Articles

Electrophilic Methylplatinum Complexes: First Structure of a Hydroxytris(pentafluorophenyl)borate Complex

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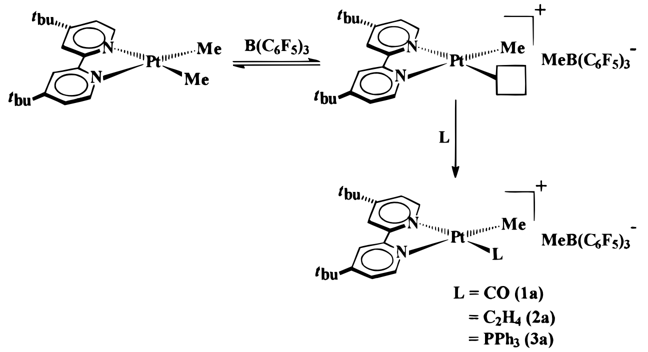
Treatment of [$PtMe_2$(bu_2bpy)] (bu_2bpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine) with $B(C_6F_5)_3$ in the presence of the ligand L gives, under anhydrous conditions, [PtMeL(bu_2bpy)][MeB-$(C_6F_5)_3$] {L = CO (**1a**), C_2H_4 (**2a**), PPh_3 (**3a**)}. Similar reactions performed in the presence of H_2O afford [PtMeL(bu_2bpy)][HOB$(C_6F_5)_3$] {L = CO (**1b**), C_2H_4 (**2b**), PPh_3 (**3b**)}. In the absence of L, the treatment of [$PtMe_2$(bu_2bpy)] with $B(C_6F_5)_3$ and H_2O gives [Pt{H*O*B$(C_6F_5)_3$}Me(bu_2bpy)] (**4**), the first published example of a hydroxytris(pentafluorophenyl)borate complex. All of the complexes are fully characterized by NMR and IR spectroscopy and, in the case of complex **4**, by an X-ray analysis which confirms the attachment of the $[HOB(C_6F_5)_3]^-$ ligand to the square-planar platinum atom *via* a Pt−O bond of 2.062(2) Å. We propose that, in the presence of water, $B(C_6F_5)_3$ forms an adduct $[H_2OB(C_6F_5)_3]$ (which acts as a strong acid $H[HOB(C_6F_5)_3]$) and this then protonates a Pt−Me bond of [$PtMe_2$(bu_2bpy)] forming CH_4 and $[PtMe(bu_2bpy)]^+[HOB(C_6F_5)_3]^-$. This protonolysis methodology provides an alternative route to the well-established electrophilic methyl-ligand abstraction by $B(C_6F_5)_3$ for the production of late transition-metal cations.

Introduction

There has been increasing interest in electrophilic cationic transition-metal complexes as they often possess unique and highly desirable catalytic properties. For example, early transition-metal metallocenium and *ansa*-metallocenium cations[1] as well as late transition-metal cations of the type $[MMe(N-N)]^+$ (M = Ni, Pd; N−N = diimine)[2] are highly active catalysts for the polymerization of ethylene and α-olefins.

One of the most common methods used to produce transition-metal cations is by direct electrophilic attack on a M−Me bond by the powerful Lewis acid $B(C_6F_5)_3$, to produce $[M]^+[MeB(C_6F_5)_3]^-$. This methodology was introduced several years ago for creating vacant sites in early transition-metal complexes[3] but has only been recently applied to late transition-metal systems.[4] For example, we have shown that under anhydrous conditions, methyl-ligand abstraction from [$PtMe_2$(bu_2bpy)] by $B(C_6F_5)_3$ in the presence of the ligand L affords the complexes [PtMeL(bu_2bpy)][MeB$(C_6F_5)_3$] {L = CO (**1a**), C_2H_4 (**2a**); bu_2bpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine}[4] and we now show that in the presence of PPh_3 it leads to the formation of [PtMe(PPh_3)(bu_2bpy)][MeB$(C_6F_5)_3$] (**3a**) (Scheme 1).

Scheme 1



In this paper we also report that in the presence of water $B(C_6F_5)_3$ does not directly attack a Pt−Me bond of [$PtMe_2$(bu_2bpy)] but forms an adduct $[H_2OB(C_6F_5)_3]$ (which acts as a strong acid $H[HOB(C_6F_5)_3]$) which rapidly protonates a Pt−Me bond to form CH_4 and the proposed cationic intermediate $[PtMe(bu_2bpy)]^+$-$[HOB(C_6F_5)_3]^-$. This protonation methodology provides an alternative synthetic route to transition-metal cations which still uses $B(C_6F_5)_3$ as the key reagent. The

