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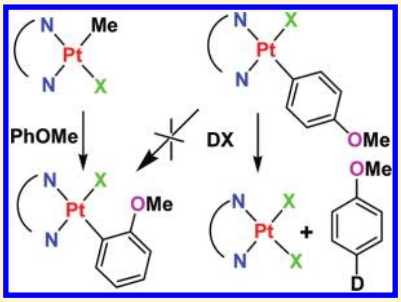
Activation of Anisole by Organoplatinum(II) Complexes: Evidence for Rate-Determining C−H Activation

Kevin J. Bonnington, Fenbao Zhang, Mahmoud M. Abd Rabo Moustafa, Benjamin F. T. Cooper, Michael C. Jennings, and Richard J. Puddephatt*

Department of Chemistry, University of Western Ontario, London, Canada N6A 5B7

Supporting Information

ABSTRACT: A study of the basis of selectivity of C−H bond activation of anisole by electrophilic methylplatinum(II) complexes is reported. Anisole reacts with [PtXMe(NN)] in trifluoroethanol solvent to give methane and [PtXAr(NN)], Ar = 2-, 3-, and 4-anisyl, in 90:8:2 ratio when X = $HOB(C_6F_5)_3$ and NN = $(2\text{-}C_5H_4N)_2CO$ (DPK) but not when NN = 2,2′-bipyridine. Similar results are obtained when X = triflate or when NN = $(2\text{-}C_5H_4N)_2NH$. Competition between reaction of anisole and anisole-d_8 with [PtXMe(NN)], X = $HOB(C_6F_5)_3$ and NN = DPK, in trifluoroethanol gave an isotope effect k_H/k_D = 3.6. Several 4-anisyl complexes, [PtClAr(NN)], [$PtAr_2$(NN)], and [PtMeAr(NN)], NN = DPK, DPA, or bipy, were prepared and reacted with HX [X = Cl, OTf, or $HOB(C_6F_5)_3$]. Reaction of [PtMeAr(NN)], NN = DPK or bipy, with HX gave a detectable hydride [PtXHMeAr(NN)] when X = Cl, followed by loss of methane to give [PtClAr(NN)], but only [Pt(OTf)Ar(NN)] was detected when X = OTf. Reaction with more HOTf gave anisole and [PtX_2(NN)], X = OTf, and no isomerization of the 4-anisyl group to the more favored 2-anisyl group was observed at any stage. The similar reaction of [PtMeAr(NN)] and HOTf in CD_3OD/CD_2Cl_2 gave CH_nD_{4-n} (n = 0−4) and mostly 4-$MeOC_6H_4D$. It is argued that the anisole C−H bond cleavage step in anisole activation, or the anisyl−H bond forming step in protonolysis, is responsible for the observed selectivity in these reactions.

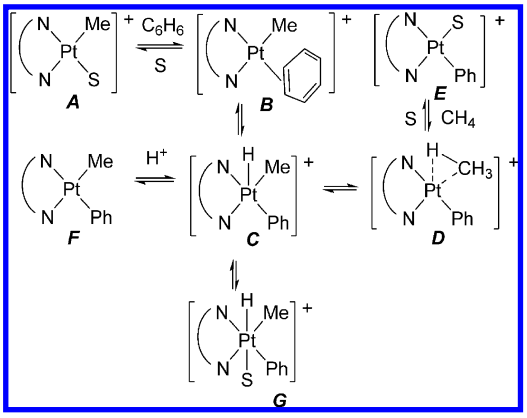


INTRODUCTION

The selective functionalization of hydrocarbons is of great current interest, and the activation of carbon−hydrogen bonds by platinum(II) complexes has played an important role in this field.[1] The carbon−hydrogen bond activation can occur by metathesis or by oxidative addition,[1,2] but reactions with reagents of the type $[PtMe(S)(NN)]^+$, where NN is a chelating bis(nitrogen-donor) ligand and S is a weakly coordinated solvent molecule, with benzene generally occur by the oxidative addition mechanism shown in Scheme 1.[1−11] The key steps are coordination of benzene to give ***B***, C−H oxidative addition to give ***C***, reductive coupling to give a methane complex ***D***, and loss of methane to give ***E***. Depending on the ligand, solvent, and anion, the rate-determining step may be the coordination of benzene, the oxidative addition of the C−H bond, or the loss of methane.[1−5] In addition, the coordination and dissociation steps can be associative or dissociative, hydrogen exchange with protic solvent can occur through reversible proton loss from ***C*** to give ***F***, and the 16-electron platinum(IV) intermediate ***C*** can be reversibly trapped by solvent coordination to give ***G***. The key intermediate ***C*** can also be formed by protonation of the methyl(phenyl)platinum(II) complex ***F***. There is typically easy fluxionality between coordinated C═C bonds of benzene in ***B*** or C−H bonds of methane in ***D*** so that H/D exchange between labeled phenyl and methyl groups or between protic solvent and methyl or phenyl groups can occur.[1−4]

Pioneering mechanistic work has been carried out with complexes in which the diimine ligands, NN in Scheme 1, are

Scheme 1[a]



[a]NN = diimine ligand, S = solvent.

ArN═CR−CR═NAr, Ar = aryl, R = H or Me. For example, in the case with Ar = $2,6\text{-}Me_2C_6H_3$, R = Me, and solvent = CF_3CH_2OH, rapid exchange between intermediates ***B***, ***C*** and ***D*** led to almost complete H/D scrambling between labeled methylplatinum and coordinated benzene or phenyl groups, but with no H/D scrambling of methyl or benzene groups with solvent, indicating that benzene coordination was the

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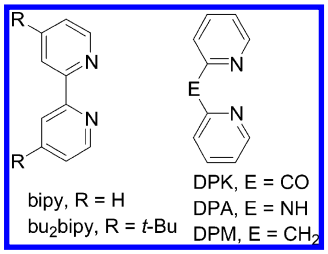
rate-determining step in conversion of ***A*** to ***E*** (Scheme 1).[3a] In this system, reaction of ***F*** with $H[BF_4]$ gave ***A*** and ***E*** in 18% and 82% yields, respectively, reflecting the slightly higher barrier to associative displacement of benzene from ***B*** compared to methane from ***D*** (Scheme 1).[3a] With less sterically hindered complexes (such as when the diimine is ArN═CH−CH═NAr, with Ar = 3,5-*t*-$Bu_2C_6H_3$), the benzene coordination is faster and then the C−H bond cleavage step is rate determining.[3d] In another study, using the diimine ligand ArN═CMe−CMe═NAr with Ar = 3,5$(CF_3)_2C_6H_3$, it was shown that reaction of ***A*** (Scheme 1) with toluene gave tolylplatinum(II) complexes (analogous to ***E***) with a preference for the *meta* isomer.[4d] In this system, reaction of any isomer (*o*-, *m*-, or *p*-) of $[Pt(tolyl)_2(NN)]$ with $H[BF_4]$ gave the same mixture of isomers of $[Pt(tolyl)(S)(NN)]^+$, with the *meta* isomer predominating, indicating easy exchange between $[PtH(tolyl)_2(NN)]^+$ and $[Pt(tolyl)(toluene)(NN)]^+$ isomers prior to displacement of toluene. In the presence of acetonitrile, less isomerization of tolyl groups was observed because the rate of associative displacement of toluene increased.[4d] Several authors have noted that activation of an aryl C−H bond of toluene gives mostly *m*-tolylplatinum complexes and that parallel or subsequent activation of a methyl C−H bond may give the benzylplatinum isomer.[1,3,4,9]

In earlier studies of reactions of Scheme 1, it was found that with the ligand NN = 2,2′-bipyridine, bipy, or its substituted derivatives such as 4,4′-di-*tert*-butyl-2,2′-bipyridine, no arene activation was observed under mild conditions,[12] whereas, with NN = $(2\text{-}C_5H_4)_2E$ (E = C═O, NH, or CH_2), Chart 1, benzene

Chart 1. Ligand Abbreviations

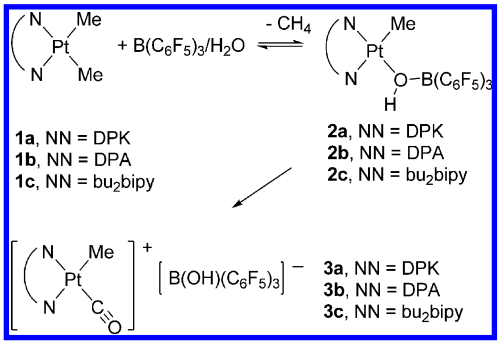


activation was observed to give the corresponding complex ***E*** (Scheme 1).[11] In the successful reactions, toluene gave mostly the *m*-tolylplatinum complex, while anisole gave mostly the *o*-anisylplatinum complex.[11] This article reports a detailed study of the reactions with anisole aimed at understanding the selectivity of the reaction[13] and the reasons for the low reactivity when NN = bipy.

