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Cationic platinum(II) complexes: platinum–alkyl bond cleavage by a powerful Lewis acid†

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Treatment of [PtCl(Me)(dbbipy)] or [$PtCl_2$(dbbipy)] (dbbipy = 4,4′-di-*tert*-butyl-2,2′-bipyridine) with AgX (X = SO_3CF_3 or O_2CCF_3) gave the complexes [PtMe(SO_3CF_3)(dbbipy)] **1**, [Pt$(SO_3CF_3)_2$(dbbipy)] **2** and [Pt$(O_2CCF_3)_2$(dbbipy)] **5**. The complexes [PtCl(SO_3CF_3)(dbbipy)] **3** and [PtMe(O_2CCF_3)(dbbipy)] **4** were prepared by the addition of HX to [$PtCl_2$(dbbipy)] or [$PtMe_2$(dbbipy)], respectively. Complex **1** reacted with CO to give the cationic carbonyl complex [PtMe(CO)(dbbipy)][SO_3CF_3] **6a**, which reacted with NEt_2H to give an equilibrium with the corresponding carbamoyl complex [Pt($CONEt_2$)Me(dbbipy)] **7**. In the first example of alkyl-ligand abstraction from a late-transition-metal complex by the powerful Lewis acid $B(C_6F_5)_3$, the complexes [PtMeL(dbbipy)][$BMe(C_6F_5)_3$] (L = CO **6b** or C_2H_4 **8**) were readily prepared from [$PtMe_2$(dbbipy)] and $B(C_6F_5)_3$ in the presence of L.

There is increasing interest in the synthesis and properties of electrophilic transition-metal complexes, since they show promise for catalytic activity, for example in the selective functionalization of alkanes by intermolecular activation of C–H or C–C bonds.[1,2] This article describes studies of cationic platinum(II) complexes containing a bipyridine ligand as stabilizing group and a study of their properties as electrophiles. It complements earlier studies which have shown that neutral organoplatinum(II) complexes of the type [$PtMe_2$(L–L)] (L–L is a diimine ligand such as 2,2′-bipyridine) are electron-rich and react as very active metal-based nucleophiles.[3]

The high reactivity of the complexes [$PtMe_2$(L–L)] has been attributed to the electron-releasing properties of the methyl groups and to the low steric requirements of the diimine ligands.[3] It was considered that these low steric requirements should also be a positive feature for electrophilic reactivity if the electronic properties at platinum could be changed from electron-rich to electron-poor. The obvious way to achieve this end is to synthesize cationic diimineplatinum(II) centres and this paper reports several ways in which such compounds can be prepared. The most original of these methods involves the use of $B(C_6F_5)_3$ as a reagent to abstract Me^- and hence to convert a MePt group into $[Pt]^+[BMe(C_6F_5)_3]^-$. This methodology was pioneered for creating vacant sites in early-transition-metal complexes, for example by reaction with [ZrL_2Me_2] (L = C_5H_5 or C_5Me_5) to give electrophilic cations which are very effective catalysts for the polymerization of alkenes,[4] but does not appear to have been applied to create electrophilic derivatives of late transition metals. The closest analogy of which we are aware is the formation of cationic palladium(II) complexes by treatment of [MMe_2(L–L)] (M = Ni or Pd, L–L = diimine) with the oxonium acid $[H(OEt_2)_2]^+[B\{C_6H_3(CF_3)_2\text{-}3,5\}_4]^-$; these cations are active catalysts for α-olefin and ethylene polymerization.[5]

There are already indications that electrophilic derivatives of late transition metals have useful properties.[6,7] For example, the intermolecular activation of a C–H bond of benzene has been achieved by the electrophilic complex *trans*-[Pt(CH_2Bu^t)(SO_3CF_3)$(PMe_3)_2$].[7a]

Results and Discussion

Synthesis of triflate and trifluoroacetate complexes 1–5

Treatment of [PtClMe(dbbipy)] (dbbipy = 4,4′-di-*tert*-butyl-2,2′-bipyridine) with $AgSO_3CF_3$ gave [PtMe(SO_3CF_3)(dbbipy)] **1** in very high yield (Scheme 1). Similarly, the complexes [PtX_2(dbbipy)] (X = SO_3CF_3 **2** or O_2CCF_3 **5**) were prepared by the reaction of [$PtCl_2$(dbbipy)] with 2 equivalents of AgX (Scheme 2). The complexes [PtCl(SO_3CF_3)(dbbipy)] **3** and [PtMe(O_2CCF_3)(dbbipy)] **4** were prepared by the addition of HX to [$PtCl_2$(dbbipy)] or [$PtMe_2$(dbbipy)], respectively (Scheme 2). In both cases, only one of the ligands Z (Z = Cl or Me) is replaced by the weakly co-ordinating anion X, even when neat acid is employed in the preparation of the complexes. The attempted preparation of **1** by this method was unsuccessful since reaction of [$PtMe_2$(dbbipy)] with triflic acid (CF_3SO_3H) gave a complex mixture of products.