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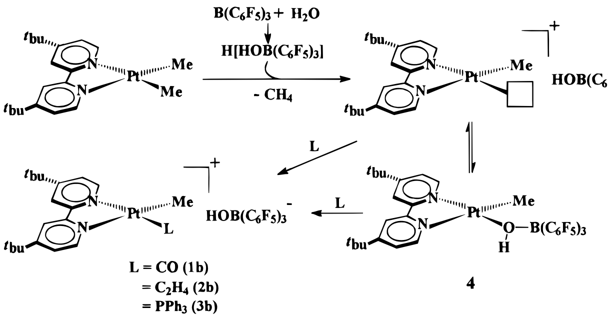
Scheme 2



closest analogies to this system of which we are aware employ either the trialkylammonium acid[5] $[HNBu_3]^+[B(C_6F_5)_4]^-$ or the oxonium acid[6] $[H(OEt_2)_2]^+[\{3,5\text{-}(CF_3)_2C_6H_3\}_4B]^-$. The protonation of a zirconium−methyl bond in $[(Cp^*)_2ZrMe_2]$ by $[HNEt_3][HOB(C_6F_5)_3]$ gives *not* a cationic species but the zirconoxyborane $[(Cp^*)_2ZrOB(C_6F_5)_3]$.[7]

Results and Discussion

Under anhydrous conditions, electrophilic methyl-ligand abstraction from $[PtMe_2(bu_2bpy)]$ by the powerful Lewis acid $B(C_6F_5)_3$ in the presence of the ligand L gives the complexes $[PtMeL(bu_2bpy)][MeB(C_6F_5)_3]$ {L = CO (**1a**), C_2H_4 (**2a**), PPh_3 (**3a**); bu_2bpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine}. The synthesis and characterization of complexes **1a** and **2a** have been reported previously.[4] Complex **3a** is an orange hygroscopic solid that can be isolated in good yield and has been characterized on the basis of NMR spectroscopic (^1H, ^{11}B, and ^{31}P) and microanalytical data. The ^1H NMR spectrum shows the expected two *tert*-butyl resonances and six sets of aromatic resonances due to the inequivalent nature of the two pyridyl moieties of the bu_2bpy ligand. The Pt−Me ligand resonates at $\delta = 0.71$ with $^2J(PtH) = 72.0$ Hz, typical of other cationic platinum(II) complexes.[4] The ^{31}P NMR spectrum shows the expected singlet at $\delta = 20.0$. This resonance is flanked by ^{195}Pt satellite signals with $^1J(PtP) = 4343$ Hz, typical of other cationic platinum(II)−phosphine complexes.[9] The ^{11}B NMR spectra of complexes **1a**, **2a**, and **3a** show a singlet at $\delta = -15.1$, indicative of the $[MeB(C_6F_5)_3]^-$ anion.[3,7,10]

During the initial preparations of complexes **1a**, **2a**, and **3a**, it was noted that some of the corresponding complex, $[PtMeL(bu_2bpy)][HOB(C_6F_5)_3]$ {L = CO (**1b**), C_2H_4 (**2b**), PPh_3 (**3b**)}, was often produced (Scheme 2). The cause of this is most certainly the introduction of adventitious H_2O into the reaction vessel since these $[HOB(C_6F_5)_3]^-$ complexes are formed exclusively if 1 equiv of H_2O is added during the initial stages of the reaction. Complexes **1b**, **2b**, and **3b** give very similar NMR spectra to complexes **1a**, **2a**, and **3a**, respectively, with the exception of the ^{11}B NMR which shows a singlet at $\delta = -4.4$, indicative of the $[HOB(C_6F_5)_3]^-$ anion.[7] The infrared spectra of complexes **1b**, **2b**, and **3b** show a strong O−H stretching band at 3684 cm^{-1} that is absent in the otherwise very similar infrared spectra of **1a**, **2a**, and **3a**, respectively.

In the absence of the ligand L, the low-temperature reaction of $[PtMe_2(bu_2bpy)]$ with $B(C_6F_5)_3$ and 1 equiv of water produces CH_4 and the {hydroxytris(pentafluorophenyl)borato}platinum(II) complex **4** in high yield (Scheme 2).[11] To our knowledge, the only other example of a transition-metal complex incorporating the $[HOB(C_6F_5)_3]^-$ group is $[(Cp^*)_2Ta(OH)Me][HOB(C_6F_5)_3]$, which is formed upon treatment of $[(Cp^*)_2TaMe_2]SO_3CF_3$ with $[NaB(C_6F_5)_4]$ and in which the $[HOB(C_6F_5)_3]^-$ group is not coordinated.[8] Thus, complex **4** provides the first published example of a transition-metal complex containing a coordinated $[HOB(C_6F_5)_3]^-$ ligand, though such species have been mentioned in the patent literature.[7] The ^1H NMR spectrum of complex **4** shows the expected two *tert*-butyl resonances and six sets of aromatic resonances due to the inequivalent nature of the two pyridyl moieties of the bu_2bpy ligand. The Pt−Me ligand resonates at $\delta = 0.81$ with $^2J(PtH) = 78.9$ Hz. The PtO(*H*)B group gives a broad resonance at $\delta = 3.21$ which does not show any resolvable splitting even at −90 °C. No coupling of the PtO(*H*)B group to ^{195}Pt is observed, and we assume that this is due to a rapid exchange process. This PtO(*H*)B resonance disappears upon treatment of an Et_2O solution of complex **4** with D_2O and is absent in the otherwise identical ^1H NMR spectrum of $[Pt\{DOB(C_6F_5)_3\}Me(bu_2bpy)]$ prepared from $[PtMe_2(bu_2bpy)]$, $B(C_6F_5)_3$, and D_2O. The infrared spectrum of complex **4** shows a sharp O−H stretching band at 3640 cm^{-1}. This band is replaced by a weak absorption at 2673 cm^{-1} in the infrared spectrum of $[Pt\{DOB(C_6F_5)_3\}Me(bu_2bpy)]$. At room temperature, rapid rotation about the O−B and B−C bonds renders the three pentafluorophenyl moieties of **4** equivalent, and the ^{19}F NMR spectrum shows only three sets of resonances, one set for each of the *ortho*-, *meta*-, and *para*-fluorine atoms. However, at −90 °C these three sets resolve into eight separate resonances, indicating that the three pentafluorophenyl moieties are no longer equivalent. This low-temperature phenomenon is certainly a result of the steric interference introduced upon coordination of the $[HOB(C_6F_5)_3]^-$ ion to platinum, since none of the compounds which contain either the free $[MeB(C_6F_5)_3]^-$ ion (in complexes **1a**, **2a**, **3a**) or $[HOB(C_6F_5)_3]^-$ ion (in complexes **1b**, **2b**, **3b**) shows any further resolution in the ^{19}F NMR at −90 °C due to inequivalent pentafluorophenyl groups.