RESULTS AND DISCUSSION

Carbon−Hydrogen Bond Activation of Anisole. The reaction of $B(C_6F_5)_3$ with water impurity in organic solvents gives $H[B(OH)(C_6F_5)_3]$, and this can cleave a methylplatinum bond of the complex $[PtMe_2(NN)]$, **1**,[14] to give the corresponding complex $[PtMe\{HOB(C_6F_5)_3\}(NN)]$, **2**, according to Scheme 2.[11,12] The hydroxotris(pentafluorophenyl)borate anion is weakly coordinating, and it was easily displaced by carbon monoxide to give the corresponding complex $[PtMe(CO)(NN)][HOB(C_6F_5)_3]$, **3** (Scheme 2). The carbonyl stretching frequencies follow the sequence **3a** (2119 cm^{-1}) > **3c** (2109 cm^{-1})[12] > **3b** (2105 cm^{-1}), indicating that the ligand donor ability follows the sequence DPA > bu_2bipy > DPK. The corresponding cations $[PtMe(CO)(NN)]^+$ with

Scheme 2



NN = ArN═CR−CR═NAr give CO stretching frequencies in the range 2103−2116 cm^{-1}, showing that they have a similar range of donor abilities.[3d] Differences in reactivity are therefore likely to be a result of steric effects.

The structure of complex **2a** was determined and is shown in Figure 1. The platinum center in **2a** is square planar, and the

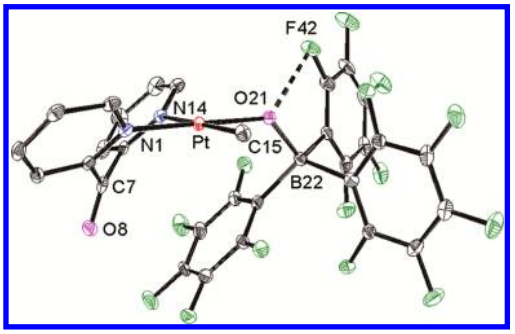


Figure 1. View of the structure of complex **2a**. Selected bond parameters (distances in Å, angles in deg): Pt−N(1) 1.975(5); Pt−N(14) 2.122(5); Pt−C(15) 2.044(7); Pt−O(21) 2.047(4); N(1)−Pt−N(14) 88.5(2).

pyridyl groups are twisted out of the plane by 44.9° (N1 ring) and 43.5° (N14 ring). There is a hydrogen bond between the OH group and an *ortho*-fluorine atom of the $HOB(C_6F_5)_3$ group with O(21)···F(42) = 2.70(1) Å. The ^1H NMR spectrum at room temperature gave a septet for the OH proton, with J(HF) = 3 Hz, due to coupling with all six *ortho*-fluorine atoms, indicating rapid rotation of the C_6F_5 groups and of the $B(C_6F_5)_3$ unit. However, at −80 °C, this resonance appeared as a broad doublet with ^1J(HF) = 20 Hz, as expected for the structure of Figure 1. In addition, at room temperature the ^{19}F NMR spectrum contained only three resonances (*o*-, *m*-, *p*-F), but each resonance split into several at low temperature as the fluxionality was frozen out. These data show clearly that the anion remains coordinated in solution and is not displaced by solvent CD_2Cl_2.

The structure of complex **3b** is shown in Figure 2. There was disorder of the methylplatinum and platinum carbonyl groups, and only one of the components is shown, for clarity. There are two hydrogen bonds, with N(7)···O(20) = 2.71(1) Å and O(20)···F(46) = 2.80(1) Å. The platinum center in **3b** is square planar, and the pyridyl groups are twisted out of the plane by 35.5° (N1 ring) and 38.5° (N13 ring).

The carbon−hydrogen bond activation of anisole was most conveniently carried out by reaction of complex **1a** and anisole with $B(C_6F_5)_3$ in CF_3CH_2OH solvent. The reaction involves formation of **2a** *in situ* (Scheme 2) followed by reaction with

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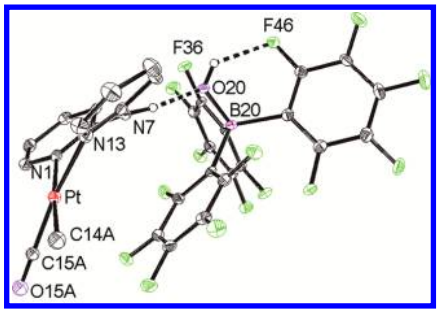
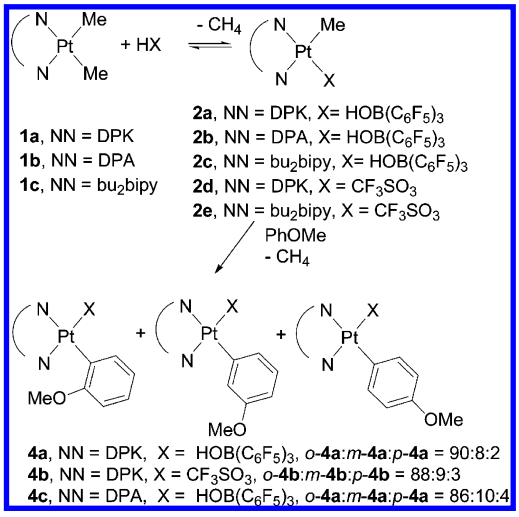


Figure 2. View of the structure of complex **3b**. Selected bond parameters (distances in Å; angles in deg): Pt–N(1) 2.110(6); Pt–N(13) 2.083(6); Pt–C(14A) 2.08(2); Pt–C(15A) 1.82(1); C(15A)–O(15A) 1.14(1); N(1)PtN(13) 87.2(2).

anisole accompanied by loss of methane (Scheme 3). The product $[Pt(C_6H_4OMe)\{HOB(C_6F_5)_3\}(DPK)]$, **4a**, was

Scheme 3



isolated as a mixture of *o*-, *m*-, and *p*-isomers in a ratio of 90:8:2. Analysis by NMR of samples taken from the reaction solution, evaporated to dryness and redissolved in CD_2Cl_2, showed similar relative amounts of the isomers. The pure *ortho* isomer *o*-**4a** was obtained by crystallization. Complex **4a** was also obtained, again with similar isomer ratio, by reaction of isolated complex **2a** with anisole. In these reactions, the anion remains coordinated in the isolated product, but otherwise the reaction is analogous to the diimine system of Scheme 1.[1,3,4] What is important is that it must be possible to displace the solvent (Scheme 1) or anion (Scheme 3) with the arene at intermediate stages of reaction (Scheme 1).[3,4] A carbon–hydrogen bond of anisole could also be activated by reaction of **1a** and anisole with triflic acid in CF_3CH_2OH solvent, but it was not possible to grow crystals of the product **4b**; a similar ratio of isomers was found (Scheme 3). Reaction of complex **1b** and anisole with $B(C_6F_5)_3$ in CF_3CH_2OH solvent gave complex **4c**, again with the *ortho* isomer preferred (Scheme 3). For comparison, activation of anisole by an organotungsten reagent has been shown to give $[WCp^*(NO)(CH_2\text{-}t\text{-}Bu)(C_6H_4OMe)]$ with selectivity *o*:*m*:*p* = 87:7:6.[13f]

