DALTON
FULL PAPER

Transition metal complexes incorporating the BF_2 ligand formed by oxidative addition of the B–B bond in B_2F_4

Norman Lu, Nicholas C. Norman, A. Guy Orpen, Michael J. Quayle, Peter L. Timms and George R. Whittell

The University of Bristol, School of Chemistry, Cantock's Close, Bristol, UK BS8 1TS

Received 9th August 2000, Accepted 19th September 2000
First published as an Advance Article on the web 26th October 2000

The reactions between B_2F_4 and the platinum and iridium complexes $[Pt(PPh_3)_2(\eta\text{-}C_2H_4)]$, $[Pt(dppb)(\eta\text{-}C_2H_4)]$ [dppb = 1,4-bis(diphenylphosphino)butane] and *trans*-$[IrCl(CO)(PPh_3)_2]$ afforded the difluoroboryl complexes *cis*-$[Pt(BF_2)_2(PPh_3)_2]$, *cis*-$[Pt(BF_2)_2(dppb)]$ and *fac*-$[Ir(BF_2)_3(CO)(PPh_3)_2]$ respectively all of which have been characterised by X-ray crystallography. The isoelectronic platinum dppb nitrito complex *cis*-$[Pt(NO_2)_2(dppb)]$ has also been prepared and structurally characterised.

Transition metal boryl compounds, in which the metal is bonded to one or more BR_2 groups,[1] were first studied in detail by Nöth and co-workers, but in recent years there has been renewed interest not least because of the importance of these compounds in metal catalysed hydro- and diboration reactions.[2] Many metal boryl species have now fully been characterised by multinuclear NMR and by X-ray crystallography although the variety of boron substituents employed is still relatively modest. In fact, most structurally characterised compounds incorporate either an alkanediolate or catecholate group although some thiocatecholate and phenylenediamine derivatives have been described.[1b] We note also, with particular relevance to this study, a number of dihalogenoboryl (BX_2, X = Cl, Br or I) complexes originally described by Nöth and co-workers [1a,b,3] and the osmium dichloroboryl species recently prepared by Roper and co-workers.[4]

Our interest in this area has focused largely on what is a key synthetic route to metal boryls, namely oxidative addition of the B–B bond in diborane(4) compounds which affords metal *cis*-(bis)boryl complexes. This interest coupled with an additional interest in low-valent boron fluoride chemistry and a desire to extend the range of known boryl ligands led us to investigate the chemistry of B_2F_4 with various transition metal compounds. In preliminary work we studied the reaction between B_2F_4 and the platinum(0) compound $[Pt(PPh_3)_2(\eta\text{-}C_2H_4)]$ which afforded the first crystallographically characterised example of a difluoroboryl ligand in the complex *cis*-$[Pt(BF_2)_2(PPh_3)_2]$ **1**.[5] Herein we describe further and more detailed studies on the reactivity of B_2F_4 towards low oxidation state transition metal complexes.

Results and discussion

The reaction between $[Pt(PPh_3)_2(\eta\text{-}C_2H_4)]$ and a slight excess of B_2F_4 [6] in toluene solution afforded, after work-up, pale yellow crystals of the platinum(II) complex *cis*-$[Pt(BF_2)_2(PPh_3)_2]$ **1** characterised by multinuclear NMR and X-ray crystallography as described in ref. 5.† The platinum centre in **1** adopts the expected square-planar coordination geometry (maximum atom deviation from the PtP_2B_2 mean plane is 0.025 Å) with the BF_2 groups in a *cis* configuration. Metric parameters of note are the Pt–B bond distances [Pt–B(1) 2.058(6) and Pt–B(2) 2.052(6) Å] together with the B–Pt–B [78.2(3)°] and P–Pt–P [99.4(1)°] angles. The angles defined by the boron ligand planes and the mean platinum square plane are 81.1 and 87.4° for B(1) and B(2) respectively showing that the boryl ligands are essentially orthogonal to the platinum square plane. The B···B separation is 2.591(9) Å. All of these values fall in or close to ranges observed for other structurally characterised platinum(II) *cis*-(bis)boryl compounds.[1b] Within the BF_2 groups themselves, we note that the F–B–F angles [av. 110.7 Å] are significantly smaller than the Pt–B–F angles [av. 124.6 Å].

An analogous reaction between B_2F_4 and $[Pt(dppb)(\eta\text{-}C_2H_4)]$ [dppb = 1,4-bis(diphenylphosphino)butane] afforded the complex *cis*-$[Pt(BF_2)_2(dppb)]$ **2**. Spectroscopic data were similar in all respects to those of **1** and the structure was confirmed by X-ray crystallography (Fig. 1). Pertinent metric information includes the Pt–B bond distances [Pt–B(1) 2.044(6) and Pt–B(2) 2.047(6) Å], the B–Pt–B [81.5(2)°] and P–Pt–P [95.70(7)°] angles, the maximum atom deviation from the PtP_2B_2 mean plane [0.081 Å], the angles defined by the boron ligand

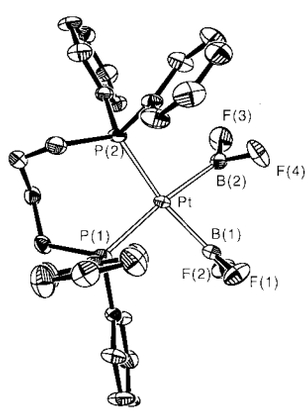


Fig. 1 A view of the molecular structure of complex **2** with key atoms labelled. Hydrogen atoms are omitted for clarity. Ellipsoids are drawn at the 50% level. Selected bond lengths (Å) and angles (°) include: Pt–B(1) 2.044(6), Pt–B(2) 2.047(6), Pt–P(1) 2.335(2), Pt–P(2) 2.341(2), B(1)–F(1) 1.351(7), B(1)–F(2) 1.325(6), B(2)–F(3) 1.339(6) and B(2)–F(4) 1.322(7); B(1)–Pt–B(2) 81.5(2), P(1)–Pt–P(2) 95.70(7), F(1)–B(1)–F(2) 110.2(5), Pt–B(1)–F(1) 120.9(4), Pt–B(1)–F(2) 128.9(4), F(3)–B(2)–F(4) 110.6(5), Pt–B(2)–F(3) 124.6(4) and Pt–B(2)–F(4) 124.8(4).

† Full experimental details for the preparation are given in the Experimental section of this paper and spectroscopic data are reproduced for comparison with other complexes. The crystal structure is not republished here although pertinent metric parameters are given to aid comparison with other structures.