The structure of **4** has been confirmed by X-ray analysis (Figure 1). The *cis*-N_2CO donor set which surrounds the Pt atom departs significantly from ideal square-planar coordination: as expected, the N−Pt−N angle narrows to accommodate the restricted bite of the bu_2bpy ligand and there is also a slight tetrahedral distortion, with donor atoms lying alternately 0.04 Å above and below the coordination plane. The Pt−N bond lengths (Table 1) differ by 0.117(3) Å, reflecting the high *trans*-influence of σ-CH_3 and the low *trans*-

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(11) CH_3D was detected by GC-MS when the reaction was performed in the presence of D_2O.

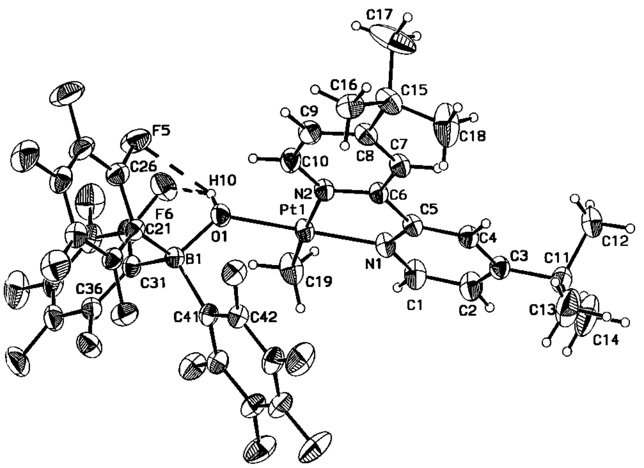

Figure 1. Molecular structure of [Pt{H*O*B(C_6F_5)$_3$}Me(bu$_2$-bpy)], **4**. Displacement ellipsoids of 30% are shown except for hydrogen atoms which are displayed as spheres of arbitrary size. The disorder of the methyl carbon atoms attached to C11 is not illustrated. Phenyl carbon atoms are numbered cyclically C21−C26, C31−C36, and C41−C46, in each case starting from the atom bonded to B1. The atoms F1−F5 are attached in sequence to C22−C26, F6−F10 to C32−C36, and F11−F15 to C42−C46.

influence of oxygen donor ligands,[9,12] thereby confirming less precise results of the only previous structural study of a platinum(II) compound with a *cis*-(sp^2-N)$_2$CO donor set.[13] The Pt−O bond length in **4** [2.062(2) Å] is a little longer than the mean Pt(II)−OH distance obtained from a database survey [2.006 Å],[14] while the reverse is true of the Pt−CH$_3$ distance [2.037(3) Å in **4** compared with a database value of 2.107 Å].

The bu$_2$bpy ligand contains two rigorously planar pyridyl rings (rms, Δ < 0.004 Å) twisted about the central single bond [C5−C6 = 1.476(3) Å] so that the C4−C5−C6−C7 torsion angle is 6.9(4)°. This twist still leaves a short H4···H7 contact of 2.16 Å; it may explain the tetrahedral distortion of the Pt coordination. The acuteness of the endocyclic C−C−C angles at C3 and C8 [115.7(3) and 115.8(2)°] can be attributed to electron release by the *tert*-butyl substituents.[15] Each of the three methyl groups attached to C11 is disordered over two sites with occupancy ratio *ca.* 4:1. The methyl groups attached to C15 show physically unreasonable displacement parameters [e.g. $U_{\max}$ = 0.27 Å^2 for C17] suggestive of disorder which is not *explicitly* accounted for in the final structural model.