Spectroscopic properties of complexes 1–5

The *tert*-butyl substituents on the bipy ligand greatly assist in the solubility of the novel complexes in common organic solvents, and are effective probes for ^1H NMR spectroscopic studies. Complexes **1** and **4** give Pt–Me signals with coupling constants $^2J_{PtH}$ = 70 and 78 Hz, respectively. The magnitudes of $^2J_{PtH}$ are significantly lower than for the electron-rich platinum(II) complex [$PtMe_2$(dbbipy)] ($^2J_{PtH}$ = 86.0 Hz),[7] indicating a strong *cis* influence of the O-donor ligand on the magnitude of the coupling.[3,8,9]

The IR data for complexes **1**–**3** clearly indicate the presence of the triflate group (ν 1350–1020 cm^{-1}), but do not define if it is co-ordinated.[6a] However, co-ordination of triflate to the metal centre in the solid state is deduced from the microanalytical data (no solvent present).

Reactivity of complexes 1–5

All the complexes prepared in this work are oxygen-stable but moisture-sensitive at room temperature. The solid products can be stored at room temperature without decomposition, but several decompose rapidly in organic solvents. For example, complexes **2** and **3** decompose rapidly at room temperature in acetone and in chlorinated solvents, respectively, while **1** decomposes within a few minutes at room temperature in all common organic solvents, except diethyl ether (in which it is sparingly soluble). For this reason, the reactions must be carried out under carefully controlled conditions. For example, during its preparation in benzene solution, all manipulations of

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† *Non-SI units employed:* atm = 101 325 Pa, mmHg ≈ 133 Pa.

1 must be performed rapidly at a temperature close to the freezing point of the solvent (*ca.* 5 °C).

The complexes **1**–**5** were surprisingly inert as electrophilic reagents. Consider first the reactivity of **1**. As described below, it readily reacted with CO; also with ethylene, benzene and various silanes (*e.g.* $SiMe_3Cl$, $SiEt_3H$ and $SiPh_2H_2$), but the products were insufficiently stable to be characterized. The reactivity of complexes **2**–**5** paralleled that of **1**, except no reaction occurred with ethylene, benzene or CO (1 atm).

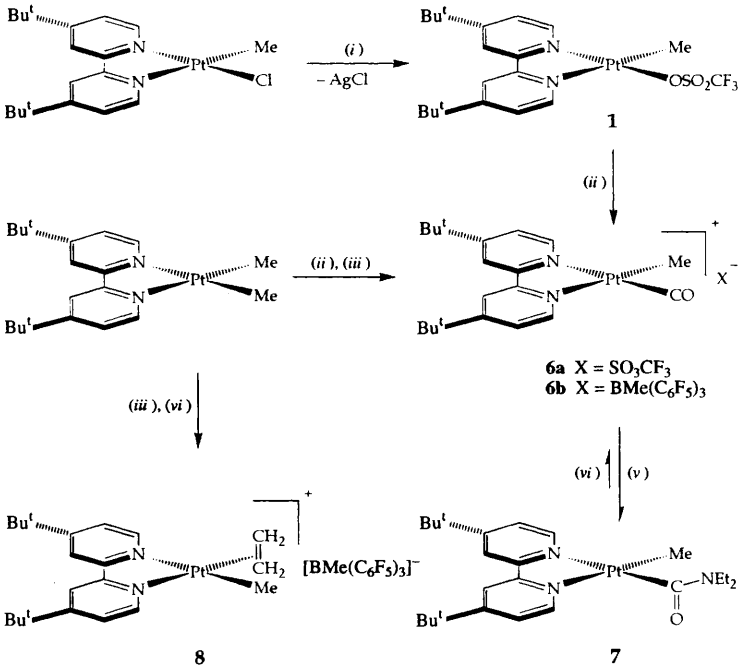
Synthesis, spectroscopic data, and reactivity of complexes 6 and 7

Treatment of complex **1** with CO (1 atm) in diethyl ether solution gave the cation **6a** in good yield (Scheme 1). The ^1H NMR contained a Pt–Me resonance with $^2J_{PtH}$ = 68.1 Hz similar to that of the parent complex **1** (70.0 Hz). The $^{13}C\text{-}\{^1H\}$ NMR spectrum of ^{13}CO-labelled **6** shows the expected CO resonance at δ 164.3 with $^1J_{PtC}$ = 1935.0 Hz. The Pt–Me signal appears at δ −12.1 with $^1J_{PtC}$ = 536.0 Hz. The IR spectrum shows the distinctive ν(CO) band at 2109 cm^{-1}.[10]