The structure of complex *o*-**4a** is shown in Figure 3. The conformation adopted has the methoxy group *anti* to the carbonyl group of the DPK ligand and *syn* to the hydroxyl group of the $B(OH)(C_6F_5)_3$ ligand. The OH group appears to

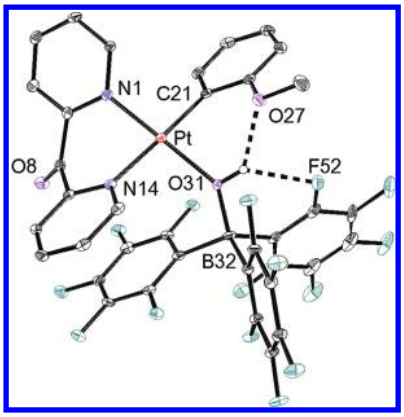


Figure 3. View of the structure of complex *o*-**4a**. Selected bond parameters (distances in Å; angles in deg): Pt–N(1) 1.988(4); Pt–N(14) 2.083(4); Pt–C(21) 2.004(5); Pt–O(31) 2.056(3) Å; N(1)–Pt–N(14) 87.6(2). H-bond distances: O(31)···O(27) 2.681(5); O(31)···F(52) 2.786(5).

act as a hydrogen bond donor to both the methoxy oxygen atom and one of the fluorine atoms (Figure 3). It is noteworthy that the anisyl aromatic group is almost coplanar with its *trans*-pyridyl group (angle = 1°) and that the angle to the plane of the platinum atom is 48°. The pyridyl groups are twisted out of the platinum plane by 45° (N1 group) and 47° (N14 group).

Mechanistic Studies Using Anisole-d_8. It is known that selectivity in carbon–hydrogen bond activation can be determined by either kinetic or thermodynamic factors, and it is important to determine which of these factors is dominant in the reactions of Scheme 3. The reaction of **1a** with anisole-d_8, with $B(C_6F_5)_3/H_2O$ as acid in CF_3CH_2OH, gave mostly **4a**-d_7 with only minor hydrogen content in the anisylplatinum group. In the major *ortho* isomer, about 8% and 6% hydrogen incorporation was observed at the 5- and 3-positions of the 2-methoxyphenylplatinum complex **4a**-d_7, with undetectable hydrogen content in the 4,6-positions or in the CD_3O group. This is attributed largely to H/D exchange through conventional electrophilic substitution *para* or *ortho* to the activating methoxy group, with a small preference for *para*, consistent with analysis of the remaining anisole. The methane was analyzed by GC-MS and shown to be CH_4 (94%) and CH_3D (6%) with negligible $CH_{4-n}D_n$ with $n > 1$. This experiment suggests that the C–D bond cleavage is largely irreversible under the reaction conditions and that there is no easy exchange between intermediates analogous to ***B***, ***C***, and ***D*** of Scheme 1, which would lead to multiple H–D exchange between the methyl and arylplatinum groups.[3,4] In addition, the observation of CH_4 rather than CH_3D as major product suggests that H/D exchange between hydridoplatinum and protic solvent is somewhat faster than methane loss (Scheme 1). No reaction occurred between **4a** and anisole-d_8, or between $[PtPh\{HOB(C_6F_5)_3\}(DPK)]$[11] and anisole, with $B(C_6F_5)_3/H_2O$ as acid in CF_3CH_2OH, showing that aryl–aryl exchange does not occur under mild conditions. The deuterium isotope effect on the reaction rate was determined by the reaction, using $B(C_6F_5)_3/H_2O$ in CF_3CH_2OH as acid, of complex **1a** with equimolar amounts of anisole/anisole-d_8, followed by analysis of the H/D content of the isolated product by ^1H NMR spectroscopy. The reaction of **1a** and $B(C_6F_5)_3/H_2O$ in CF_3CH_2OH with anisole gave a kinetic isotope effect k_H/k_D = 3.6, which suggests that the C–H cleavage step is rate determining.[2c,3,4]

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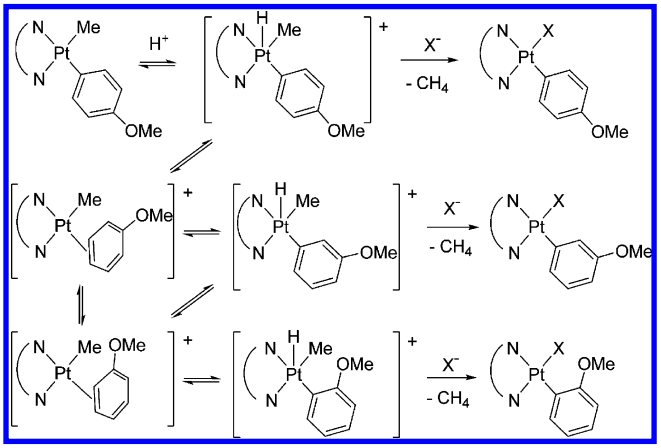
Studies Using 4-Anisylplatinum Complexes. The above study suggests that the C−H bond cleavage of anisole is the rate-determining step and thus that the selectivity is determined by kinetic factors. A further test was made on the basis of gaining access to the reaction intermediates by protonation of a neutral methyl(4-anisyl)platinum(II) complex [PtMe(4-C_6H_4OMe)(NN)], as shown in Scheme 4.[3,4] If the

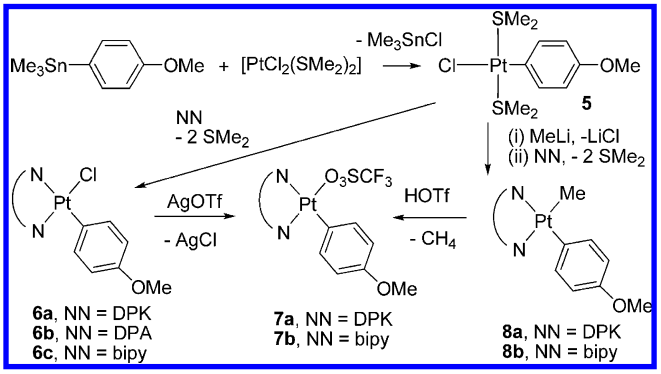
Scheme 4



arene complex intermediate was formed reversibly, then the product would be expected to contain all isomers of [PtX(C_6H_4OMe)(NN)], but, if not, only the isomer [PtX(4-C_6H_4OMe)(NN)] would be formed. If the selectivity was determined by thermodynamic factors, the isomer [PtX(2-C_6H_4OMe)(NN)] would be the dominant product.

The reagents needed for this study were prepared according to Scheme 5. Reaction of $[PtCl_2(SMe_2)_2]$[15] with Me_3Sn-4-C_6H_4OMe[16]

Scheme 5



gave *trans*-[PtCl(4-C_6H_4OMe)(SMe_2)$_2$], **5**. The *trans* stereochemistry was proved by the presence of a single resonance for the SMe_2 protons. The aryl protons *ortho* to platinum displayed satellite peaks due to the coupling ^3J(PtH) = 45 Hz. Reaction of complex **5** with bidentate ligands then gave the complexes **6a**−**6c** in good yield. Complexes **7a** and **7b** were obtained by reaction of the corresponding complex **6** with silver triflate, but the reaction was not successful for the DPA complex **6b**. The syntheses of complexes **8a** and **8b** were carried out by reaction of **5** with methyllithium in dimethylsulfide solvent, to prevent scrambling of methyl and aryl groups,[17] followed by reaction with DPK or bipy. Again the reaction was not successful with DPA.

The structures of complexes **6a**−**6c** were determined (Figure 4) in order to compare the ligand and aryl conformations (Table 1).