The [HOB(C_6F_5)$_3$]$^-$ ligand in **4** is much the most novel feature of the structure. The analysis allowed the hydrogen atom attached to O1 to be successfully, though not very accurately, located. The central boron atom has a somewhat distorted tetrahedral coordination and forms B−C bonds whose lengths [1.636(4)−1.659(4) Å] cluster about the database mean[14] for the corresponding bonds in BPh$_4^-$ (1.643 Å). The B−O bond length [1.526(3) Å] may be slightly lengthened by coordination to Pt: corresponding values in structures containing the uncomplexed [HOB(C_6F_5)$_3$]$^-$ anion are 1.487(3) Å in [Et$_3$NH][HOB(C_6F_5)$_3$] and 1.490(10) Å in [(Cp*)$_2$TaMe(OH)] [HOB(C_6F_5)$_3$].[7,8] It has been shown by a crystal structure analysis of [H$_2$OB(C_6F_5)$_3$]·2H$_2$O that only one water molecule is directly attached to boron, forming the conjugate acid of [HOB(C_6F_5)$_3$]$^-$.[16] However in [Re^{V}O$_2$(C$_{10}$H$_{24}$N$_4$)]Cl·2[H$_2$OBPh$_3$] the B−O distance [1.602(6) Å] is much longer than in **4**.[17] The only other structure related to **4** of which we are aware is [(Cp*)$_2$Zr^{IV}(OB(C_6F_5)$_3$] in which the conjugate base of [HOB(C_6F_5)$_3$]$^-$ is bonded to zirconium through an *ortho* fluorine atom as well as through oxygen [B−O 1.460(6) Å]; the B−O−Zr angle of 151.2(3)° in this structure is substantially more obtuse than the B−O−Pt angle of 128.2(2)° in **4**.[7] However, it may also be worth noting here that there is a single structural report of the attachment of OBPh$_3^{2-}$ to a tungsten(VI) cation.[18]

Table 1. Selected Distances (Å) and Angles (deg) in [Pt{H*O*B(C_6F_5)$_3$}Me(bu$_2$bpy)], 4

(a) Bond Lengths

Pt1−O1	2.062(2)	Pt1−N1	1.980(2)
Pt1−N2	2.097(2)	Pt1−C19	2.037(3)
C21−B1	1.659(4)	O1−B1	1.526(3)
C41−B1	1.636(4)	C31−B1	1.654(3)

(b) Bond Angles

O1−Pt1−N1	172.6(1)	O1−Pt1−N2	93.3(1)
O1−Pt1−C19	90.6(1)	N1−Pt1−N2	80.1(1)
N1−Pt1−C19	96.1(1)	N2−Pt1−C19	175.7(1)
Pt1−O1−N10	115(3)	Pt1−O1−B1	128.2(2)
H1O−O1−B1	111(3)	O1−B1−C21	108.3(2)
O1−B1−C31	111.7(2)	O1−B1−C41	103.2(2)
C21−B1−C31	104.3(2)	C21−B1−C41	115.2(2)
C31−B1−C41	114.3(2)		

(c) Torsion Angles

C19−Pt1−O1−B1	73.8(2)	Pt1−O1−B1−C21	132.5(2)
Pt1−O1−B1−C31	−113.2(2)	Pt1−O1−B1−C41	10.0(3)
C22−C21−B1−O1	−140.5(2)	C26−C21−B1−O1	46.2(3)
C32−C31−B1−O1	−14.0(4)	C36−C31−B1−O1	170.5(2)
C42−C41−B1−O1	70.2(3)	C46−C41−B1−O1	−100.6(3)

(d) Hydrogen Bonds

bond	O···F	O−H	H···F	O−H···F
O1−H1O···F5	2.722(3)	0.67(4)	2.32(4)	120(4)
O1−H1O···F6	2.692(3)	0.67(4)	2.18(4)	135(5)

The conformation of the [HOB(C_6F_5)$_3$]$^-$ ligand in **4** is such that B1 lies far from the coordination plane of the metal atom (C19−Pt1−O1−B1 = 74°). The Pt1−O1−B1−C41 chain is nearly planar (torsion angle 10°) so that the C41 ring lies above the coordination plane of Pt1; however, the shortest contact between the C41 ring and the metal [Pt1···C41 = 3.185(2) Å] is clearly nonbonding. This arrangement leaves the face of the Pt1 coordination plane opposite to the C41 ring relatively exposed, and in consequence there is a short intermolecular Pt···Pt contact of 4.1201(4) Å with a centrosymmetrically related molecule.

One further feature of the conformation adopted by the [HOB(C_6F_5)$_3$]$^-$ ligand in **4** requires comment. The OH group is contained in a cleft between the C21 and C31 C_6F_5 rings so that a weak bifurcated intramolecular

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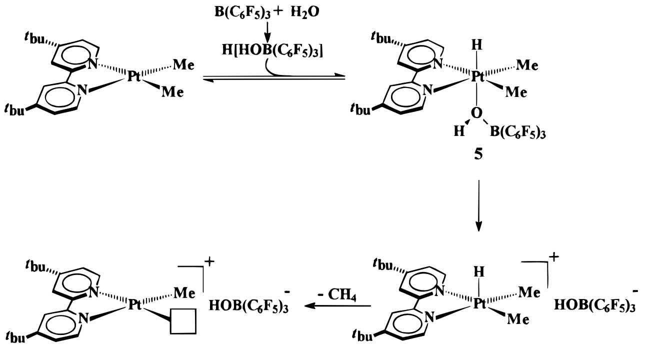
hydrogen bond is formed involving F5 and F6 as acceptors (Table 1d). Interestingly, the C−F5 and C−F6 bond lengths [1.366(4) and 1.362(3) Å] are very slightly longer than the other 13 C−F bond lengths [1.343(4)−1.355(3) Å]. Although the 11 atoms of each C_6F_5 ring barely deviate from planarity (rms $\Delta < 0.02$ Å) the displacements of the boron atom from the ring planes [respectively 0.113(3), 0.026(3), and 0.186(3) Å for the C21, C31, and C41 rings] are irregular and in two cases highly significant. The acuteness of the endocyclic C−C−C angles subtended by the atoms C21, C31, and C41 [113.0(3)−113.5(3)°] is compensated by an increase to 123.9(3)−124.5(3)° of the adjacent angles at carbon atoms *ortho* to boron. These features have been noted previously in the free $[HOB(C_6F_5)_3]^-$ anion[8] and may be ascribed to the difference in the electronegativities of B and F.[15]