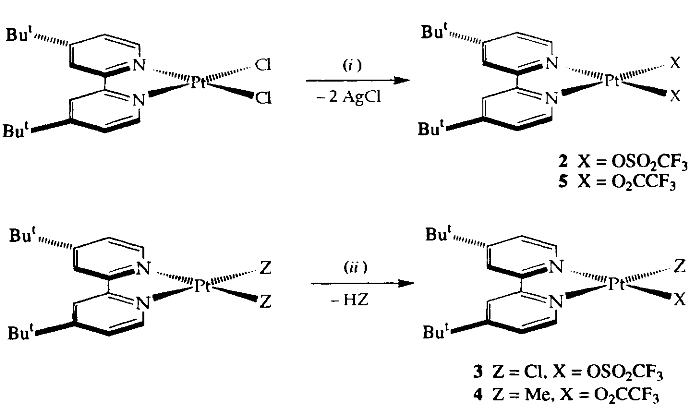
Treatment of complex **6a** with a slight excess of NEt_2H in $(CD_3)_2CO$ solution immediately resulted in the formation of the carbamoyl (carboxamido) complex **7** due to nucleophilic attack of the amine on the electrophilic carbon atom of the carbonyl ligand (Scheme 1).[11] The reaction is an equilibrium and attempted isolation of **7** always gave partial reversion to **6a**. The equilibrium is favourable, as expected on the basis of related studies,[11b,12] and so the product **7** can be formed essentially quantitatively in solution. The ^1H NMR spectrum displays some interesting features, and is presented in Fig. 1. The quartet at δ 2.96 is due to the methylene protons of both free NEt_2H and $NEt_2H_2^+$, with rapid proton exchange between the two species at room temperature, thus rendering them equivalent on the NMR time-scale. The triplet at δ 1.15 is due to the free (and protonated) NEt_2H methyl groups.

The triplets at δ 1.09 and 1.02 are assigned to the two inequivalent methyl groups of the diethylamino moiety of **7**. Two sets of signals are observed due to restricted rotation about the C–N partial double bond.[11b] The ABX_3 multiplet at δ 4.03 is due to the two diastereotopic protons of one of the methylene groups in the diethylamino moiety of **7**. The other methylene group resonates as a quartet at δ 3.45, and its apparent simplicity is due to coincidental overlap of the two diastereotopic proton signals. In the $^{13}C\text{-}\{^1H\}$ NMR spectrum the Pt–C(O) resonance is located at δ 186.0 ($^1J_{PtC}$ = 1430.0 Hz).[13]

Attempts at preparing carbamoyl complexes other than **7** by reaction of **6a** with the amines diisopropylamine, isopropylamine, and *tert*-butylamine were unsuccessful owing to immediate decomposition of the products. In contrast, the weaker base aniline did not react with **6a**.[11b]



Scheme 1 (*i*) $AgSO_3CF_3$; (*ii*) CO; (*iii*) $B(C_6F_5)_3$; (*iv*) C_2H_4; (*v*) 2 NEt_2H; (*vi*) $[NEt_2H_2]X$