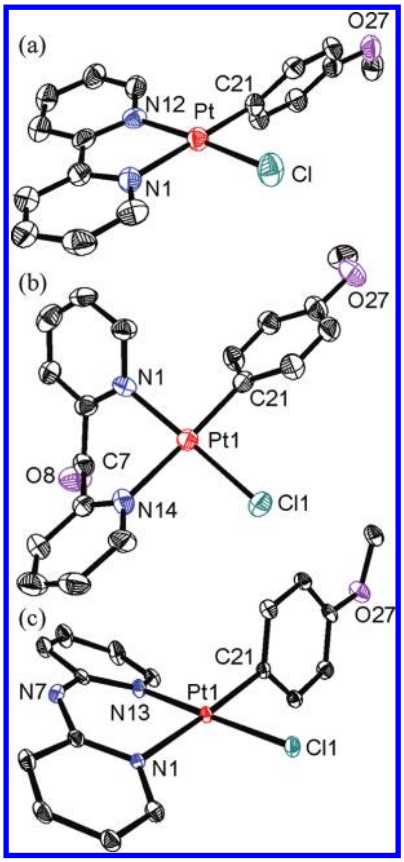


Figure 4. Views of the structures of the complexes (a) **6c**, (b) **6a**, and (c) **6b**. Selected bond parameters are in Table 1.

Table 1. Selected Bond Parameters and Twist Angles for Complexes 6a−6c

	6a(1)[d]	**6a**(2)[d]	**6b**(1)[d]	**6b**(2)[d]	**6c**
Pt−C/Å	2.01(1)	2.00(1)	2.004(5)	2.021(5)	2.004(7)
Pt−Cl/Å	2.286(3)	2.297(3)	2.301(1)	2.303(1)	2.285(2)
Pt−N[a]/Å	2.02(1)	2.02(1)	2.017(4)	2.025(4)	1.989(6)
Pt−N[b]/Å	2.12(1)	2.11(1)	2.125(4)	2.125(4)	2.107(6)
N−Pt−N/deg	87.6(4)	88.7(4)	89.6(1)	89.0(2)	80.1(3)
Θ(aryl)[c]/deg	49	57	89	86	55
Θ(py)[a,c]/deg	50	42	31	35	6
Θ(py)[b,c]/deg	47	41	28	32	3

[a] *trans*-Cl. [b] *trans*-aryl. [c] Θ is the angle between the aromatic group and the platinum plane. [d] Data for two crystallographically independent molecules.

There are many similarities in the bond parameters for the three complexes (note that there are two independent molecules in the structures of **6a** and **6b**). For example, the Pt−N bond *trans* to chloride is shorter than the one *trans* to the 4-anisyl group as a result of different *trans* influences. As expected, the N−Pt−N bite angle is smaller for the five-membered ring of the bipy complex **6c** than for the six-membered rings of **6a** and **6b**. The twist of the pyridyl ligands out of the square plane of the platinum atom followed the

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sequence DPK (mean 45°) > DPA (mean 31°) > bipy (mean 4°) and is much greater for the six-membered rings.[11,14,18] The twist of the anisyl group out of the square plane of the platinum atom followed the sequence DPA (mean 87°) > bipy (55°) > DPK (mean 53°). Only for the DPA complex **6b** is the aryl group close to orthogonal to the platinum plane (Table 1), the conformation that is expected to give maximum aryl-platinum π-overlap. The complexes pack in very different ways in the lattices, and so some of the differences in conformations may be related to packing forces. The differences in conformations observed between nonequivalent molecules of **6a** and **6b** (Table 1) support this interpretation. There is π-stacking of bipy groups in **6c** and NH···Cl intermolecular hydrogen bonding in **6b**, leading to formation of a supramolecular polymer (Figure 5).

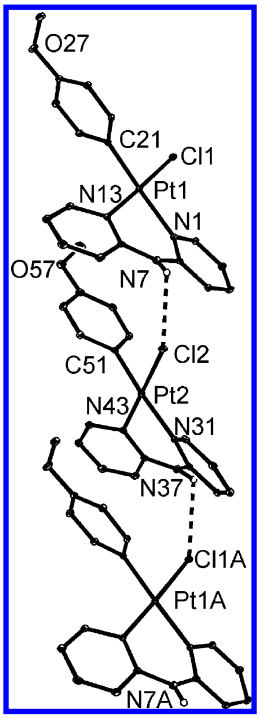
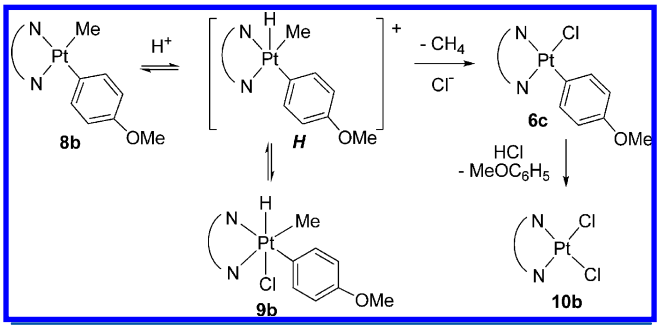


Figure 5. Supramolecular polymer formed by NH···Cl hydrogen bonding in **6b**. H-bonding distances (Å): N(7)···Cl(2) 3.384(4); N(37)···Cl(1) 3.351(4).

The reaction of the complex [PtMe(4-C_6H_4OMe)(bipy)], **8b**, with HCl is outlined in Scheme 6. If the reaction with one

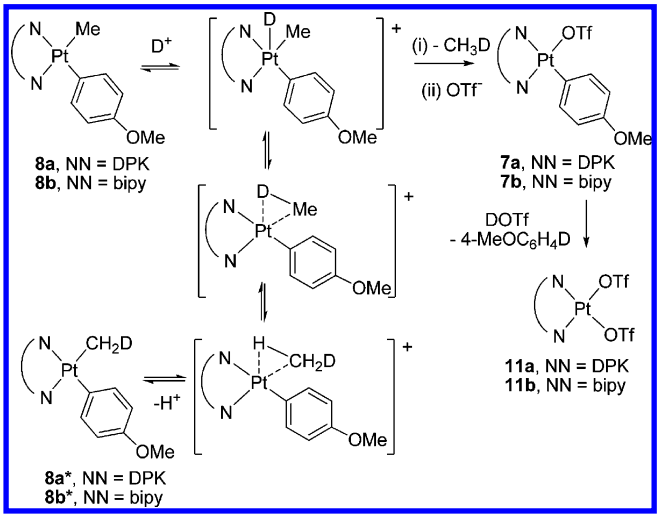
Scheme 6



equivalent of HCl was carried out at −80 °C in CD_2Cl_2 solution and monitored by ^{1}H NMR spectroscopy, the first compound observed was the platinum(IV) hydride complex **9b**. This was characterized by a platinum hydride resonance at δ = −20.37, with ^1J(PtH) = 1578 Hz, a methylplatinum resonance at δ = 1.47, with ^2J(PtH) = 66 Hz, and anisyl resonances at δ = 3.73 (MeO) and 6.59, 6.74 (aryl). As the solution was warmed to 0 °C, loss of methane occurred (δ = 0.24) and complex **6c** was formed. No [PtClMe(bipy)] or free anisole were detected by ^{1}H NMR, showing higher selectivity than the reaction of Scheme 1, which gave only 82% selectivity for methylplatinum bond cleavage from **F**.[3a] If the reaction was carried out with three equivalents of HCl, the first stage occurred in the same way to give complex **6c**, but this then reacted with more HCl to give [$PtCl_2$(bipy)], **10b**, and anisole. The high selectivity for methylplatinum rather than arylplatinum bond cleavage in reactions that occur by the oxidative addition/reductive elimination mechanism has been observed previously[19] and can be used to distinguish this mechanism from the direct S_E2 cleavage mechanism.[19,20] However, the case is more complex if the C−H bond formation is not rate determining, such as when displacement of alkane or arene from platinum is the slow step.[3a] Hydridoplatinum(IV) intermediates have been observed in several previous studies of cleavage of platinum−carbon σ-bonds by acids,[1−4,21] and five-coordinate platinum(IV) complexes such as **H** (Scheme 6) are most commonly intermediates in concerted reductive elimination reactions.[1,3,4,21,22]

