, $N = 6.3$ Hz, 2,5-borole); ^{31}P-{^{1}H} (121 MHz, toluene-d_8), δ 50.6 (s, 1 P). IR: see Table 2.

***trans*-[Fe]–Pt(4-Mepy)$_2$–[Fe] 6.** Solid [PtBr$_2$(4-Mepy)$_2$] (167 mg, 0.31 mmol) was added to a solution of [NBu$_4$][Fe] (306 mg, 0.62 mmol) at −78 °C in CH$_2$Cl$_2$ (5 mL). After the stirred reaction mixture had reached room temperature, it was filtered through silica gel. Crystallization from CH$_2$Cl$_2$–toluene at −25 °C afforded **6** (73 mg, 0.08 mmol, 27%) as ruby-red crystals. Slow decomposition of the sample, also observed during crystallization, prevented correct elemental analysis (Found: C, 47.03; H, 3.87; N, 3.32. C$_{36}$H$_{34}$B$_2$Fe$_2$N$_2$O$_4$Pt ($M = 887.09$) requires C, 48.74; H, 3.86; N, 3.16%). ^{1}H NMR (200 MHz, CD$_2$Cl$_2$), δ 8.4 (d, 4 H, $^3J_{\mathrm{HH}} = 6$ Hz, 2,6-H from 4-Mepy), 7.4 (m, 4 H, phenyl), 7.15 (m, 6 H, phenyl), 7.1 (d, 4 H, $^3J_{\mathrm{HH}} = 6$ Hz, 3,5-H from 4-Mepy), 4.66 (m, 4 H, 3,4-borole), 4.42 (s, 6 H, CH$_3$), 2.57 (m, 4 H, 2,5-borole), −14.74 (s with Pt-satellites, 2 H, $^1J_{\mathrm{HPt}} = 919$ Hz, hydride). IR (KBr): 1967s, 1914s cm^{-1}. FIR (polyethylene): 398w, 387m, 377w, 338w, 328m, 316w, 294m, 256w, 204m, 159m, 135m cm^{-1}. Mass spectrum (FAB$^+$, NBA): *m*/*z* 887 (M$^+$, 0.2%), 381 (M$^+$ − 2[Fe], 25%), 288 (M$^+$ − 2[Fe] − (4-Mepy), 21%).

Reaction of [NBu$_4$][Fe] with *cis*-[PtCl$_2$(PEt$_3$)$_2$]. A solution of [NBu$_4$][Fe] (94 mg, 0.19 mmol) in CH$_2$Cl$_2$ (2 mL) was cooled to −78 °C and solid [PtCl$_2$(PEt$_3$)$_2$] (48 mg, 0.10 mmol) was added. After the mixture had reached room temperature, it was taken to dryness and the solid was extracted with diethyl ether. This solution was filtered and taken to dryness, affording a solid identified by ^{1}H and ^{31}P-{^{1}H} NMR spectroscopy and comparison with the literature data, as *trans*-[PtHCl(PEt$_3$)$_2$].[27]

Reaction of [NBu$_4$][Fe] with *cis*-[PtCl$_2$(PPh$_3$)$_2$]. To a solid mixture of [NBu$_4$][Fe] (126 mg, 0.25 mmol) and *cis*-[PtCl$_2$(PPh$_3$)$_2$] (101 mg, 0.13 mmol) cooled to −78 °C was added precooled CH$_2$Cl$_2$ (5 mL). After the mixture had reached room temperature, it was taken to dryness and the solid was extracted with diethyl ether. This solution was filtered and taken to dryness, affording an ochre solid (97 mg) which was shown by ^{1}H and ^{31}P-{^{1}H} NMR spectroscopy and comparison with the literature data to contain mostly *trans*-[PtHCl(PPh$_3$)$_2$].[28]