Scheme 2 (*i*) 2AgX; (*ii*) HX

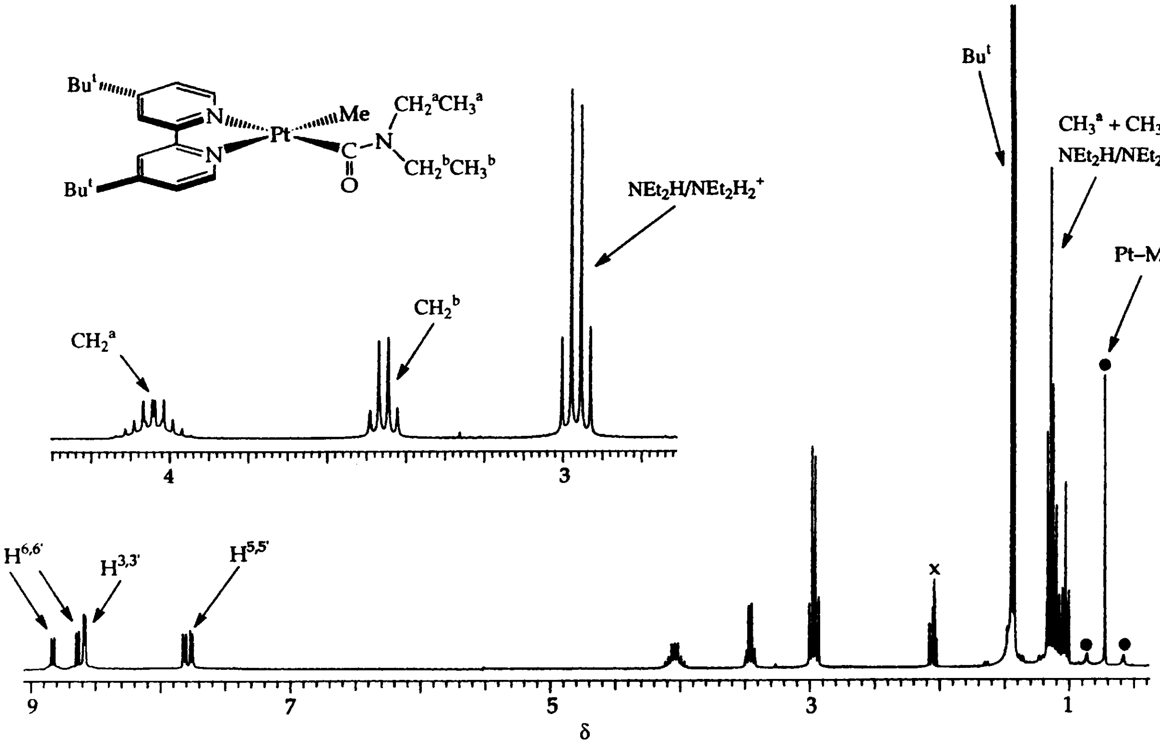


Fig. 1 The ^1H NMR spectrum of complex 7 in $(CD_3)_2CO$. The x denotes the residual protons of the solvent

Methyl group abstraction by $B(C_6F_5)_3$

Since the triflate and trifluoroacetate complexes **1**–**5** showed limited reactivity as electrophiles, attempts were made to generate more reactive platinum(II) cations. It was found that **6b** can be prepared by methyl-ligand abstraction from $[PtMe_2(dbbipy)]$ using the powerful Lewis acid $B(C_6F_5)_3$ in the presence of CO (1 atm). This reaction was rapid and gave the product in high yield, indicating that it should be the preferred method for generating cationic platinum(II) complexes.*

Complex **8** was prepared in a similar manner to **6b**, using C_2H_4 in place of CO. It is very stable with respect to loss of ethylene, even under high vacuum. It is noteworthy that the synthesis of $[PtMe(C_2H_4)(dbbipy)]^+$ using this method is successful whereas the attempted synthesis from **1** and ethylene was not, thus clearly indicating the superiority of the $B(C_6F_5)_3$ method of generating platinum(II) cations. The ^1H NMR spectrum of **8** displays many similar features to those of **6**. In addition a broad signal at δ 4.25 is assigned to the η^2-co-ordinated ethylene. This signal was unchanged in the NMR spectrum obtained at −78 °C. The observation of only one resonance for the ethylene ligand could be attributed either to rapid rotation or to its rapid, reversible dissociation, but, since no ^{195}Pt–^1H coupling was resolved even at −78 °C, the latter interpretation appears more probable. It is presumably this lability of the co-ordinated ethylene which precludes formation of $[PtMe(C_2H_4)(dbbipy)]^+$ in the presence of even weakly co-ordinating anions such as triflate.

The unusually intense colours associated with complexes **6b** and **8** are in marked contrast to those observed for the other complexes prepared in this work. Note especially that **6a** is not intensely coloured. Since the structures of the cations of **6a** and **6b** are identical the difference in colour must be attributed to the anion. We believe that the intense colours of **6b** and **8** are caused by π-stacking interactions between the dbbipy ligand and the pentafluorophenyl substituent(s) of the anion, leading to charge-transfer phenomena.[14] A solution of **6b** at high concentrations is deep red (λ_{max} = 484 nm) and, upon dilution, it changes to light yellow (λ_{max} = 418 nm). The latter transition is attributed to the Pt(5d)→π*(dbbipy) metal-to-ligand charge transfer, and is also observed for **6a**. The observation that the spectra are concentration dependent strongly supports the interpretation in terms of π-stacking interactions, since the cation–anion association would be expected to be diminished upon dilution of **6b**.

In conclusion, several cationic platinum(II) complexes and neutral platinum(II) complexes with weakly co-ordinating ligands have been prepared and characterized and their reactivity as electrophilic reagents studied. They exhibit only weak electrophilic properties, probably because the strong electron-donating nature of the dbbipy ligand limits the electrophilic character. The use of the strong Lewis acid $B(C_6F_5)_3$ to abstract an alkyl ligand from a late transition-metal complex has been established as the best method for generating reactive platinum(II) cations.

Experimental

All reactions were performed under a nitrogen atmosphere using standard Schlenk techniques. All solvents were freshly distilled, dried and degassed prior to use. The NMR spectra were recorded by means of a Varian Gemini (^1H at 300.10, ^{13}C at 75.45, ^{19}F at 282.32 MHz) spectrometer. Chemical shifts are reported in ppm with respect to $SiMe_4$ as reference (^1H and ^{13}C) or $CFCl_3$ (^{19}F). All ^1H, ^{13}C-{^1H}, and ^{19}F NMR spectra are referenced to the residual protons of the deuteriated solvents, the solvent peak, and $CFCl_3$ contained in a coaxial insert, respectively. The IR spectra (Nujol mull or CD_2Cl_2 solution) were recorded in the range 4000–400 cm^{-1} on a Perkin-Elmer 2000 FT-IR instrument. Elemental analyses were by Guelph Chemical Laboratories, Canada.