 DOI: 10.1039/b006535h

planes and the mean platinum square plane [80.9 and 76.8° for B(1) and B(2) respectively], the B···B separation [2.670(8) Å] and the F–B–F [av. 110.4 Å] and Pt–B–F [av. 124.8 Å] angles. All these data are similar to the corresponding values in **1**; additional data are given in the caption to Fig. 1.

The reaction between Vaska's compound, *trans*-[IrCl(CO)-$(PPh_3)_2$], and B_2F_4 afforded a complex characterised by X-ray crystallography as the iridium(III) (tris)boryl species $[Ir(BF_2)_3(CO)(PPh_3)_2]$ **3** (Fig. 2). The molecular structure of **3** comprises an octahedral iridium(III) centre bonded to three BF_2 groups in a *fac* configuration, two *cis* phosphines and one carbonyl ligand. A degree of positional disorder involving the carbonyl group and the *trans* related BF_2 ligand was present.‡ The Ir–B bond lengths [Ir–B(1) 2.066(10), Ir–B(2) 2.083(6), Ir–B(3) 2.088(5) Å] are similar to those in other iridium boryls.[1b] Of the bond angles around the iridium centre we note that the P(1)–Ir–P(2) angle [105.87(3)°] deviates most from an ideal value presumably for steric reasons although the deviation is larger than that for the *cis*-PPh_3 groups in **1**. Angles around each boron centre follow the same pattern as that seen in the platinum complexes **1** and **2** in that the F–B–F angle is significantly smaller than the Ir–B–F angles; all relevant angles for **3** are given in the caption to Fig. 2.

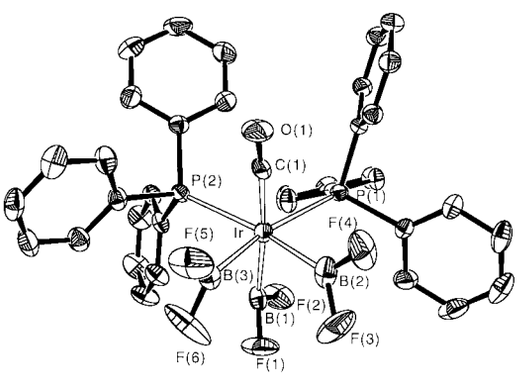
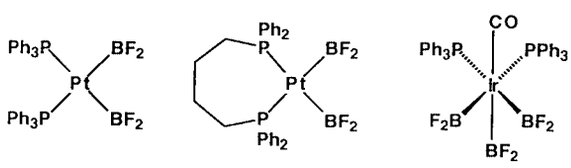


Fig. 2 A view of the molecular structure of complex **3** with key atoms labelled. Hydrogen atoms are omitted for clarity. Ellipsoids are drawn at the 50% level. Selected bond lengths (Å) and angles (°) include: Ir–B(1) 2.066(10), Ir–B(2) 2.083(6), Ir–B(3) 2.088(5), Ir–C(1) 2.009(8), Ir–P(1) 2.4416(10) and Ir–P(2) 2.4508(10); B(1)–Ir–B(2) 86.2(5), B(1)–Ir–B(3) 82.4(4), B(2)–Ir–B(3) 80.7(2), B(1)–Ir–C(1) 170.2(4), B(1)–Ir–P(1) 96.0(4), B(1)–Ir–P(2) 89.0(5), B(2)–Ir–C(1) 85.9(4), B(2)–Ir–P(1) 86.0(2), B(2)–Ir–P(2) 167.6(2), B(3)–Ir–C(1) 90.7(3), B(3)–Ir–P(1) 166.68(14), B(3)–Ir–P(2) 87.35(14), C(1)–Ir–P(1) 89.1(2), C(1)–Ir–P(2) 97.6(3), P(1)–Ir–P(2) 105.87(3), Ir–B(1)–F(1) 123.1(8), Ir–B(1)–F(2) 123.5(8), Ir–B(2)–F(3) 123.8(5), Ir–B(2)–F(4) 126.5(5), Ir–B(3)–F(5) 127.0(4), Ir–B(3)–F(6) 124.3(4), F(1)–B(1)–F(2) 113.4(8), F(3)–B(2)–F(4) 109.7(5) and F(5)–B(3)–F(6) 108.7(4).



1 **2** **3**

The configuration of the ligands in complex **3** warrants comment for two reasons. First, we note that the *fac* arrangement of the boryl groups is consistent with previous observations that in (bis)- or (tris)-boryl compounds boryls are never observed to be *trans*, presumably as a result of their large *trans* influence.[1] Secondly, and associated with the first point, the *fac* configuration adopted by the BF_2 groups forces a *cis* arrangement of the two phosphines which is unusual for iridium(III) (bis)triphenylphosphine complexes for which a mutually *trans* arrangement is more common.

The formation of complex **3** is clearly not as simple as in the platinum examples in that a (tris)boryl complex has been formed and the chloride group in the iridium starting material has been lost. Attempts to prepare an intermediate species by treating *trans*-[IrCl(CO)$(PPh_3)_2$] with no more than one equivalent of B_2F_4 afforded only mixtures of unchanged Vaska's compound and **3** and we were unable to obtain even spectroscopic data for a 1:1 reaction product. Reaction between *trans*-[IrCl(CO)$(PPh_3)_2$] and two equivalents or more of B_2F_4 afforded **3** in high yield. As far as a mechanism is concerned we can only speculate. As a first step we can envisage oxidative addition of B_2F_4 to give an iridium(III) species $[IrCl(BF_2)_2(CO)(PPh_3)_2]$ **A**. A σ-bond metathesis reaction involving the B–B bond of a second molecule of B_2F_4 and the Ir–Cl bond would then afford **3** and $BClF_2$. Alternatively, the above reaction sequence could be reversed affording an intermediate iridium(I) species $[Ir(BF_2)(CO)(PPh_3)_2]$ **B** and $BClF_2$ as initial products of which **B** then reacts with a second equivalent of B_2F_4 to form the iridium(III) product **3**.