X-Ray crystallography

Crystal data for complex 1. C$_{26}$H$_{18}$B$_2$HgO$_6$Re$_2$; $M = 1021.1$; $a = 10.911(4)$, $b = 8.467(3)$, $c = 15.374(6)$ Å, $\beta = 110.13(3)°$, $V = 1333.6(9)$ Å^3, $T = 253$ K, monoclinic space group $P2_1/n$ (no. 14), $Z = 2$, $D_c = 2.543$ g cm^{-3}, Mo-Kα radiation ($\lambda = 0.71073$ Å); graphite monochromator, $\mu_{\mathrm{lin}} = 15.0$ mm^{-1}. ENRAF-Nonius CAD4 diffractometer; green translucent crystal fragment of size 0.25 × 0.25 × 0.20 mm, ω scans with $3 < \theta < 23°$ in the index range $0 < h < 16$, $0 < k < 6$, $-16 < l < 15$; 1532 reflections. Correction for Lorentz and polarization effects and empirical absorption correction (min. transmission 0.090, max. transmission 0.107) based on azimuthal scans.[29] 1191 unique ($R_{\mathrm{int}} = 0.068$) observations with $I > 1.0\sigma(I)$ for structure solution[30] by Patterson and subsequent Fourier difference syntheses. Least-squares refinement on F[30] with anisotropic displacement parameters for the metal and oxygen atoms, isotropic displacement parameters for the remaining non-hydrogen atoms, hydrogen atoms in calculated positions (C–H = 0.98 Å). Convergence (maximum $\Delta/\sigma = 0.005$) for 100 variables and 1191 observed data at $R = 0.059$, $R_w = 0.059$ ($w^{-1} = \sigma^2 F_o$). A final difference Fourier map showed a local maximum of 1.6 e Å^{-3} close to the Hg atom.

Crystal data for complex 6. $C_{36}H_{34}B_2Fe_2N_2O_4Pt$; $M = 887.09$; $a = 8.532(2)$, $b = 10.445(3)$, $c = 10.430(3)$ Å, $\alpha = 100.75(2)$, $\beta = 101.13(2)$, $\gamma = 101.15(2)°$, $V = 870.3(4)$ Å^3, $T = 248$ K, triclinic space group $P\bar{1}$ (no. 2), $Z = 1$, $D_c = 1.69$ g cm^{-3}, Mo-Kα radiation ($\lambda = 0.71073$ Å); graphite monochromator, $\mu_{lin} = 4.91$ mm^{-1}. ENRAF-Nonius CAD4 diffractometer; red parallelepipedic crystal of size 0.15 × 0.15 × 0.15 mm, ω scans with $3 < \theta < 27°$ in the index range $-10 < h < 10$, $-13 < k < 13$, $0 < l < 12$, 3248 reflections. Correction for Lorentz and polarization effects and empirical absorption correction (min. transmission 0.770, max. transmission 0.992) based on azimuthal scans.[29] 2477 unique ($R_{int} = 0.018$) reflections for structure solution with the Patterson method. Both unit cell metric and symmetry of the diffraction pattern are in close agreement with a monoclinic symmetry which, however, would require extensive disorder and partial occupancy for most atoms. Refinement of the disordered structure model gives satisfactory agreement factors but results in unreasonably short intermolecular contacts. We hence prefer to describe the crystal as a pseudo-merohedral twin. For completion of the structure model and the twin refinement the SHELXL 93 program was used.[31] Least-squares refinement on intensities with anisotropic displacement parameters for all non-hydrogen atoms, isotropic displacement parameter for the hydrido H atom, remaining hydrogen atoms in calculated positions (C–H = 0.98 Å). Convergence (maximum $\Delta/\sigma = 0.004$) was obtained for 220 variables and 2477 data at $R = 0.030$, $wR2 = 0.089$ $\{w^{-1} = \sigma^2(F_o^2) + [0.0667(\max(F_o^2,0) + 2F_c^2)/3]^2\}$. A final difference Fourier map showed fluctuations <1.1 e Å^{-3} close (0.7 Å) to Pt.

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See http//www.rsc.org/suppdata/dt/1999/2807/ for crystallographic files in .cif format.

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