The compounds $[PtMe_2(dbbipy)]$,[8] $[PtCl_2(dbbipy)]$[9] and $[PtClMe(dbbipy)]$[9] were prepared by the literature methods; $B(C_6F_5)_3$ was obtained commercially (Strem).

Preparations

(4,4′-Di-*tert*-butyl-2,2′-bipyridine)methyl(trifluoromethanesulfonato)platinum(II), $[PtMe(SO_3CF_3)(dbbipy)]$ 1. All oper-

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* For this chemistry to be observed materials must be rigorously dried.

ations must be carried out at *ca.* 5 °C, as decomposition of the product in solution ensues after several minutes at room temperature. To a Schlenk tube (100 cm^3) charged with $AgSO_3CF_3$ (0.406 g, 1.58 mmol) was added a suspension of [PtCl(Me)(dbbipy)] (0.812 g, 1.58 mmol) in C_6H_6 (30 cm^3). The mixture was stirred at *ca.* 5 °C for 10 min, whereupon it was filtered over Celite filter-aid. Addition of C_6H_6 (20 cm^3) to the lemon-yellow filtrate, followed by addition of pentane (60 cm^3) gave a bright yellow precipitate. The solid was washed with pentane (3 × 50 cm^3), and the solvents were evaporated *in vacuo* to afford a bright yellow powder (0.973 g, 98%). Owing to the facile decomposition of the product in all common organic solvents (see above) its recrystallization was not possible and thus reproducible microanalyses could not be obtained. $\delta_H(C_6D_6)$ 9.52 [1 H, d, $^3J(H^{6'}H^{5'})$ 6.0, $H^{6'}$], 9.01 [1 H, d, $^3J(H^6H^5)$ 6.4, H^6], 7.82 [1 H, d, $^4J(H^{3'}H^{5'})$ 1.8, $H^{3'}$], 7.81 [1 H, d, $^4J(H^3H^5)$ 1.8, H^3], 7.63 [1 H, dd, $^3J(H^{5'}H^{6'})$ 6.0, $^4J(H^{5'}H^{3'})$ 1.8, $H^{5'}$], 7.35 [1 H, dd, $^3J(H^5H^6)$ 6.4, $^4J(H^5H^3)$ 1.8 Hz, H^5], 1.33 (3 H, s, Pt–Me), 1.13 (9 H, s, Bu^t) and 1.12 (9 H, s, Bu^t). $\delta_H(CD_2Cl_2)$ 9.04 [1 H,d,$^3J(H^{6'}H^{5'})$ 5.8, $H^{6'}$], 8.71 [1 H, d, $^3J(H^6H^5)$ 6.3, H^6], 8.02 [1 H, d, $^4J(H^{3'}H^{5'})$ 1.8, $H^{3'}$], 8.01 [1 H, d, $^4J(H^3H^5)$ 1.7, H^3], 7.71 [1 H, dd, $^3J(H^{5'}H^{6'})$ 5.8, $^4J(H^{5'}H^{3'})$ 1.8, $H^{5'}$], 7.54 [1 H, dd, $^3J(H^5H^6)$ 6.3, $^4J(H^5H^3)$ 1.7, H^5], 1.44 (9 H, s, Bu^t), 1.43 (9 H, s, Bu^t), and 0.90 [3 H, s, $^2J(PtH)$ 70.0 Hz, Pt–Me]. $\delta_F(CD_2Cl_2)$ −79.0 (s). $\tilde{\nu}_{max}/cm^{-1}$ (SO_3CF_3) 1260(br)s, 1159s and 1027s (Nujol).

(4,4′-Di-*tert*-butyl-2,2′-bipyridine)bis(trifluoromethanesulfonato)platinum(II), $[Pt(SO_3CF_3)_2(dbbipy)]$ 2. To a stirred solution of $[PtCl_2(dbbipy)]$ (0.500 g, 0.936 mmol) in CH_2Cl_2 (50 cm^3) was added $AgSO_3CF_3$ (0.478 g, 1.86 mmol). The mixture was stirred in the absence of light for 1 h at room temperature, and then filtered over Celite filter-aid to afford a pale yellow filtrate. The solvent was removed *in vacuo* to give a pale yellow solid, which could be recrystallized from CH_2Cl_2–pentane to afford pale yellow microcrystals (0.667 g, 94%) (Found: C, 31.4; H, 3.4; N, 3.8. $C_{20}H_{24}F_6N_2O_6PtS_2$ requires C, 31.5; H, 3.2; N, 3.7%). $\delta_H(CD_2Cl_2)$ 8.61 [2 H, d, $^3J(H^6H^5)$ 6.3, H^6], 7.94 [2 H, d, $^4J(H^3H^5)$ 2.0, H^3], 7.67 [2 H, dd, $^3J(H^5H^6)$ 6.3, $^4J(H^5H^3)$ 2.0 Hz, H^5] and 1.45 (18 H, Bu^t); δ_F −79.0 (s). $\tilde{\nu}_{max}/cm^{-1}$ (SO_3CF_3) 1345vs, 1235s, 1197s and 1033s (Nujol).