Reactions between B_2F_4 and the complexes *trans*-[IrCl-$(CO)(PMe_3)_2$], *trans*-[RhCl(CO)$(PPh_3)_2$], $[\{RhCl(PPh_3)_2\}_2]$, $[Co(PMe_3)_4]$, [AuCl(PPh_3)] and [AuMe(PPh_3)] were also investigated. In the case of the iridium and two rhodium complexes, analysis by ^{31}P and ^{11}B NMR spectroscopy indicated the formation of several species. No pure materials could be isolated and none of the signals could unambiguously be assigned to an iridium or rhodium difluoroboryl species although ^{11}B NMR shifts of δ 33.3 and 33.9 for the reactions involving *trans*-[IrCl(CO)$(PMe_3)_2$] and *trans*-[RhCl(CO)-$(PPh_3)_2$] respectively are consistent with the presence of co-ordinated BF_2 groups. The reaction of B_2F_4 with paramagnetic $[Co(PMe_3)_4]$ afforded mixtures of yellow and deep green crystals which were characterised by X-ray crystallography as the starting cobalt(0) complex $[Co(PMe_3)_4]$ and the cobalt(I) salt $[Co(PMe_3)_4][BF_4]$ respectively. Crystallographic details for the latter are given in the Experimental section; data for $[Co(PMe_3)_4]$ were of poor quality but the refinement, although hampered by disorder problems, was sufficient to establish the identity of the complex. In the case of the two gold complexes, reactions clearly occurred although spectroscopic evidence was not consistent with the formation of any gold–BF_2 compounds and no pure materials could be isolated.

One aspect of the structures of complexes **1** and **2**, and indeed all other platinum complexes of the general formula *cis*-$[Pt(PPh_3)_2(BR_2)_2]$, concerns the acute B–Pt–B and obtuse P–Pt–P angles, ranges for which are 72.9–81.0 and 100.72–107.14° respectively.[1b] (Theoretical studies which reproduce the observed geometries are described in ref. 7.) We were interested to compare the structures of **1** and **2** with those of the complexes in which the BF_2 ligand is replaced by the isoelectronic NO_2 group. Treatment of $K_2[Pt(NO_2)_4]$ with two equivalents of PPh_3 afforded the *trans* isomer of $[Pt(NO_2)_2(PPh_3)_2]$[8]§ but the reaction between $K_2[Pt(NO_2)_4]$ and dppb afforded the complex *cis*-$[Pt(NO_2)_2(dppb)]$ **4**. Spectroscopic and analytical data for **4** were in accord with its expected formulation and the structure was confirmed by X-ray crystallography (Fig. 3). Pertinent metric information includes the Pt–N bond distances [Pt–N(1) 2.13(2) and Pt–N(2) 2.089(9) Å], the N–Pt–N [84.6(7)°] and P–Pt–P [94.95(11)°] angles, the maximum atom deviation from the PtP_2N_2 mean plane [0.069 Å], the angles defined by the

‡ The metric parameters associated with B(1) and the carbonyl carbon C(1) are for the configuration with the major site occupancy. Full details are given in the Experimental section.

§ Ref. 8 describes the preparation of *cis*-$[Pt(NO_2)_2(PPh_3)_2]$ by this synthetic route although there is some uncertainty concerning whether a *cis* or *trans* isomer was in fact formed. An X-ray structural study performed on a crystal of $[Pt(NO_2)_2(PPh_3)_2]$ prepared in this study revealed a *trans* configuration although the data were of poor quality and will not be further addressed here.

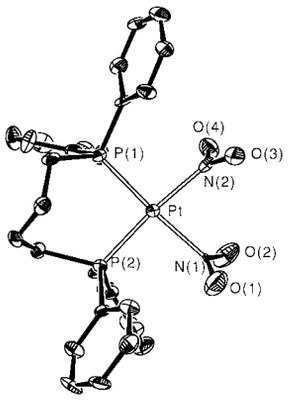
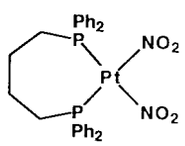


Fig. 3 A view of the molecular structure of complex **4** with key atoms labelled. Hydrogen atoms are omitted for clarity. Ellipsoids are drawn at the 50% level. Selected bond lengths (Å) and angles (°) include: Pt–N(1) 2.13(2), Pt–N(2) 2.089(9), Pt–P(1) 2.265(3), Pt–P(2) 2.271(3), N(1)–O(1) 1.17(2), N(1)–O(2) 1.20(2), N(2)–O(3) 1.218(9) and N(2)–O(4) 1.239(9); N(1)–Pt–N(2) 84.6(7), P(1)–Pt–P(2) 94.95(11), O(1)–N(1)–O(2) 126(2), Pt–N(1)–O(1) 119(2), Pt–N(1)–O(2) 113.9(14), O(3)–N(2)–O(4) 121.0(9), Pt–N(2)–O(3) 122.9(7) and Pt–N(2)–O(4) 116.1(7).

nitrite ligand planes and the mean platinum square plane [65.7 and 75.7° for N(1) and N(2) respectively], the N···N separation [2.837(25) Å] and the O–N–O [121.0(9)° for N(2)] and Pt–N–O [av. 119.5° for N(2)] angles. Unfortunately there is some compositional disorder in the structure of **4** involving one of the NO_2 groups and what appears to be residual chloride. Despite any associated uncertainties, these structural data are broadly similar to those of **2** (further data are given in the caption to Fig. 3).



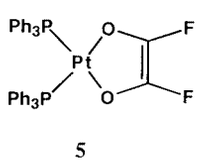
4

While the dppb bite angle is essentially unchanged on replacement of BF_2 by NO_2, the Pt–P distances are reduced by 0.07 Å. The N–O distances in complex **4** are shorter than the B–F lengths in **2** (by *ca.* 0.1 Å) and the O–N–O angles larger than the F–B–F angles (by *ca.* 10°) with the Pt–N–O angles correspondingly smaller than Pt–B–F by *ca.* 5°. The slightly larger N–Pt–N than B–Pt–B angle (by *ca.* 3°) and similarity of Pt–N and Pt–B lengths leads to an increased N···N distance in **4** compound to the B···B distance in **2**.

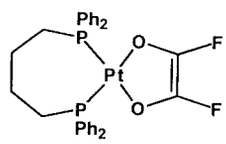
The origin of many of these differences in the structures of these strictly isoelectronic species can be traced to the electronegativity of the component atoms (B < N < O < F) and consequent effects on orbital energies. The greater electronegativity difference between B and F compared with N and O would be expected[9] to lead to larger F–B–F angles in BF_2^- than in NO_2^-. This difference is apparently preserved in their complexes. The lower electronegativity of B leads to BF_2 being a better σ donor than NO_2 and hence exerting a greater *trans* influence. As noted previously[1b] there is little evidence from the Pt–B bond lengths for significant Pt–B π bonding in **1** or **2** and one would expect even less Pt–N π-back bonding in **4**.