The reactions of complexes **8a** and **8b** with triflic acid or with $B(C_6F_5)_3/H_2O$ were carried out under several different conditions, including reactions in CF_3CH_2OD and CD_3OD, which mimicked those used in the CH activation (Scheme 3). They gave similar results (Scheme 7), so only representative

Scheme 7



examples are described. The reaction of **8b** with one equivalent of triflic acid in CD_3OD occurred rapidly to give [Pt(O_3SCF_3)-(4-C_6H_4OMe)(bipy)], **7b**, and methane as a mixture of CH_4, CH_3D, CH_2D_2, and CHD_3 (and presumably CD_4) as identified by the ^{1}H NMR spectrum.[1,3,4,14,21] Scheme 7 shows only the formation of CH_3D, but easy equilibration between the cationic hydridomethylplatinum(IV) and methane-platinum(II) complexes can lead to extensive H/D exchange by way of **8b*** and then further reversible addition of D^+.[1,3,4] No significant deuterium incorporation into the anisyl group of **7b** was observed, and no isomerization to the *ortho*- or *meta*-anisyl group occurred. This result indicates that there is an easy equilibrium between methyl(hydrido)platinum(IV) and methane-platinum(II)

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intermediates, as well as easy exchange between the hydride and deuterium from solvent CD_3OD to give multiple deuterium incorporation into the methane, but that there is no reductive elimination (either reversible or irreversible) involving the anisyl group. When the reaction was carried out at −80 °C, a very similar result was obtained and the presumed hydride intermediate analogous to **9b** was not detected. Similar reactions of **8a** gave **7a** and CH_nD_{4-n}. The selectivity for methylplatinum rather than arylplatinum bond cleavage is again very high.

The reaction of **8b** with excess (five equivalents) of triflic acid in CD_2Cl_2/CD_3OD occurred in two distinct steps. The first step was very fast and occurred as above to give methane-d_n (n = 1−4) and **7b**, but the second step occurred much more slowly to give $[Pt(O_3SCF_3)_2(bipy)]$, **11b**,[23,24] and anisole, which was very largely anisole-4-d_1. This step was complete in about four days at room temperature. The reaction of triflic acid with **7b**, prepared according to Scheme 5, occurred in the same way as in the second step above. The reactions of **8a** and **7a** with excess triflic acid occurred similarly (Figure 6), the only

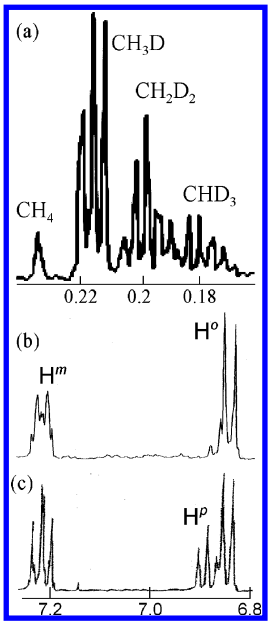
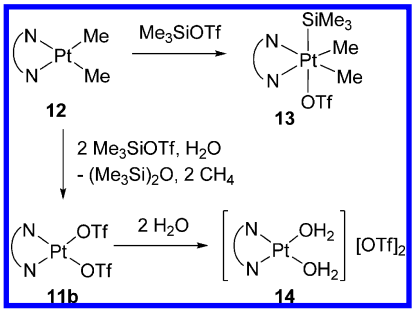


Figure 6. ^1H NMR spectra from reaction of **8a** with triflic acid in CD_2Cl_2/CD_3OD of (a) methane-d_n and (b) anisole (mostly 4-$MeOC_6H_4D$); (c) reference spectrum of anisole ($MeOC_6H_5$) in $CDCl_3$.

significant difference being that the reaction with **7a** to give anisole and $[Pt(O_3SCF_3)_2(DPK)]$, **10b**,[23] was complete in about five hours at room temperature, which is significantly faster than the reaction with **7b**. Similarly, the reaction of $[Pt(4\text{-}C_6H_4OMe)_2(bipy)]$[25] with triflic acid in CD_2Cl_2/CD_3OD occurred in two steps to give **7b** and then $[Pt(O_3SCF_3)_2(bipy)]$, with anisole-4-d_1 as the major organic product in both steps.

The nature of the triflate complexes[23] was investigated by reaction of $[PtMe_2(bipy)]$, **12**, with trimethylsilyl triflate under varying conditions (Scheme 8). Under rigorously dry conditions in CD_2Cl_2 solution, as monitored by ^1H NMR spectroscopy, the reaction occurred easily at −78 °C to give a green-black solution in which the chief product was identified as the trimethylsilylplatinum(IV) complex $[Pt(OTf)Me_2(SiMe_3)(bipy)]$, **13**, by comparison of the NMR parameters with those of similar compounds $[PtXMe_2(SiMe_3)(bipy)]$.[26,27] Complex **13**

Scheme 8. ([a])



[a]NN = bipy.

had limited thermal stability and decomposed to give an unidentified black precipitate on warming the solution. Complex **13** was characterized by a trimethysilylplatinum resonance at δ = −0.16, with $^3J(PtH)$ = 21 Hz, and by a methylplatinum resonance at δ = 1.23, with $^2J(PtH)$ = 62 Hz.[26] If a solution of **13** at 0 °C was allowed to stand while exposed to moist air, the anhydrous triflate complex $[Pt(OTf)_2(bipy)]$, **11b**, crystallized slowly and was structurally characterized (Figure 7a).

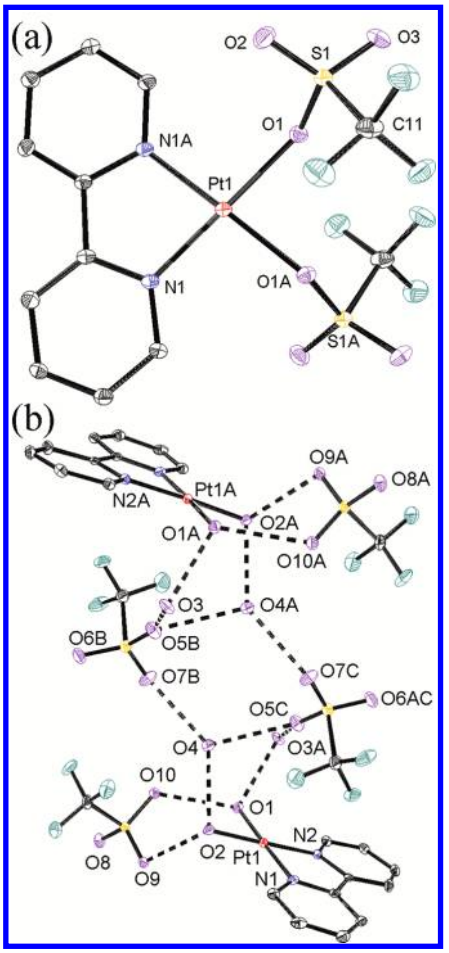


Figure 7. Views of the structure of (a) $[Pt(O_3SCF_3)_2(bipy)]$, **11b**. Selected bond parameters (distances in Å; angles in deg): Pt(1)−N(1) 1.982(5); Pt(1)−O(1) 2.054 Å; N(1)−Pt−N(1A) 81.9(3); O(1)−Pt−O(1A) 84.1(2). (b) $[Pt(OH_2)_2(bipy)](CF_3SO_3)_2(H_2O)_2$. Selected bond parameters (distances in Å; angles in deg): Pt(1)−N(1) 1.976(7); Pt(1)−N(2) 1.976(7); Pt(1)−O(1) 2.042(6); Pt(1)−O(2) 2.041(6) Å; N(2)−Pt(1)−N(1) 81.9(3); O(2)−Pt(1)−O(1) 90.0(2).