Chloro(4,4′-di-*tert*-butyl-2,2′-bipyridine)(trifluoromethanesulfonato)platinum(II), $[PtCl(SO_3CF_3)(dbbipy]$ 3. $[PtCl_2(dbbipy)]$ (1.00 g, 1.87 mmol) was added to anhydrous CF_3SO_3H (10.0 cm^3). Dry nitrogen gas was passed over the dark yellow solution as it was heated to 100 °C for 2.5 h. The solution was concentrated by vacuum distillation (53 °C, *ca.* 10 mmHg) to *ca.* one-third volume, and then cooled in an ice-bath. Diethyl ether (80 cm^3) was added dropwise to give a cloudy solution, and the mixture was stored for 16 h at 2 °C to afford a bright yellow precipitate. The product was filtered off, washed with diethyl ether (3 × 50 cm^3), and dried *in vacuo* (1.11 g, 92%). Reproducible microanalyses could not be obtained for the product owing to its extremely hygroscopic nature. $\delta_H[(CD_3)_2CO]$ 9.15 [1 H, d, $^3J(PtH^{6'})$ *ca.* 41 (br), $^3J(H^{6'}H^{5'})$ 6.3, $H^{6'}$], 8.70 [1 H, d, $^4J(H^{3'}H^{5'})$ 1.9, $H^{3'}$], 8.66 [1 H, d, $^4J(H^3H^5)$ 2.1, H^3, 8.40 [1 H, d, $^3J(H^6H^5)$ 6.1, H^6], 7.87 [1 H, dd, $^3J(H^{5'}H^{6'})$ 6.3, $^4J(H^{5'}H^{3'})$ 1.9, $H^{5'}$], 7.85 [1 H, dd, $^3J(H^5H^6)$ 6.1, $^4J(H^5H^3)$ 2.1 Hz, H^5], 1.46 (9 H, s, Bu^t) and 1.45 (9 H, s, Bu^t); $\delta_F[(CD_3)_2CO]$ −79.0 (s). $\tilde{\nu}_{max}/cm^{-1}$ (SO_3CF_3) 1250 (vbr) s, 1224s, 1161(br) s and 1026s (Nujol).

(4,4′-Di-*tert*-butyl-2,2′-bipyridine)methyl(trifluoroacetato)-platinum(II), $[PtMe(O_2CCF_3)(dbbipy)]$ 4. To a stirred suspension of $[PtMe_2(dbbipy)]$ (0.231 g, 0.467 mmol) in diethyl ether (50 cm^3) was added CF_3CO_2H (80 µl, 1.04 mmol) dropwise over a period of 2 min. The orange mixture was stirred for 2 h at room temperature to afford a yellow precipitate. The supernatant solution was decanted, and the solid was washed with diethyl ether (2 × 25 cm^3), and dried *in vacuo* at room temperature for several hours (0.249 g, 90%) (Found: C, 42.3; H, 4.5; N, 4.9. $C_{21}H_{27}F_3N_2O_2Pt$ requires C, 42.6; H, 4.6; N, 4.7%). $\delta_H[(CD_3)_2CO]$ 8.88 [1 H, d, $^3J(PtH^{6'})$ *ca.* 63 (br), $^3J(H^{6'}H^{5'})$ 6.2, $H^{6'}$], 8.57 [1 H, d, $^4J(H^3H^5)$ 1.95, H^3], 8.50 [1 H, d, $^4J(H^{3'}H^{5'})$ 2.2, $H^{3'}$], 8.47 [1 H, d, $^3J(H^6H^5)$ 5.8, H^6], 7.86 [1 H, dd, $^3J(H^5H^6)$ 5.8, $^4J(H^5H^3)$ 1.95 H^5], 7.65 [1 H, dd, $^3J(H^{5'}H^{6'})$ 6.2, $^4J(H^{5'}H^{3'})$ 2.2, $H^{5'}$], 1.44 (9 H, s, Bu^t), 1.43 (9 H, s, Bu^t) and 0.86 [s, 3 H, $^2J(PtH)$ 78.0 Hz, Pt–Me]; $\delta_F[(CD_3)_2CO]$ −74.0 (s).