Another ligand isoelectronic with BF_2 is the fluoroacyl group, COF.¶ A small number of fluoroacyl compounds are known in which the COF ligand results from fluorine addition to coordinated CO, the fluorine source being XeF_2; an example is the cationic iridium(III) complex $[IrF(COF)(CO)_2(PEt_3)_2]^+$ {angles around the fluoroacyl carbon atom: Ir–C–O [125.4(4)], Ir–C–F [118.9(4)] and O–C–F [115.7(5)°]}.[11] By analogy with the B_2F_4 reactions described above, we sought to prepare a platinum (bis)fluoroacyl complex by oxidative addition of the C–C bond in oxalyl fluoride, $C_2O_2F_2$.‖ The platinum complexes $[Pt(PPh_3)_2(\eta\text{-}C_2H_4)]$ and $[Pt(dppb)(\eta\text{-}C_2H_4)]$ were both treated with $C_2O_2F_2$ in toluene solution and the solid products obtained after work-up analysed by multinuclear NMR and infrared spectroscopy; no crystalline products suitable for X-ray crystallography were obtained. In the former reaction the ^{31}P NMR spectrum revealed several products but only one signal, at δ 8.2, had platinum satellites. However, the Pt–P coupling constant ($^1J_{PtP} = 3806$ Hz) was more than twice that observed for **1** although it is quite similar to that found for the platinum catecholate complex $[Pt(PPh_3)_2(1,2\text{-}O_2C_6Cl_4)]$ ($^1J_{PtP} = 3613$ Hz).[13] The ^{19}F spectrum revealed a signal at δ −64.9 with coupling to phosphorus (3 Hz) and platinum (93 Hz). Other signals present in both spectra were attributed to phosphine degradation products most likely arising from the effects of traces of HF in the reaction mixture. An infrared spectrum of the reaction mixture showed absorptions at 1707 and 1670 cm^{-1} which are similar to those assigned to C–O vibrations in platinum(II) catecholate complexes.[14] On the basis of these data, therefore, the most likely structure for the product of this reaction is an enediolate complex $[Pt(PPh_3)_2\text{-}(1,2\text{-}O_2C_2F_2)]$ **5**. This results from a formal reduction of oxalyl fluoride by Pt^0 and is therefore analogous to reactions between platinum(0) complexes and *ortho*-quinones which afford platinum(II) catecholate complexes.[13]

Spectroscopic data for the major product from the reaction between the platinum dppb complex and $C_2O_2F_2$ were similar to those described above for **5**, *viz.* ^{31}P NMR δ 3.4 ($^1J_{PtP} = 3620$ Hz), ^{19}F NMR δ −64.4 ($^4J_{PF} = 3$, $^3J_{PtF} = 90$ Hz) and ν(C–O) 1706, 1669 cm^{-1}, albeit with less decomposition evident. An analogous structure $[Pt(dppb)(1,2\text{-}O_2C_2F_2)]$ **6** is therefore proposed.



5



6

Having established synthetic routes to the BF_2 complexes **1**–**3** a number of reactivity studies were carried out, primarily on **1**. The reaction between **1** and CO in CH_2Cl_2 afforded the complex $[PtH(CO)(PPh_3)_2][BF_4]$[15] (NMR: δ_P 23.3, $^1J_{PtP} = 2546$ Hz; δ_H −4.34, $^2J_{PH} = 10$, $^1J_{PtH} = 898$ Hz; δ_B −2.9; δ_F −153.1) as the only identifiable species. Simple phosphine substitution was observed, however, in the reaction between **1** and an excess of PCy_3 (Cy = cyclohexyl) in CH_2Cl_2 which afforded the boryl complex *cis*-$[Pt(BF_2)_2(PPh_3)(PCy_3)]$ (NMR: δ_P 35.6, $^1J_{PtP} = 1634$; 19.7, $^1J_{PtP} = 1587$ Hz, P–P coupling unresolved; δ_B 43.5; δ_F −15.4, $^2J_{PtF}$ 934; −15.8, $^2J_{PtF}$ 1138 Hz). Similar monosubstitution by PCy_3 has been observed before in the synthesis of *cis*-$[Pt\{B(cat)\}_2(PPh_3)(PCy_3)]$ (cat = 1,2-$O_2C_6H_4$) from *cis*-$[Pt\{B(cat)\}_2(PPh_3)_2]$ and PCy_3.[16]

Platinum boryls are efficient alkyne diboration catalysts[17] and although B_2F_4 is known to undergo uncatalysed addition to alkynes[18] the reaction between complex **1** and two equivalents of the alkyne di-*p*-tolylethyne was investigated. Little reaction in dichloromethane was evident from a ^{31}P NMR spectrum of the reaction mixture although signals due to the complex [Pt-(η-*p*-$MeC_6H_4C{\equiv}CC_6H_4Me$-*p*)$(PPh_3)_2$][19] (NMR: δ_p 27.1, $^1J_{PtP} =$

¶ We note also the osmium hydroxyboryl complex $[Os\{B(OH)_2\}Cl(CO)(PPh_3)_2]$ containing the $B(OH)_2$ ligand; Os–B 2.046(7), B–O 1.362(8), 1.396(9) Å; Os–B–O 116.5(5), 127.3(5), O–B–O 116.2(5)°.[10]

‖ Carbon–carbon bond activation, particularly for unstrained C–C bonds, is a topic of considerable current interest some aspects of which have recently been reviewed.[12]

3443 Hz) were present. No BF_2 containing products could unambiguously be identified. Although toluene is undoubtedly a better solvent for these reactions than CH_2Cl_2, the use of toluene in this case was not possible due to the low solubility of **1** in this solvent.

Alcoholysis reactions were carried out between complex **1** and both pinacol and catechol in CH_2Cl_2 solution in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) with a view to effecting fluoride substitution at the boron centre. Little evidence for simple substitution was apparent from monitoring these reactions by NMR, however. In the former case the only identifiable products were $[Pt(PPh_3)_3]$[20] (δ_P 49.5, $^1J_{PtP} = 4453$ Hz), $[PtH(Cl)(PPh_3)_2]$[17e,21] (δ_P 26.8, $^1J_{PtP} = 3002$ Hz) and $B_2(pin)_2$ (pin = pinacolate) (δ_B 30.4), whereas in the latter case the species identified were $[Pt(PPh_3)_3]$, $[PtH(Cl)(PPh_3)_2]$ and $[B(cat)_2]^-$ the latter being a typical decomposition product in transition metal B(cat) chemistry.[22] Fluoride substitution using alkoxide anions was attempted in two reactions. First, **1** was treated with $Li_2[pin]$ in CH_2Cl_2 and although analysis by ^{31}P and ^{11}B NMR spectroscopy indicated the presence of new products the reaction solution consisted largely of unchanged **1**. The reaction between compound **2** and Na[OMe] in dichloromethane, however, afforded a mixture of compounds, spectroscopic data [^{19}F NMR: δ_F −17.2, $^2J_{PtF} = 967$ (unchanged **2**); −19.0, $^2J_{PtF} = 981$; −24.6, $^2J_{PtF} = 396$; −37.3, $^2J_{PtF} = 881$ Hz] consistent with partial substitution of F by OMe, *i.e.* $[Pt\{BF_x(OMe)_y\}_2(dppb)]$ $[2(x + y) = 4]$.