The $[HOB(C_6F_5)_3]^-$ ligand in complex **4** is only weakly coordinated to platinum as treatment of **4** with CO, C_2H_4, and PPh_3 gives the complexes **1b**, **2b**, and **3b**, respectively (Scheme 2). Similar complexes of the type $[PtMeX(bu_2bpy)]$ ($X = O_3SCF_3$, O_2CCF_3) do not react with C_2H_4, illustrating that the $[HOB(C_6F_5)_3]^-$ ligand is an even poorer ligand than triflate or trifluoroacetate for platinum.[4]

In the synthesis of complexes **1a**, **2a**, and **3a**, $B(C_6F_5)_3$ acts as a powerful Lewis acid and directly attacks a Pt−Me bond in $[PtMe_2(bu_2bpy)]$ to form $[PtMe(Bu_2bpy)]^+$-$[MeB(C_6F_5)_3]^-$. However, in the presence of water a different mechanism must be followed because the corresponding $[PtMe(bu_2bpy)]^+[HOB(C_6F_5)_3]^-$ complex is preferentially formed. Although $B(C_6F_5)_3$ has often been described as a "water-tolerant Lewis acid",[19] it has been shown that, in the presence of H_2O, $B(C_6F_5)_3$ forms the hydrate $[H_2OB(C_6F_5)_3]\cdot 2H_2O$ with one molecule of H_2O directly coordinated to boron.[16] In the presence of a suitable base, Nu, this hydrate can be deprotonated to form the acid $[HNu]^+[HOB(C_6F_5)_3]^-$.[7,16] It has been shown that the highly nucleophilic complex $[PtMe_2(bu_2bpy)]$ reacts rapidly with a variety of protic acids, resulting in protonation of the Pt−Me bond to initially form CH_4 and $[PtMe(bu_2bpy)]^+$.[20] Thus, in the synthesis of complexes **1b**, **2b**, and **3b**, $[PtMe_2(bu_2bpy)]$ most probably acts as Nu and deprotonates $H_2OB(C_6F_5)_3$ to form CH_4 and $[PtMe(bu_2bpy)]^+[HOB(C_6F_5)_3]^-$. This complex can either react with L to form $[PtMeL(bu_2bpy)][HOB(C_6F_5)_3]$ {L = CO (**1b**), C_2H_4 (**2b**), PPh_3 (**3b**)} or, in the absence of L, form the hydroxytris(pentafluorophenyl)borate complex (**4**) (Scheme 2). In the reaction with D_2O in place of H_2O, the organic products contained CH_3D but no CH_2D_2, indicating that exchange between PtH and $PtCH_3$ protons does not occur to a significant extent in this reaction.[21]

It has been well established that the protonation of the Pt−C bond follows an oxidative addition/reductive elimination mechanism proceeding through an alkyl(hydrido)platinum(IV) intermediate.[20,21] The most definitive evidence for the proposed protonation mechanism for the production of complexes **1b**, **2b**, **3b**, and **4** would be the detection of the methyl(hydrido)platinum(IV) intermediate **5** (Scheme 3). In an attempt to detect this intermediate, the reaction of $B(C_6F_5)_3$ and water with $[PtMe_2(bu_2bpy)]$ in CD_2Cl_2 was monitored by low-temperature ^1H NMR spectroscopy (−90 °C). A resonance was detected at $\delta = -18.5$, suggestive of a (hydrido)platinum species.[20,21] Unfortunately, the stability of this hydrido species was poor and at any given time the concentration was not high enough to discern the ^{195}Pt satellite signals.[22] Since the order of stability toward CH_4 reductive elimination from the methyl(hydrido)platinum(IV) complexes $[PtX(H)Me_2(bu_2bpy)]$ ($X = Cl, Br, I, O_2CCF_3, SO_3CF_3$) follows the order of the Pt−X bond strength, i.e. Cl > Br > I > O_2CCF_3, SO_3CF_3, it is not unexpected that complex **5**, containing the weakly bound $[HOB(C_6F_5)_3]^-$ ion, would be highly unstable.[20] Nevertheless, this low-frequency resonance in the ^1H NMR spectrum is highly suggestive of a transient (hydrido)platinum intermediate and, thus, provides further evidence for the protonation mechanism proposed in Scheme 3.