(4,4′-Di-*tert*-butyl-2,2′-bipyridine)bis(trifluoroacetato) platinum(II), $[Pt(O_2CCF_3)_2(dbbipy)]$ 5. To a stirred solution of $[PtCl_2(dbbipy)]$ (0.413 g, 0.773 mmol) in CH_2Cl_2 (60 cm^3) was added AgO_2CCF_3 (0.340 g, 1.54 mmol). The flask was stirred in the absence of light for 1 h at room temperature, and the mixture was then filtered over Celite filter-aid to afford a yellow filtrate. The solvent was removed *in vacuo* to give a pale yellow solid (0.49 g, 92%) (Found: C, 38.2; H, 3.2; N, 3.8. $C_{22}H_{24}F_6N_2O_4Pt$ requires C, 38.3; H, 3.5; N, 4.1%). $\delta_H(CD_2Cl_2)$ 8.21 [2 H, d, $^3J(H^6H^5)$ 6.2, H^6], 7.99 [2 H, d, $^4J(H^3H^5)$ 2.1, H^3], 7.53 [2 H, dd, $^3J(H^5H^6)$ 6.2, $^4J(H^3H^5)$ 2.1 Hz, H^5] and 1.43 (18 H, s, Bu^t); $\delta_F(CD_2Cl_2)$ −75.0 (s).

Carbonyl(4,4′-di-*tert*-butyl-2,2′-bipyridine)methylplatinum(II) trifluoromethanesulfonate, $[PtMe(CO)(dbbipy)][SO_3CF_3]$ 6a. A suspension of complex **1** (0.222 g, 0.357 mmol) in diethyl ether (30 cm^3) was stirred under CO (1 atm) for 18 h at room temperature to give a milky white mixture. The solvent was removed *in vacuo*, and the off-white solid residue was dissolved in CH_2Cl_2 (20 cm^3). The cloudy solution was filtered through Celite filter-aid, and the pale yellow filtrate concentrated to *ca.* one-quarter volume. Addition of pentane (75 cm^3) gave a pale yellow solid. The colourless supernatant solution was removed by syringe, and the solid washed with pentane (2 × 30 cm^3). The pale yellow product was dried *in vacuo* for several hours at room temperature (0.167 g, 72%) (Found: C, 38.4; H, 4.0; N, 4.2. $C_{21}H_{27}F_3N_2O_4PtS$ requires C, 38.5; H, 4.15; N, 4.3%). $\delta_H[(CD_3)_2CO]$ 9.10 [1 H, d, $^3J(PtH^{6'})$ *ca.* 18, $^3J(H^{6'}H^{5'})$ 5.8, $H^{6'}$], 8.98 [1 H, d, $^3J(H^6H^5)$ 6.1, H^6], 8.88 [1 H, d, $^4J(H^{3'}H^{5'})$ 2.0, $H^{3'}$], 8.87 [1 H, d, $^4J(H^3H^5)$ 2.0, H^3], 8.09 [1 H, dd, $^3J(H^5H^6)$ 6.1, $^4J(H^5H^3)$ 2.0, H^5], 8.00 [1 H, dd, $^3J(H^{5'}H^{6'})$ 5.8, $^4J(H^{5'}H^{3'})$ 2.0, $H^{5'}$], 1.48 (9 H, s, Bu^t), 1.47 (9 H, s, Bu^t) and 1.28 [3 H, s, $^2J(PtH)$ 68.1, Pt–Me]; $\delta_C[(CD_3)_2CO]$ 164.3 [$^1J(PtC)$ 1935.0, Pt–CO] and −12.1 [$^1J(PtC)$ 536.0 Hz, Pt–Me]; $\delta_F[(CD_3)_2CO]$ −79.0 (s). $\tilde{\nu}_{max}/cm^{-1}$ (CO) 2109vs; (SO_3CF_3) 1286s, 1264s, 1154s and 1030s.

Carbonyl(4,4′-di-*tert*-butyl-2,2′-bipyridine)methylplatinum(II) methyltris(pentafluorophenyl)borate, $[PtMe(CO)(dbbipy)][BMe(C_6F_5)_3]$ 6b. To a CO-saturated solution of $[PtMe_2(dbbipy)]$ (0.100 g, 0.203 mmol) in CH_2Cl_2 (5 cm^3) at −78 °C was added a solution of $B(C_6F_5)_3$ (0.105 g, 0.203 mmol) in CH_2Cl_2 (8 cm^3). After warming the deep red solution to room temperature the solvent was removed *in vacuo* to afford a brown-red solid. Yield 0.21 g (99%) (Found: C, 45.0; H, 2.9; N, 2.7. $C_{39}H_{30}BF_{15}N_2OPt$ requires C, 45.3; H, 2.9; N, 2.7%). The ^1H NMR spectrum of complex **6b** is identical to that reported for **6a**, with an additional resonance at δ 1.45 (3 H, s) due to the Me group of the anion. $\delta_F(CD_2Cl_2)$ −136.1 [d, $^3J(FF)$ = 22.8], −163.9 [t, $^3J(FF)$ = 20.2 Hz] and −167.1 (m).