Finally, diborane(4) exchange reactions were attempted. Compound **1** showed no reactivity towards $B_2(pin)_2$ or $B_2(thiocat)_2$ (thiocat = 1,2-$S_2C_6H_4$) in CH_2Cl_2 but with $B_2(cat)_2$ some spectroscopic evidence for $[Pt(BF_2)\{B(cat)\}(PPh_3)_2]$ (NMR: δ_P 27.9, $^1J_{PtP}$ 1622; δ_F −19.3, $^2J_{PtF} = 998$ Hz) and $[Pt\{B(cat)\}_2(PPh_3)_2]$[17e] (NMR: δ_P 28.7, $^1J_{PtP}$ 1639 Hz) was obtained. The observation of the mixed boryl species $[Pt(BF_2)\{B(cat)\}(PPh_3)_2]$, albeit only a tentative assignment, indicates that more than just a simple reductive elimination/oxidative addition pathway is operating.[17e,23]

Experimental

General procedures

Except where indicated all operations were carried out under dry dinitrogen or argon atmospheres using standard Schlenk and vacuum line techniques. All non-deuteriated solvents used were distilled over appropriate drying agents prior to use. Deuteriated solvents were dried over molecular sieves and degassed by three freeze–pump–thaw cycles under nitrogen.

High field NMR spectra were recorded using JEOL GX-400 and Lambda 300 spectrometers. Chemical shifts are reported in ppm relative to external standards; ^{31}P, ^{11}B and ^{19}F spectra were referenced to 85% H_3PO_4, $BF_3{\cdot}Et_2O$ and $CFCl_3$ respectively.

The compounds B_2F_4,[5] $[Pt(PPh_3)_2(\eta\text{-}C_2H_4)]$,[24] $[Pt(dppb)(\eta\text{-}C_2H_4)]$,[24] *trans*-$[IrCl(CO)(PPh_3)_2]$,[25] $K_2[Pt(NO_2)_4]$,[26] *trans*-$[IrCl(CO)(PMe_3)_2]$,[27] *trans*-$[RhCl(CO)(PPh_3)_2]$,[28] $[\{RhCl(PPh_3)_2\}_2]$,[29] $[Co(PMe_3)_4]$,[30] $[AuMe(PPh_3)]$,[31] $B_2(pin)_2$,[32] $B_2(cat)_2$[33] and $B_2(thiocat)_2$[33] were prepared according to literature methods. All other materials (including $[AuCl(PPh_3)]$) were procured commercially and used without further purification unless otherwise stated. Oxalyl fluoride was supplied by Lancaster and was vacuum distilled before use until determined to be pure by gas phase IR [ν(C–O) 1876, 1862 cm^{-1} [34]].

Preparations and reactions

***cis*-[Pt(BF$_2$)$_2$(PPh$_3$)$_2$] 1.** A sample of $[Pt(PPh_3)_2(\eta\text{-}C_2H_4)]$ (0.326 g, 0.436 mmol) was dissolved in toluene (5 cm^3) in a Young's tap tube after which the reaction flask was cooled in a liquid nitrogen Dewar. A sample of B_2F_4 (*ca.* 0.92 mmol) was then condensed into the Young's tap tube and the contents were allowed to warm to room temperature with stirring once the solvent had melted. A white precipitate formed at about −50 °C and once at room temperature stirring was continued for 30 min. After this time all volatiles were removed from the (orange) solution by vacuum affording a cream solid which was redissolved in CH_2Cl_2 (*ca.* 8 cm^3) resulting in a cloudy pale yellow solution. This solution was then filtered and diluted with toluene (30 cm^3) after which the solvent volume was reduced to *ca.* 4 cm^3 by vacuum resulting in a pale brown precipitate. This precipitate was collected by vacuum filtration, washed with toluene (*ca.* 2 cm^3) and hexane (*ca.* 15 cm^3) and dried by vacuum to yield pale brown microcrystalline complex **1** (0.269 g, 76%). Recrystallisation by solvent diffusion of toluene into a CH_2Cl_2 solution of **1** over 7 days at −30 °C afforded pale yellow crystals one of which was used for X-ray crystallography. NMR data (CD_2Cl_2): $^{31}P\text{-}\{^1H\}$ δ 24.3 (br t, $^1J_{PtP} = 1607$ Hz); $^{11}B\text{-}\{^1H\}$ δ 42.3; ^{19}F δ −17.8 (br t, $^2J_{PtF} = 1032$ Hz); $^{13}C\text{-}\{^1H\}$ δ 134.4 (d, *o*-C of PPh_3, $^2J_{PC} = 12$), 130.8 (s, *p*-C of PPh_3), 128.8 (d, *m*-C of PPh_3, $^3J_{PC} = 11$ Hz), *ipso*-carbon not observed; ^1H δ 7.32 (m, 18H, PPh_3) and 7.21 (m, 12H, PPh_3). $C_{36}H_{30}B_2F_4P_2Pt$ requires C, 52.90; H, 3.70. Found C, 54.60; H, 3.90%. Mass spectrum (FAB): *m*/*z* 719, $[Pt(PPh_3)_2]^+$.