Scheme 3



It is has been suggested that the reaction of H_2O with $[PtMe_2(N-N)]$ (N−N = 2,2′-bipyridine, 1,10-phenanthroline) proceeds through the hydroxy(hydrido)platinum(IV) intermediate $[PtH(OH)Me_2(N-N)]$[23] (Scheme 4). It is thus conceivable that complex **5** is formed by an initial reaction of H_2O with $[PtMe_2(bu_2bpy)]$, forming $[PtH(OH)Me_2(bu_2bpy)]$, which then reacts with $B(C_6F_5)_3$ to give complex **5**. However, the reaction of H_2O with $[PtMe_2(N-N)]$ is slow, taking several hours to reach completion,[23] whereas the reaction of Scheme 2 is very rapid, so this mechanism can immediately be eliminated. Since $H[HOB(C_6F_5)_3]$ is a strong acid, it is expected to react with $[PtMe_2(bu_2bpy)]$ much more rapidly than water itself would.

Conclusions

In addition to the well-established methyl-ligand abstraction by $B(C_6F_5)_3$ to form $[M]^+[MeB(C_6F_5)_3]^-$, we have shown that, in the presence of water, $B(C_6F_5)_3$ protonates a Pt−Me bond of $[PtMe_2(bu_2bpy)]$ to form $[PtMe(bu_2bpy)]^+[HOB(C_6F_5)_3]^-$. In the presence of the

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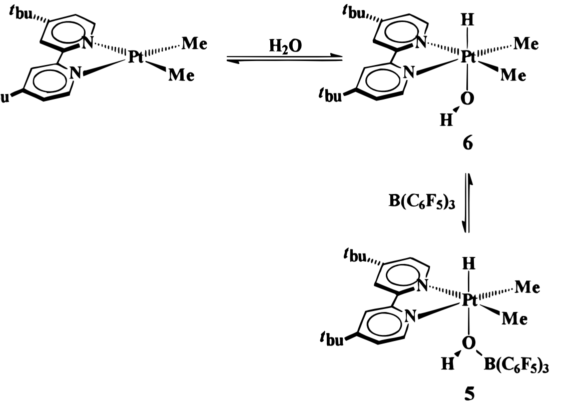
[20] Hill, G. S.; Rendina, L. M.; Puddephatt, R. J. *Organometallics* **1995**, *14*, 4966.

[21] (a) Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1995**, *117*, 9371; **1996**, *118*, 5961. (b) De Felice, V.; De Renzi, A.; Panunzi, A.; Tesauro, D. *J. Organomet. Chem.* **1995**, *488*, C13.

[22] Monitoring similar reactions by low-temperature ^1H NMR (−90 °C) with either CH_3OH or C_6H_5OH in place of H_2O resulted in no observable hydride resonances.

[23] (a) Canty, A. J.; Fritsche, S. D.; Jin, H.; Honeyman, R. T.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1996**, *510*, 281. (b) Canty, A. J.; Fritsche, S. D.; Jin, H.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1995**, *490*, C18. (c) Canty, A. J.; Honeyman, R. T.; Roberts, A. S.; Traill, P. R.; Colton, R.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1994**, *471*, C8. (d) Appleton, T. G.; Hall, J. R.; Neale, D. W.; Williams, M. A. *J. Organomet. Chem.* **1984**, *276*, C73. (e) Monaghan, P. K.; Puddephatt, R. J. *Organometallics* **1984**, *3*, 444.

Scheme 4



ligand L (L = CO, C_2H_4, PPh_3) the corresponding cationic complex, $[PtMeL(bu_2bpy)][HOB(C_6F_5)_3]$, is formed. However, in the absence of L, the $[HOB(C_6F_5)_3]^-$ anion coordinates to platinum to form the first published example of a hydroxytris(pentafluorophenyl)borate complex (**4**), which has been fully characterized by NMR spectroscopy and X-ray crystallography. This procedure provides an additional route to the production of late transition-metal cations by the powerful Lewis acid $B(C_6F_5)_3$.

Experimental Section

General Procedures. All reactions were performed under a N_2 atmosphere using standard Schlenk techniques, unless otherwise stated. All solvents were freshly distilled, dried, and degassed prior to use. NMR spectra were recorded using a Varian Gemini spectrometer (^1H at 300.10 MHz, ^{11}B at 64.17 MHz, ^{19}F at 282.32 MHz, ^{31}P at 121.44 MHz, and ^{195}Pt at 42.99 MHz). Chemical shifts are reported in ppm with respect to TMS (^1H), $BF_3{\cdot}Et_2O$ (^{11}B), $CFCl_3$ (^{19}F), H_3PO_4/D_2O (^{31}P), or $K_2[PtCl_4]/D_2O$ (^{195}Pt). The ^1H, ^{11}B, ^{19}F, ^{31}P, and ^{195}Pt NMR spectra are referenced to the residual protons of the deuterated solvents or to $BF_3{\cdot}Et_2O$, $CFCl_3$, H_3PO_4/D_2O, or $K_2[PtCl_4]/D_2O$ contained in a coaxial insert, respectively. IR spectra (Nujol mull) were recorded in the range 4000−400 cm^{-1} using a Perkin-Elmer 2000 FT-IR instrument. Elemental analyses were determined by Guelph Chemical Laboratories, Guelph, Canada.

$[PtMe_2(bu_2bpy)]$,[24] $[PtMe(CO)(bu_2bpy)][MeB(C_6F_5)_3]$,[4] and $[Pt(Me)(C_2H_4)(bu_2bpy)][MeB(C_6F_5)_3]$[4] were prepared by the literature methods. $B(C_6F_5)_3$ was obtained commercially (Strem).