(Diethylcarbamoyl)(4,4′-di-*tert*-butyl-2,2′-bipyridine)methylplatinum(II), $[Pt(CONEt_2)Me(dbbipy)]$ 7. To a solution of complex **6a** (0.0208 g, 0.0317 mmol) in $(CD_3)_2CO$ (0.4 cm^3) was added NEt_2H (6.9 µl, 0.067 mmol), resulting in an immediate change from yellow to deep orange. The ^1H NMR spectrum was recorded immediately. Removal of the solvent *in vacuo*, or attempted precipitation of the product from solution by addition of pentane, resulted in the formation of a mixture of **6a** and **7**. $\delta_H[(CD_3]_2CO]$ 8.83 [1 H, d, $^3J(PtH)$ *ca.* 22.0, $^3J(H^{6'}H^{5'})$ 5.8, $H^{6'}$], 8.64 [1 H, d, $^3J(H^6H^5)$ 5.8, H^6], 8.60 [1 H, d, $^4J(H^{3'}H^{5'})$ 1.8, $H^{3'}$], 8.58 [1 H, d, $^4J(H^3H^5)$ 1.8, H^3] 7.81 [1 H, dd, $^4J(H^{5'}H^{3'})$ 1.8, $^3J(H^{5'}H^{6'})$ 5.8, $H^{5'}$], 7.76 [1 H, dd, $^4J(H^5H^3)$ 1.8, $^3J(H^5H^6)$ 5.8, H^5], 4.03 [2 H, m, $C(O)NCH_2{}^aCH_3{}^a$], 3.45 [2 H, q, $^3J(HH)$ 7.1, $C(O)NCH_2{}^bCH_3{}^b$], 2.96 [q, $^3J(HH)$ 7.2, $NEt_2H/NEt_2H_2{}^+$], 1.44 (9 H, s, Bu^t), 1.42 (9 H, s, Bu^t), 1.15 [t, $^3J(HH)$ 7.2, $NEt_2H/NEt_2H_2{}^+$] 1.09 [3 H, t, $^3J(HH)$ 7.1, $C(O)NCH_2{}^bCH_3{}^b$], 1.02 [3 H, t, $^3J(HH)$ 7.1, $C(O)NCH_2{}^aCH_3{}^a$] and 0.71 [3 H, t, $^2J(PtH)$ 87.0, Pt–Me]; $\delta_C(CD_2Cl_2)$ 186.0 [$^1J(PtC)$ 1430.0 Hz, Pt–C(O)] and −19.8 (Pt–Me). $\tilde{\nu}_{max}/cm^{-1}$ (C=O) 1546m (CD_2Cl_2).

(4,4′-Di-*tert*-butyl-2,2′-bipyridine)(ethylene)methylplatinum(II) methyltris(pentafluorophenyl)borate, $[PtMe(C_2H_4)(dbbipy)][BMe(C_6F_5)_3]$ 8. To a C_2H_4 saturated solution of $[PtMe_2(dbbipy)]$ (0.100 g, 0.203 mmol) in CH_2Cl_2 (5 cm^3) at −78 °C was added a solution of $B(C_6F_5)_3$ (0.105 g, 0.203 mmol) in CH_2Cl_2 (8 cm^3). After warming the bright red solution to room temperature the solvent was removed *in vacuo* to afford a bright red solid. Yield 0.21 g (99%) (Found: C, 46.3; H, 3.6; N, 2.4. $C_{40}H_{34}BF_{15}N_2Pt$ requires C, 46.5; H, 3.3; N, 2.7%). $\delta_H(CD_2Cl_2)$ 8.72 [1 H, d, $^3J(PtH^{6'})$ *ca.* 48, $^3J(H^{6'}H^{5'})$ 5.9, $H^{6'}$], 8.22 [1 H, d, $^4J(H^{3'}H^{5'})$ 2.0, $H^{3'}$], 8.15 [1 H, d, $^4J(H^3H^5)$ 2.0, H^3], 7.99 [1 H, d, $^3J(H^6H^5)$ 6.0, H^6], 7.80 [1 H, dd, $^3J(H^5H^6)$ 6.0, $^4J(H^5H^3)$ 2.0, H^5], 7.72 [1 H, dd, $^3J(H^{5'}H^{6'})$ 6.0, $^4J(H^{5'}H^{3'})$ 2.0, $H^{5'}$], 4.25 (4 H, br s, C_2H_4) 1.47 (9 H, s, Bu^t), 1.43 (3 H, s, MeB), 1.42 (9 H, s, Bu^t) and 0.74 [3 H, s, $^2J(PtH)$ 70.3 Hz, Pt–Me]; $\delta_F(CD_2Cl_2)$ −136.1 [d, $^3J(FF)$ = 22.8], −163.9 [t, $^3J(FF)$ = 20.2 Hz] and −167.1 (m).

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