***cis*-[Pt(BF$_2$)$_2$(dppb)] 2.** A sample of $[Pt(dppb)(\eta\text{-}C_2H_4)]$ (0.166 g, 0.256 mmol) was dissolved in toluene (5 cm^3) in a Young's tap tube after which the reaction flask was cooled in a liquid nitrogen Dewar. A sample of B_2F_4 (*ca.* 0.44 mmol) was then condensed into the Young's tap tube and the contents were allowed to warm to room temperature with stirring once the solvent had melted. A white precipitate formed at about −50 °C and once at room temperature stirring was continued for 1 h. After this time all volatiles were removed from the (yellow) solution by vacuum affording a cream solid which was redissolved in CH_2Cl_2 (*ca.* 6 cm^3) resulting in a cloudy pale yellow solution. This solution was then filtered and diluted with toluene (10 cm^3) and hexane (10 cm^3) after which the solvent volume was reduced to *ca.* 3 cm^3 by vacuum resulting in a cream precipitate. This precipitate was collected by vacuum filtration, washed with hexane (*ca.* 10 cm^3) and dried by vacuum to yield cream microcrystalline complex **2** (0.126 g, 69%). Recrystallisation by solvent diffusion of toluene into a CH_2Cl_2 solution of **2** over 7 days at −30 °C afforded pale yellow crystals one of which was used for X-ray crystallography. NMR data (CD_2Cl_2): $^{31}P\text{-}\{^1H\}$ δ 18.8 (br t, $^1J_{PtP} = 1526$ Hz); $^{11}B\text{-}\{^1H\}$ δ 43.9; ^{19}F δ −17.4 (br t, $^2J_{PtF} = 1040$ Hz); $^{13}C\text{-}\{^1H\}$ δ 136.1 (d, *ipso*-C of PPh_2, $^1J_{PC} = 48$), 133.2 (dt, *o*-C of PPh_2, $^2J_{PC} = 12$ and 19), 131.0 (d, *p*-C of PPh_2, $^4J_{PC} = 1$), 129.2 (d, *m*-C of PPh_2, $^3J_{PC} = 10$), 28.2 (d, PCH_2, $^1J_{PC} = 25$) and 23.9 (dd, PCH_2CH_2, $^2J_{PC} = 4$ and 3 Hz); ^1H δ 7.55 (m, 8H, PPh_2), 7.45 (m, 12H, PPh_2), 2.66 (br s, 4H, PCH_2CH_2) and 1.76 (br d, 4H, PCH_2, $J_{PH} = 19$ Hz). $C_{28}H_{28}B_2F_4P_2Pt$ requires C, 46.75; H, 3.90. Found C, 47.05; H, 4.00%.

***fac*-[Ir(BF$_2$)$_3$(CO)(PPh$_3$)$_2$] 3.** A sample of *trans*-$[IrCl(CO)(PPh_3)_2]$ (0.100 g, 0.128 mmol) was dissolved in toluene (5 cm^3) in a Young's tap tube after which the reaction flask was cooled in a liquid nitrogen Dewar. A sample of B_2F_4 (*ca.* 0.28 mmol) was then condensed into the Young's tap tube and the contents were allowed to warm to room temperature with stirring once the solvent had melted. After stirring for 1 h the reaction mixture comprised a clear yellow solution which was then refrozen to allow expansion of any volatile reaction components into a gas phase infrared cell. Upon rethawing the reaction mixture a white precipitate was observed which was collected by vacuum filtration, washed with toluene (*ca.* 1 cm^3) and hexane (3 × 3 cm^3) and then dried by vacuum to yield a white microcrystalline complex **3** (0.043 g, 41%). Recrystallisation by solvent diffusion of toluene into a CH_2Cl_2 solution of **3** over 7 days at −30 °C afforded colourless crystals one of which was used for X-ray crystallography. NMR data (CD_2Cl_2): $^{31}P\text{-}\{^1H\}$ δ −7.1 (br t, $^3J_{PF} = 56$ Hz); $^{11}B\text{-}\{^1H\}$ δ 32.4;

^{19}F δ −8.1 (br s, 2F, BF_2 *trans* to CO) and −10.0 (br s, 4F, BF_2 *trans* to PPh_3); ^{13}C-{^{1}H} δ 135.2 (d, *ipso*-C of PPh_3, $^1J_{PC}$ = 46), 134.1 (d, *o*-C of PPh_3, $^2J_{PC}$ = 12), 131.1 (s, *p*-C of PPh_3) and 128.9 (d, *m*-C of PPh_3, $^3J_{PC}$ = 10 Hz); ^{1}H δ 7.39 (m, 8H, PPh_3) and 7.29 (m, 22H, PPh_3). $C_{37}H_{30}B_3F_6IrOP_2$ requires C, 49.85; H, 3.40. Found C, 49.70; H, 3.00%. IR (KBr disk): ν(CO) 2039 cm^{-1}.

***cis*-[Pt(NO$_2$)$_2$(dppb)] 4.** A solution of dppb (0.103 g, 0.242 mmol) in ethanol (30 cm^3) and thf (6 cm^3) was transferred to a pressure equalising dropping funnel fitted above a Schlenk flask containing a yellow-green solution of $K_2[Pt(NO_2)_4]$ (0.110 g, 0.241 mmol) in water (10 cm^3). Dropwise addition of the dppb solution to the stirred aqueous solution of the nitritoplatinate salt at room temperature resulted in the immediate formation of a white precipitate. After stirring for 16 h the white solid was collected by vacuum filtration (in air), washed with distilled water (4 × 10 cm^3), ethanol (3 × 10 cm^3) and Et_2O (2 × 10 cm^3) and then dried by vacuum affording complex **4** as a white microcrystalline solid (0.084 g, 49%). NMR data (d_6-dmso): ^{31}P-{^{1}H} δ −3.1 (t, $^1J_{PtP}$ = 3026 Hz). IR (KBr disk): 1417s, 1331s and 820s cm^{-1}. $C_{28}H_{28}N_2O_4P_2Pt$ requires C, 47.15; H, 3.95; N, 3.95. Found C, 47.10; H, 3.90; N, 3.30%.

[Pt(PPh$_3$)$_2$(1,2-O$_2$C$_2$F$_2$)] 5. A Young's tap tube containing a stirrer bead and a solution of $[Pt(PPh_3)_2(\eta\text{-}C_2H_4)]$ (0.122 g, 0.163 mmol) in toluene (2 cm^3) was frozen in liquid nitrogen and evacuated. A sample of $C_2O_2F_2$ (0.25 mmol) was then condensed into the Young's tube which was resealed under vacuum, allowed to warm to 0 °C by placing the tube in an ice bath and the solution was stirred. After 30 min the reaction mixture comprised an orange solution which was allowed to warm to room temperature and stir for 48 h. After this time the reaction mixture consisted of an orange solution and an off-white precipitate. The solid was collected by vacuum filtration, washed with toluene (1 cm^3) and hexane (2 cm^3) and then dried by vacuum affording an off-white solid (0.064 g). NMR data (CD_2Cl_2): ^{31}P-{^{1}H} δ 8.2 (t, $^1J_{PtP}$ = 3806 Hz); ^{19}F δ −64.9 (tt, $^4J_{PF}$ = 3, $^3J_{PtF}$ = 93 Hz); ^{13}C-{^{1}H} δ 136.5–128.0 (PPh_3); ^{1}H δ 7.85–7.00 (PPh_3) IR (KBr disk): ν(C–O) 1707, 1670 cm^{-1}. Satisfactory microanalytical data could not be obtained due to the presence of impurities in the sample.