Preparation of Complexes. 4,4′-Di-*tert*-butyl-2,2′-bipyridine{hydroxytris(pentafluorophenyl)borato}-methylplatinum(II), [Pt{H*O*B(C₆F₅)₃}Me(bu₂bpy)] (4). *All glassware must be flame-dried under vacuum prior to use.* To a 100 mL Schlenk tube charged with $[PtMe_2(bu_2bpy)]$ (10.0 mg, 0.020 mmol) and $B(C_6F_5)_3$ (10.4 mg, 0.020 mmol) was added Et_2O (5.0 mL) and distilled H_2O (0.4 μL, 0.02 mmol) immediately producing an orange to yellow color change. Removal of the solvent *in vacuo* and recrystallization from CH_2Cl_2/n-pentane gave a bright yellow microcrystalline product. Yield: 18.4 mg (92%). ^1H NMR (CD_2Cl_2): $\delta = 8.64$ [d, 1H, $^3J(H^6H^5) = 6.3$ Hz, $^3J(PtH) =$ *ca.* 60 Hz, H^6], 8.50 [d, 1H, $^3J(H^{6'}H^{5'}) = 5.6$ Hz, $H^{6'}$], 7.91 [d, 1H, $^4J(H^{3'}H^{5'}) = 1.9$ Hz, $H^{3'}$], 7.84 [d, 1H, $^4J(H^3H^5) = 2.2$ Hz, H^3], 7.58 [dd, 1H, $^4J(H^{5'}H^{3'}) = 1.9$ Hz, $^3J(H^{5'}H^{6'}) = 5.7$ Hz, $H^{5'}$], 7.35 [dd, 1H, $^4J(H^5H^3) = 2.2$ Hz, $^3J(H^5H^6) = 6.3$, H^5], 3.21 [br s, 1H, Pt−O(*H*)B], 1.41 (s, 9H, *tert*-bu), 1.39 (s, 9H, *tert*-bu), 0.81 [s, 3H, $^2J(Pt{-}H) = 78.9$ Hz, Pt−Me]. ^{11}B NMR (CD_2Cl_2): $\delta = 0.1$ (br s). ^{19}F NMR (CD_2Cl_2, 25 °C): $\delta = -124.5$ [br s, 6F, *o*-F], −160.8 [m, 3F, *p*-F], −165.8 [m, 6F, *m*-F]. ^{19}F NMR (CD_2Cl_2, −90 °C): $\delta = -132$ (br m, 3F, *o*-F), −133 (s, 1F, *o*-F), −139 (s, 1F, *o*-F), −143 (s, 1F, *o*-F), −159 (s, 1F, *p*-F), −160 (br m, 2F, *p*-F), −164 (br m, 3F, *m*-F), −165 (br m, 3F, *m*-F). ^{195}Pt NMR (CD_2Cl_2): $\delta = -1330$ [br s ($\Delta\nu^{1/2} =$ *ca.* 400 Hz)]. IR (Nujol, cm^{-1}): 3640 [s, ν(OH)]. Anal. Calcd for $C_{37}H_{28}BF_{15}N_2OPt$: C, 44.0; H, 3.1; N, 2.7. Found: C, 44.1; H, 2.8; N, 2.8.

Alternate Method for the Preparation of 4. To a suspension of $[PtMe_2(bu_2bpy)]$ (0.100 g, 0.203 mmol) in Et_2O (5.0 mL) at −78 °C was added a solution of $B(C_6F_5)_3$ (0.105 g, 0.203 mmol) in Et_2O (2.0 mL). The solution was stirred at −78 °C until the color had completely changed from orange to bright-yellow (*ca.* 2.0 h). The mixture was then allowed to warm to room temperature, and the solvent was removed *in vacuo* to give a yellow product. The product could be recrystallized from CH_2Cl_2/n-pentane to afford a yellow microcrystalline solid. Yield: 0.189 g (93%).

(4,4′-Di-*tert*-butyl-2,2′-bipyridine)methyl(triphenylphosphine)platinum(II) Methyltris(pentafluorophenyl)-borate, [PtMePPh₃(bu₂bpy)][MeB(C₆F₅)₃] (3a). *All glassware must be flame-dried under vacuum prior to use.* To a 50 mL Schlenk tube charged with $PtMe_2(bu_2bpy)]$ (0.20 g, 0.405 mmol), $B(C_6F_5)_3$ (0.208 g, 0.405 mmol), and PPh_3 (0.106 g, 0.405 mmol) was added Et_2O (10.0 mL). This bright orange mixture was stirred at room temperature for *ca.* 24 h giving a pale orange solution. Removal of the solvent *in vacuo* gave a pale orange powder. Yield: 0.510 g (99%). ^1H NMR (CD_2Cl_2): $\delta = 8.89$ [d, 1H, $^3J(H^6H^5) = 6.4$ Hz, $^3J(PtH) =$ *ca.* 35 Hz, H^6], 8.88 [d, 1H, $^3J(H^{6'}H^{5'}) = 6.2$ Hz, $^3J(PtH) =$ *ca.* 35 Hz, $H^{6'}$], 8.20 (br s, 1H, H^3), 8.11 [d, 1H, $^4J(H^{3'}H^{5'}) = 2.2$ Hz, $H^{3'}$], 7.78 [m, 6H, PPh_3)], 7.55 [dd, 1H, $^4J(H^5H^3) = 1.9$ Hz, $^3J(H^5H^6) = 6.4$ Hz, H^5], 7.50 (m, 9H, PPh_3), 7.00 [dd, 1H, $^4J(H^{5'}H^{3'}) = 2.2$ Hz, $^3J(H^{5'}H^{6'}) = 6.1$, $H^{5'}$], 1.49 [s, 9H, *tert*-bu), 1.32 (s, 9H, *tert*-bu), 0.71 [s, 3H, $^2J(PtH) = 72.0$ Hz, $^3J(PtP) = 3.7$ Hz, Pt-Me]. ^{11}B NMR (CD_2Cl_2): $\delta = -15.1$ (br s). ^{31}P NMR (CD_2Cl_2): $\delta = 20.0$ [s, $^1J(PtP) = 4343$ Hz]. Anal. Calcd for $C_{56}H_{45}BF_{15}N_2PPt$: C, 53.0; H, 3.6; N, 2.2 Found: C, 52.7; H, 3.5; N, 2.8.