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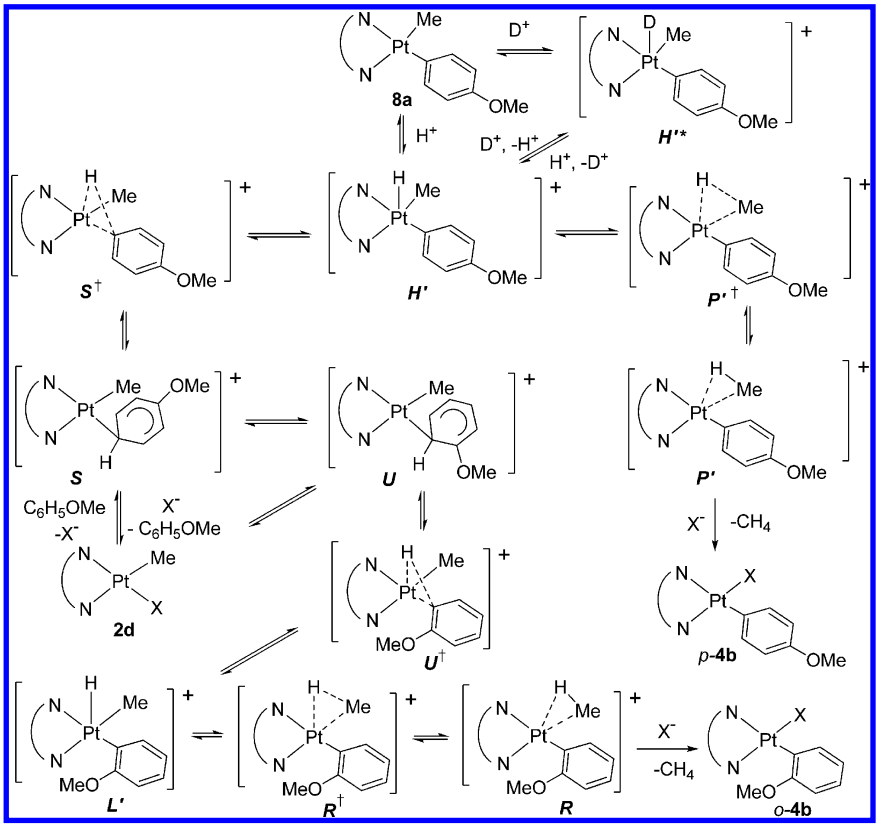
Scheme 9[a]



[a]NN = DPK, X = triflate, cationic complexes have a triflate anion.

When complex **12** was treated with triflic acid-*d*, prepared by reaction of Me_3SiOTf with CD_3OD in moist solvent, a white precipitate formed that was recrystallized to give the hydrated complex $[Pt(OH_2)_2(bipy)](CF_3SO_3)_2{\cdot}2H_2O$, **14**, whose structure is shown in Figure 7b. Complex **14** forms dimer units in the crystal through hydrogen bonding between coordinated [O(1), O(2)] and free [O(3), O(4)] water molecules and the triflate anions (Figure 7b). The ^1H NMR spectrum of **14** in acetone-d_6 solution gave a free triflate resonance at $\delta(^{19}F)$ = 79.0 and broad resonances for the bipy protons, which may be indicative of dynamic exchange between coordinated water and acetone molecules. It should be noted that the cleavage of both methylplatinum groups from **12** (Scheme 8) occurred much more rapidly than the cleavage of the anisyl ligand of **8b** (Scheme 7).

Theoretical Studies. Several theoretical studies have been made on carbon–hydrogen bond activation of methane or benzene by electrophilic platinum(II) complexes,[1−4,17,21,22,28] but there has been little computational work on the selectivity in anisole activation.[13] A DFT study of the isomers of [PtMe(anisyl)(NN)] and of the isomers formed by protonation, namely, $[PtHMe(anisyl)(NN)]^+$, $[PtMe(anisole)(NN)]^+$, and $[Pt(anisyl)(CH_4)(NN)]^+$, with NN = bipy or DPK, has therefore been carried out. Results on the ground-state structures are given in Figures 8−10 and are summarized below.

For the platinum(II) complexes [PtMe(anisyl)(NN)], the calculated stability follows the series *ortho* (*J*, *J'*) > *meta* (*I*, *I'*) > *para* (**8b**, **8a**) for both NN = bipy and DPK, but the energy differences are small. The equilibration of the *para*-anisyl derivative **8a** or **8b** with its *ortho* and *meta* isomers is therefore predicted to be thermodynamically favorable if it is allowed kinetically. Consider the case of the bipy complex **8b**. The experimental results show that isomerization does not occur, but, if it did, it is expected to occur by initial protonation. The kinetic product of protonation of **8b** is expected to be $[PtHMe(4\text{-}C_6H_4OMe)(bipy)]^+$, ***H*** (Figure 8), and there is evidence for this in the formation of **9b** (Scheme 6).[1−4,21] The *meta* and *ortho* isomers of ***H*** are ***K*** and ***L*** (Figure 8) and isomerization would be expected to occur by way of the arene isomers, which are ***M*** and ***N*** (Figure 8), formed by reductive coupling. With anisole, the arene can also bind through the oxygen atom to give the ether complex ***O***, which is calculated to be the lowest energy isomer (Figures 8, 10). The alternative reductive

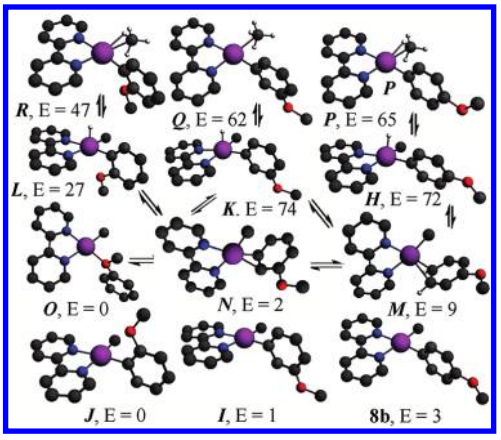


Figure 8. Calculated structures and energies (*E* in kJ mol^{-1}, with respect to ***J*** for neutral complexes or ***O*** for cationic complexes) of complexes and cationic intermediates with NN = bipy.

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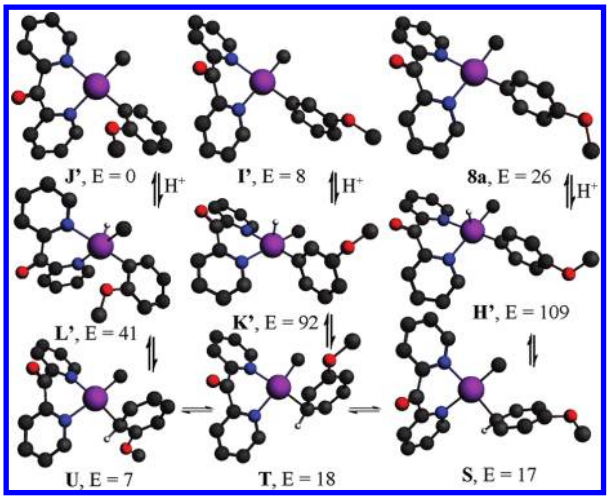

Figure 9. Calculated structures of complexes and cationic intermediates with NN = DPK.

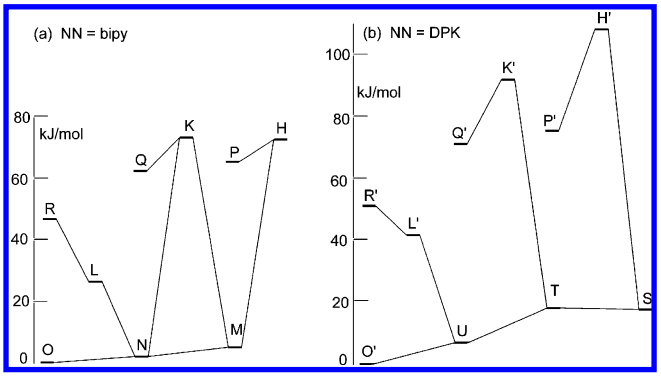

Figure 10. Relative energies (kJ mol^{-1} with respect to ***O*** or ***O′***) of cationic complexes shown in (a) Figure 8 (NN = bipy) and (b) Figure 9 (NN = DPK).

coupling is to combine the methyl and hydride groups to give the corresponding methane complexes ***P***, ***Q***, and ***R*** (Figure 8).