[Pt(dppb)(1,2-O$_2$C$_2$F$_2$)] 6. A Young's tap tube containing a stirrer bead and a solution of $[Pt(dppb)(\eta\text{-}C_2H_4)]$ (0.129 g, 0.198 mmol) in toluene (2 cm^3) was frozen in liquid nitrogen and evacuated. A sample of $C_2O_2F_2$ (0.30 mmol) was then condensed into the Young's tube which was resealed under vacuum, allowed to warm to 0 °C by placing the tube in an ice bath and the solution was stirred. After 10 min the reaction mixture comprised a pale precipitate and an orange solution which was allowed to warm to room temperature and stir for 48 h. After this time the reaction mixture consisted of an orange solution and an off-white precipitate. The solid was collected by vacuum filtration, washed with toluene (1 cm^3) and hexane (2 cm^3) and then dried by vacuum affording an off-white solid (0.087 g). NMR data (CD_2Cl_2): ^{31}P-{^{1}H} δ 3.4 (t, $^1J_{PtP}$ = 3620 Hz); ^{19}F δ −64.4 (tt, $^4J_{PF}$ = 3, $^3J_{PtF}$ = 90 Hz); ^{13}C-{^{1}H} δ 134.5–128.5 (PPh_3); ^{1}H δ 7.75–7.10 (PPh_3). IR (KBr disk): ν(C–O) 1706, 1669 cm^{-1}. Satisfactory microanalytical data could not be obtained due to the presence of impurities in the sample.

X-Ray crystallography

Crystallographic data for compound **1** are given in ref. 5. For **2**–**4** and $[Co(PMe_3)_4][BF_4]$ X-ray diffraction measurements were carried out on single crystals coated in a hydrocarbon oil mounted on a glass fibre under argon, using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) on a Bruker SMART area detector diffractometer, and the structures were solved and refined against F^2 using SHELXL 97.[35] In compound **3** positional disorder was identified between the carbonyl ligand and the BF_2 group *trans* to it. Each unit was refined anisotropically over two sites in a ratio of 67 : 33(5). In **4** disorder was observed between one of the NO_2 groups and residual chloride and was modelled in a 66 : 34(2) ratio with the chloride refined isotropically. Constraints were applied to the refinement of the NO_2 group so that the adps mirrored those of the neighbouring NO_2 ligand. In $[Co(PMe_3)_4][BF_4]$ the anion was disordered over a 3-fold rotation axis and modelled with two separate images [73 : 27(2) ratio] with F(2) having two different positions. Hydrogen atoms were included in idealised positions.

Crystal data for *cis*-[Pt(BF$_2$)$_2$(dppb)] 2. M = 719.15, triclinic, space group $P\bar{1}$ (no. 2), a = 8.924(4), b = 11.185(7), c = 14.678(12) Å, α = 85.61(6), β = 80.07(5), γ = 71.32(4)°, U = 1366.7(15) Å^3, T = 173(2) K, Z = 2, μ(Mo-Kα) = 5.29 mm^{-1}, 14332 reflections measured, 6163 unique (R_{int} = 0.044), final $R1$ = 0.034 [5100 data, $I > 2\sigma(I)$].

Crystal data for *fac*-[Ir(BF$_2$)$_3$(CO)(PPh$_3$)$_2$] 3. M = 891.18, orthorhombic, space group *Pbca* (no. 61), a = 9.9312(8), b = 18.493(2), c = 38.273(4) Å, U = 7029.4(11) Å^3, T = 173(2) K, Z = 8, μ(Mo-Kα) = 3.95 mm^{-1}, 42025 reflections measured, 8046 unique (R_{int} = 0.049), final $R1$ = 0.036 (5930 data, $I > 2\sigma(I)$).

Crystal data for *cis*-[Pt(NO$_2$)$_2$(PPh$_3$)$_2$] 4. M = 837.63, triclinic, space group $P\bar{1}$ (no. 2), a = 8.707(4), b = 10.872(5), c = 14.645(8) Å, α = 85.32(3), β = 79.59(2), γ = 72.21(4)°, U = 1297.7(11) Å^3, T = 173(2) K, Z = 2, μ(Mo-Kα) = 5.93 mm^{-1}, 13647 reflections measured, 5877 unique (R_{int} = 0.118), final $R1$ = 0.065 (3552 data, $I > 2\sigma(I)$).

Crystal data for [Co(PMe$_3$)$_4$][BF$_4$]. M = 267.82, cubic, space group $P2_13$ (no. 198), a = 13.2859(6) Å, U = 2345.16(18) Å^3, T = 173(2) K, Z = 8, μ(Mo-Kα) = 1.52 mm^{-1}, 15447 reflections measured, 1814 unique (R_{int} = 0.118), final $R1$ = 0.031 (1459 data, $I > 2\sigma(I)$).

CCDC reference number 186/2190.

See http://www.rsc.org/suppdata/dt/b0/b006535h/ for crystallographic files in .cif format.

Acknowledgements

We thank the EPSRC for research support and studentships (G.R.W. and M.J.Q.) and N.C.N. thanks Laporte plc and The Royal Society for additional supporting funds. Johnson Matthey Ltd. are thanked for generous supplies of platinum salts and we thank Jennifer Pardoe for providing samples of B_2F_4.

Note added at proof: since the submission of this manuscript we have noted a report (T. M. Peterson, J. T. Golden and R. C. Bergman, *Organometallics*, 1999, **18**, 2005) which provides spectroscopic data (δ_B 23.9, $^1J_{BF}$ 160; δ_F −23.2, $^1J_{BF}$ 154 Hz) for a compound formulated as $[IrH(BF_2)(PMe_3)(\eta\text{-}C_5Me_5)]$.

References

1 (*a*) G. Schmid, *Angew. Chem., Int. Ed. Engl.*, 1970, **9**, 819; (*b*) G. J. Irvine, M. J. G. Lesley, T. B. Marder, N. C. Norman, E. G. Robins, W. Roper, C. R. Rice, G. R. Whittell and L. J. Wright, *Chem. Rev.*, 1998, **98**, 2685; (*c*) M. R. Smith, *Prog. Inorg. Chem.*, 1999, **48**, 505; (*d*) H. Braunschweig, *Angew. Chem., Int. Ed.*, 1998, **37**, 1787.