Synthesis of Complexes 1b, 2b, and 3b. The addition of 1 equiv of H_2O during the initial stages of the preparation of complexes **1a**, **2a**, and **3a** afforded exclusively complexes **1b**, **2b**, and **3b**, respectively. The ^1H NMR spectra of the cationic platinum complexes are identical to those of the analogous $[MeB(C_6F_5)_3]^-$ complexes (**1a**, **2a**, and **3a**, respectively). ^{11}B NMR (CD_2Cl_2): $\delta = -15.1$. IR (Nujol, cm^{-1}): 3684 [s, ν(OH)].

Crystal structure analysis of 4: $C_{37}H_{28}BF_{15}N_2OPt$, fw = 1007.51, triclinic, space group $P\bar{1}$, $a = 10.7613(7)$ Å, $b = 12.2174(11)$ Å, $c = 15.9389(7)$ Å, $\alpha = 110.855(5)°$, $\beta = 96.347(4)°$, $\gamma = 98.985(6)°$, $V = 1902.7(2)$ Å^3 [from setting angles of 25 reflections with $20.7 \le \theta(\text{Mo K}\alpha) \le 22.3°$], $Z = 2$, $D_{\text{calc}} = 1.759$ Mg/m^3, $\mu = 3.794$ mm^{-1}, $F(000) = 980$.

The intensities of 12 786 reflections with $2.3 \le \theta(\text{Mo K}\alpha) \le 30°$ and $-15 \le h \le 15$, $-17 \le k \le 2$, and $-21 \le l \le 22$ were measured at 20 °C from $\omega/2\theta$ scans on an Enraf-Nonius CAD4 diffractometer with Mo Kα X-rays, $\lambda = 0.710\ 73$ Å, using a yellow, needle-shaped crystal of dimensions 0.66 × 0.36 × 0.21 mm. The mean intensity of the three standard reflections decreased by 9.4% during the experiment. Correction for this decomposition and for absorption[25] (analytical method,[26] transmission factors 0.32−0.53) and subsequent merging gave 11 037 independent reflections ($R_{\text{int}} = 0.015$). Refinement of F^2 on 536 parameters using 11 036 observations converged ($\Delta/\sigma < 0.001$) at $R_1 = 0.025$, w$R_2 = 0.059$ for 9203 reflections with $I > 2\sigma(I)$ and $R_1 = 0.040$, w$R_2 = 0.065$ for all 11 037 data with

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(25) Computer programs used for data processing were as follows. (a) GX: Mallinson, P. R.; Muir, K. W. *J. Appl. Crystallogr.* **1985**, *18*, 53. (b) PLATON: Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, 31.

(26) de Meulenaer, J.; Tompa, H. *Acta Crystallogr.* **1965**, *19*, 1014.

$|\Delta\rho| < 0.96$ e·Å^{-3} and $w = 1/[\sigma^2(F_o^2) + (0.0342P)^2 + 0.72P]$, where $P = (F_o^2 + 2F_c^2)/3$.[27]

In the final calculations the positional and anisotropic displacement parameters of 57 non-hydrogen atoms ($C_{37}BF_{15}N_2OPt$), a scale factor, an extinction parameter, and orientation parameters for seven methyl groups were refined (Supporting Information). The C12−C14 methyl carbon atoms were found to be disordered with site occupancy, α, of 0.794(5). The alternative sites C12*, C13*, and C14* were assigned occupancies 1 − α and U^{ij} parameters equal respectively to those of C13, C12, and C14; only their positional parameters were refined. Hydrogen atoms attached to C12*−C14* were not included in the calculations. Despite the disorder of the methyl groups, the hydrogen atom bonded to O1 was located in a difference map. Its positional and isotropic thermal parameters were refined freely. Other hydrogen atoms rode on their parent carbon atoms with C−H and $U(H)_{iso}$ set at SHELXL default values.[27] Atomic scattering factors and dispersion corrections were taken from ref 28.

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Supporting Information Available: For **4**, tables of atomic parameters and a complete geometry listing (9 pages). Ordering information is given on any current masthead page. X-ray data have also been deposited with the Cambridge Crystallographic Data Centre.

OM960834J

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