The following features are notable in Figures 8 and 10a:

1. The arene and ether complexes [PtMe(anisole)(bipy)]$^+$, ***M***, ***N***, and ***O***, have similar energies, they are more stable than the corresponding complexes [PtHMe(anisyl)(bipy)]$^+$ and [Pt(anisyl)(CH$_4$)(bipy)]$^+$, and they would be likely to interconvert easily (the 1- or 1,2-arene complex is calculated to have significantly higher energy). The arene–platinum binding in ***M*** (Pt–C3 = 2.44, Pt–C4 = 2.30 Å) and ***N*** (Pt–C2 = 2.29, Pt–C3 = 2.45 Å) is less symmetrical than in the corresponding benzene complexes (Pt–C = 2.30, 2.30 Å),[2a] but can still be considered as η^2-arene binding.[3–5,22f] The distortion is rationalized in terms of the electronic effects of the methoxy substituent, favoring the shorter Pt–C bond to the *ortho*-carbon in ***N*** and to the *para*-carbon in ***M***.
2. The *para* and *meta* isomers [PtHMe(anisyl)(bipy)]$^+$, ***H*** and ***K***, are the least stable complexes, but the *ortho* isomer ***L*** is considerably more stable (Figures 8, 10). In ***L***, the *o*-anisyl group bends to allow the oxygen atom to be closer to platinum, as seen by different calculated bond angles of the anisylplatinum group with Pt–C–C = 134° and 107°, compared to the respective calculated angles of 119° and 122° in ***H***. The distance Pt–O = 2.55 Å in ***L*** is too long to represent a full covalent bond, but evidently provides significant overall stabilization. These bond parameters are similar to those found experimentally in a stable iridium(III) pincer ligand (PNP) complex [IrH(2-C$_6$H$_4$OMe)(PNP)]$^+$, which has Ir–C–C = 131.1° and 112.5° and Ir···O = 2.76 Å.[13b]
3. For the *para* and *meta* isomers, the methane complexes [Pt(anisyl)(CH$_4$)(bipy)]$^+$, ***P*** and ***Q***, lie a little lower in energy than the corresponding complexes [PtHMe(anisyl)(bipy)]$^+$, ***H*** and ***K***, but, for the *ortho* isomer, the methane complex ***R*** is higher in energy than the corresponding hydrido(methyl)platinum(IV) complex ***L*** (Figures 8, 10). The difference is explained by the exceptional stabilization of ***L*** as described above.

For the DPK complexes (Figures 9, 10) the trends are similar, but there is one significant difference. The most stable calculated forms of the arene π-complexes are closer to the η^1 than to the η^2 bonding form found with the bipy ligand. Thus, complex ***U*** is calculated to have Pt–C2 = 2.27 Å but Pt–C1 = 3.00 Å and Pt–C3 = 2.82 Å, ***T*** has Pt–C3 = 2.30 Å but Pt–C2 = 2.76 Å and Pt–C4 = 2.97 Å, and ***S*** has Pt–C4 = 2.26 Å but Pt–C3 = 2.80 Å and Pt–C5 = 3.05 Å. The closest Pt···H distances of 2.51, 2.70, and 2.63 Å for ***U***, ***T***, and ***S***, respectively, are too long to indicate a bonding interaction, so these complexes have the structure of the Wheland intermediate, which can be described as an η^1-anisole complex, rather than an η^2-CH complex. There are several possible conformers in the DPK complexes, but, in the most stable ones (Figure 9), the arene groups in ***S***, ***T***, and ***U*** are oriented toward the methylplatinum group with the CH group roughly in the plane of the platinum atom. This structure would not be favored for the 2,2′-bipyridine complexes because of steric interactions.

The interpretation of the observed chemistry is summarized in Scheme 8 and Figure 11, for the case with NN = DPK and

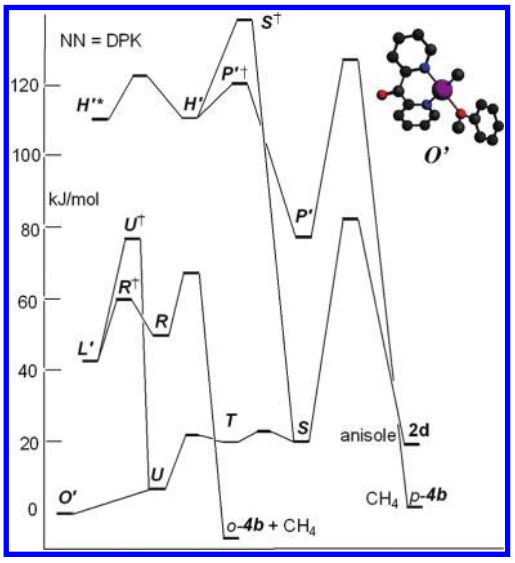

Figure 11. Proposed energies (relative to ***O′***, shown as inset) and transition states of the DPK complexes shown in Scheme 8. Cationic complexes have the triflate anion (not shown).

X$^-$ = triflate. It will be assumed that the C–H cleavage or formation reactions occur by the oxidative addition or reductive elimination reactions, respectively, although this is not strictly proved.[1–3] The kinetic product of protonation of complex **8a** is ***H′*** (Scheme 8), which can undergo reductive elimination of either methane to give the methane complex ***P′***, via transition

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state $P'^{\dagger}$, or the anisole complex S, via transition state $S^{\dagger}$. A third reaction is that it can undergo H/D exchange with solvent (CD_3OD in this case), which might occur by reversible deprotonation to **8a** or by an associative mechanism, such as by a dihydrogen complex intermediate. Associative displacement of methane from P' or anisole from S could then give *p*-**4b** or **2d**, respectively[1−4] (note that the nucleophile is shown as triflate in Scheme 8, but it could also be a solvent molecule).[23] Any of these five reactions could in principle be rate determining. The observation that methane isotopomers CH_nD_{4-n} are formed shows that the exchange between H', H'^{*}, and P' must be fast relative to methane displacement from P' to give *p*-**4b**. The observation that anisole and complex **2d** are not formed could be explained if either the anisole displacement from S or the reductive elimination to form S was rate determining. However, if S was formed reversibly, then isomerization to T (Figure 9, not shown in Scheme 8) and U would also occur and would lead eventually to formation of *o*-**4b** and to multiple deuterium incorporation into the anisyl group, neither of which was observed. It is therefore concluded that the highest activation energy in the five possible reactions is the reductive elimination to form S and that neither this step nor the subsequent displacement of anisole occurs. The possible relative activation energies are shown in Figure 11.[29] The selectivity for methane rather than arene formation is much higher than when the methane or arene displacement step is rate determining.[3a]

The mechanisms of protonolysis of **8a** and of C−H activation of anisole by complex **2d** are related by microscopic reversibility, and the C−H activation is also depicted in Scheme 8 and Figure 11. Displacement of triflate by anisole gives the anisole complexes O', U, T, and S, which are easily interconverted.[30] The easiest C−H activation occurs from U to give L' via the transition state $U^{\dagger}$, and reductive elimination from L' then gives methane and *o*-**4b** by way of $R'^{\dagger}$ and R' (Scheme 8). The rate-determining step is the C−H activation, consistent with the observed isotope effect k_H/k_D = 3.6.[2−4,31] The selectivity of C−H activation of arenes can be determined by either thermodynamic or kinetic effects.[1−4,13] In the present case, kinetic control is proposed, but we note that the product *o*-**4b** is favored by both kinetic and thermodynamic effects (Figure 11).[23]