2 T. B. Marder and N. C. Norman, *Topics in Catalysis*, eds. W. Leitner and D. G. Blackmond, Baltzer Science Publishers, Amsterdam, 1998, vol. 5, p. 63; I. Beletskaya and A. Pelter, *Tetrahedron*, 1997, **53**, 4957; K. Burgess and M. J. Ohlmeyer, *Chem. Rev.*, 1991, **91**, 1179; K. Burgess and W. A. van der Donk, in *Encyclopedia*

of Inorganic Chemistry, ed. R. B. King, Wiley, 1994, vol. 3, p. 1420; G. C. Fu, D. A. Evans and A. R. Muci, in *Advances in Catalytic Processes*, ed. M. P. Doyle, JAI, Greenwich, CT, 1995, p. 95.
3 H. Nöth and G. Schmid, *Angew. Chem.*, *Int. Ed. Engl.*, 1963, **2**, 623; H. Nöth and G. Schmid, *Z. Anorg. Allg. Chem.*, 1966, **345**, 69; G. Schmid and H. Nöth, *J. Organomet. Chem.*, 1967, **7**, 129; H. Nöth, W. Petz, W. Arloth and G. Schmid, *Angew. Chem.*, *Int. Ed. Engl.*, 1967, **6**, 696; G. Schmid, P. Powell and H. Nöth, *Chem. Ber.*, 1968, **101**, 1205; G. Schmid, *Chem. Ber.*, 1969, **102**, 191.
4 G. J. Irvine, C. E. F. Rickard, W. R. Roper, A. Williamson and L. J. Wright, *Angew. Chem.*, *Int. Ed.*, 2000, **39**, 948.
5 A. Kerr, T. B. Marder, N. C. Norman, A. G. Orpen, M. J. Quayle, C. R. Rice, P. L. Timms and G. R. Whittell, *Chem. Commun.*, 1998, 319.
6 P. L. Timms, *J. Am. Chem. Soc.*, 1967, **89**, 1629.
7 Q. Cui, D. G. Musaev and K. Morokuma, *Organometallics*, 1997, **16**, 1355; S. Sakaki and T. Kikuno, *Inorg. Chem.*, 1997, **36**, 226.
8 J. L. Burmeister and R. C. Timmer, *J. Inorg. Nucl. Chem.*, 1966, **28**, 1973.
9 B. M. Gimarc, *Molecular Structure and Bonding*, Academic Press, New York, 1979; T. A. Albright, J. K. Burdett and M.-H. Whangbo, *Orbital Interactions in Chemistry*, Wiley, New York, 1985.
10 G. J. Irvine, PhD Thesis, University of Auckland, 1996.
11 A. J. Blake, R. W. Cockman, E. A. V. Ebsworth and J. H. Holloway, *J. Chem. Soc.*, *Chem. Commun.*, 1988, 529.
12 B. Rybtchinski and D. Milstein, *Angew. Chem.*, *Int. Ed.*, 1999, **38**, 870.
13 J. A. Daldy, J. Fawcett, W. Henderson, R. D. W. Kemmit and D. R. Russell, *J. Chem. Soc.*, *Dalton Trans.*, 1994, 3383.
14 O. Gandolfi, G. Dolcetti, M. Ghedini and M. Cais, *Inorg. Chem.*, 1980, **19**, 1785.
15 W. J. Cherwinski and H. C. Clark, *Inorg. Chem.*, 1971, **10**, 2263.
16 D. Curtis, M. J. G. Lesley, N. C. Norman, A. G. Orpen and J. Starbuck, *J. Chem. Soc.*, *Dalton Trans.*, 1999, 1687.
17 (*a*) T. Ishiyama, N. Matsuda, N. Miyaura and A. Suzuki, *J. Am. Chem. Soc.*, 1993, **115**, 11018; (*b*) F. Ozaura, A. Suzuki and N. Miyaura, *Organometallics*, 1996, **15**, 713; (*c*) C. N. Iverson and M. R. Smith, *J. Am. Chem. Soc.*, 1995, **117**, 4403; (*d*) C. N. Iverson and M. R. Smith, *Organometallics*, 1996, **15**, 5155; (*e*) M. J. G. Lesley, P. Nguyen, N. J. Taylor, T. B. Marder, A. J. Scott, W. Clegg and N. C. Norman, *Organometallics*, 1996, **15**, 5137; (*f*) K. M. Anderson, M. J. G. Lesley, N. C. Norman, A. G. Orpen and J. Starbuck, *New J. Chem.*, 1999, **23**, 1053.
18 A. G. Massey, *Adv. Inorg. Chem. Radiochem.*, 1983, **26**, 1.
19 J. Chatt, B. L. Shaw and A. A. Williams, *J. Chem. Soc.*, 1962, 3269.
20 A. Sen and J. Halpern, *Inorg. Chem.*, 1980, **19**, 1073.
21 W. McFarlane, *J. Chem. Soc.*, *Dalton Trans.*, 1974, 324.
22 W. Clegg, F. J. Lawlor, T. B. Marder, P. Nguyen, N. C. Norman, A. G. Orpen, M. J. Quayle, C. R. Rice, E. G. Robins, A. J. Scott, F. E. S. Souza, G. Stringer and G. R. Whittell, *J. Chem. Soc.*, *Dalton Trans.*, 1998, 301; W. Clegg, M. R. J. Elsegood, A. J. Scott, T. B. Marder, C. Dai, N. C. Norman, N. L. Pickett and E. G. Robins, *Acta Crystallogr.*, *Sect. C*, 1999, **55**, 733.
23 T. B. Marder, N. C. Norman, C. R. Rice and E. G. Robins, *Chem. Commun.*, 1997, 53.
24 M. Camalli, F. Caruso, S. Chaloupka, E. M. Leber, H. Rimml and L. M. Venanzi, *Helv. Chim. Acta*, 1990, **73**, 2263.
25 K. Vrieze, J. P. Collman, C. J. Sears and M. Kubota, *Inorg. Synth.*, 1968, **11**, 101.
26 G. Brauer, *Handbook of Preparative Inorganic Chemistry*, Academic Press, New York, 1965.
27 J. A. Labinger and J. A. Osborn, *Inorg. Synth.*, 1978, **18**, 62.
28 D. Evans, J. A. Osborn and G. Wilkinson, *Inorg. Synth.*, 1968, **11**, 99.
29 J. A. Osborn and G. Wilkinson, *Inorg. Synth.*, 1967, **10**, 67.
30 H.-F. Klein and H. H. Karsch, *Chem. Ber.*, 1975, **108**, 944.
31 G. E. Coates and C. Parkin, *J. Chem. Soc.*, 1962, 3221.
32 H. Nöth, *Z. Naturforsch.*, *Teil B*, 1984, **39**, 1463.
33 F. J. Lawlor, N. C. Norman, N. L. Pickett, E. G. Robins, P. Nguyen, G. Lesley, T. B. Marder, J. A. Ashmore and J. C. Green, *Inorg. Chem.*, 1998, **37**, 5282.
34 D. E. Milligan, M. E. Jacox, A. M. Bass, J. J. Comeford and D. E. Mann, *J. Chem. Phys.*, 1965, **42**, 3187.
35 G. M. Sheldrick, SHELXL 97, Program for Crystal Structure Determination, University of Göttingen, 1997.