One unexplained aspect of this work is the difference between the bipy and DPK complexes. Under mild conditions used in this work, [PtXMe(NN)], X = OTf or $HOB(C_6F_5)_3$, reacts with arenes when NN = DPK but not when NN = bipy. In addition the protonolysis of the anisyl−platinum bond in [PtX(4-C_6H_4OMe)(NN)] occurs faster by an order of magnitude when NN = DPK compared to NN = bipy. However, [PtX_2(NN)], X = CF_3CO_2, in CF_3CO_2D catalyzes H/D exchange of benzene at 150 °C at similar rates when NN = bipy or DPK, showing that C−H bond activation can occur in both cases.[1j] In addition, studies using mass spectrometry have shown that [PtMe(C_6D_6)(bipy)]$^+$ can undergo easy H/D exchange between the methylplatinum group and the arene, which must involve C−D bond activation.[2a] Although the calculated ground-state structures of the π-arene complexes [PtMe(anisole)(NN)]$^+$ are different when NN = bipy (N, Figure 12) and DPK (U, Figure 12), the calculated transition states ($N^{\dagger}$, $U^{\dagger}$) can be considered as intermediate between the hydrido(2-anisyl)platinum(IV) complexes (L, L') and an η^2-CH bonded anisole complex in each case (Figure 12),[2a] and the calculated activation energies are only 5−10 kJ mol^{-1} higher

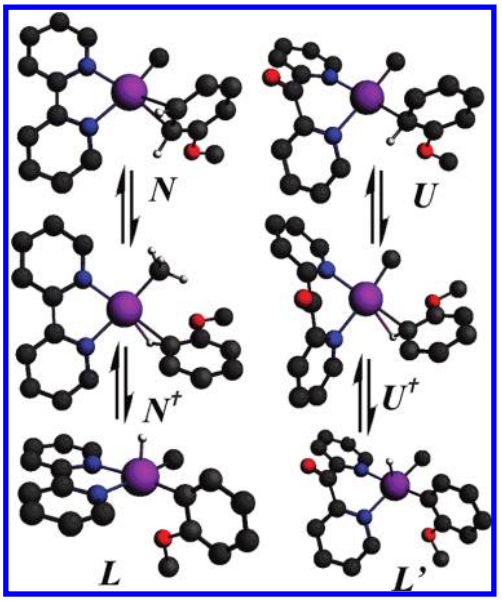

Figure 12. Calculated intermediates and transition states in the oxidative addition of a C−H bond of anisole (left bipy, right DPK complexes).

when NN = bipy. It seems likely, therefore, that C−H activation by complexes "[PtMe(bipy)]$^+$" will be possible under optimum experimental conditions.

EXPERIMENTAL SECTION

All reactions were carried out under nitrogen using standard Schlenk techniques, unless otherwise specified. NMR spectra were recorded using Varian Mercury 400 or Varian Inova 400 or 600 spectrometers. ESI mass spectra were recorded using a Micromass LCT spectrometer, with an injection flow rate of 20 μL/min, and were calibrated with NaI at a concentration of 2 μg/μL in 50:50 propan-2-ol/water. The injection flow rate of 20.0 μL/min was used throughout all experiments. The complexes [$Pt_2Me_4(\mu$-$SMe_2)_2$], [$PtMe_2$(bipy)], [$PtMe_2$(DPK)], and [Pt(4-$MeOC_6H_4)_2$(bipy)] were prepared by the literature methods.[16,18e,25]

[PtMe{HOB(C_6F_5)$_3$}(DPK)], 2a. To a solution of [$PtMe_2$(DPK)], **1a** (0.41 g, 1 mmol), in CF_3CH_2OH (30 mL) was added a solution of $B(C_6F_5)_3$ (0.54 g, 1 mmol) in CF_3CH_2OH (10 mL). The color changed from purple to yellow-orange. The mixture was stirred for 6 h, and the yellow precipitate of the product was separated by filtration, washed with ether (3 × 2 mL) and pentane (3 × 10 mL), and dried under vacuum. Yield: 86%. Anal. Calcd for $C_{30}H_{12}BF_{15}N_2O_2Pt$: C, 39.03; H, 1.31; N, 3.03. Found: C, 39.54; H, 1.34; N, 3.27. NMR in CD_2Cl_2: δ(^{1}H) = 0.96 [s, 3H, ^2J(PtH) = 73 Hz, Pt-Me]; 3.30 [m, 1H, OH]; 7.50−8.80 [8H, py]. δ(^{19}F) = −134.3 [br m, 6F, *o*-F]; −160.2 [t, 3F, *p*-F]; −165.4 [dt, 6F, *m*-F]. δ(^{13}C) = −13.9 [PtMe]; 125.4, 127.4, 129.1, 129.2, 137.8, 139.1, 149.5, 149.9, 153.5, 153.9 [py]; 135.6; 138.2; 146.5; 148.8 [C_6F_5]; 185.9 [CO].

[PtMe{HOB(C_6F_5)$_3$}(DPA)], 2b. This was prepared in a similar way from [$PtMe_2$(DPA)] and isolated as a pale brown solid. Yield: 84%. Anal. Calcd for $C_{29}H_{13}BF_{15}N_3OPt$: C, 38.26; H, 1.44; N, 4.62. Found: C, 38.59; H, 1.33; N, 4.47. NMR in CD_2Cl_2: δ(^{1}H) = 0.86 [s, 3H, ^2J(PtH) = 72 Hz, Pt-Me]; 3.70 [m, 1H, OH]; 5.70 [1H, NH]; 6.38−8.51 [8H, py]. δ(^{19}F) = −134.1 [br m, 6F, *o*-F]; −160.1 [t, 3F, *p*-F]; −165.2 [dt, 6F, *m*-F].

[PtMe(DPK)(CO)]$^+$[HOB(C_6F_5)$_3$]$^-$, 3a. Yield: 88%. NMR in CD_2Cl_2: δ(^{1}H) = 1.09 [s, 3H, ^2J(PtH) = 70 Hz, PtMe]; 4.17 [m, 1H, O(H)B]; 7.42 [t, br, 2H, Py H^5 and $H^{5'}$]; 7.92 [d, 2H, ^3J((HH) = 8 Hz, Py H^3, $H^{3'}$]; 8.03 [t, 2H, ^3J(HH) = 7 Hz, Py H^4, $H^{4'}$]; 8.60 [d, br, 2H, Py H^6, $H^{6'}$]. δ(^{19}F) = −136.3 [d, 6F, *o*-F]; −162.1 [t, br, 3F, *p*-F]; −166.6 [t, 6F, *m*-F]. IR: 2073 cm^{-1} (CO). ESI-MS (*m*/*z*): 422 (M^+).

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[PtMe(DPA)(CO)]$^+$[HOB(C$_6$F$_5$)$_3$]$^-$, 3b. Yield: 91%. NMR in CD_2Cl_2: $\delta(^1H)$ = 1.00 [s, 3H, ^2J(PtH) = 68 Hz, PtMe]; 7.10 [t, 1H, Py H^5]; 7.12 [t, 1H, Py H$^{5'}$]; 7.46 [d, 1H, Py H^4]; 7.52 [d, 1H, Py H$^{4'}$]; 7.82 [t, br, 2H, Py H^3, H$^{3'}$]; 8.17 [d, 1H, ^3J(PtH) = 34 Hz, Py H^6]; 8.28 [d, 1H, Py H$^{6'}$]; 12.08 [s, 1H, NH]. NMR (CD_2Cl_2): $\delta(^{13}C)$ = −13.9 [s, ^1J(PtC) = 520 Hz, PtMe]; 163.2 [s, ^1J(PtC) = 1821 Hz, PtCO]. $\delta(^{19}F)$ = −136.3 [d, 6F, *o*-F]; −161.8 [t, 3F, *p*-F]; −166.3 [t, 6F, *m*-F]. IR: 2105 cm^{-1} (CO). ESI-MS (*m*/*z*): 409 (M$^+$).

[Pt(C$_6$H$_4$OMe){HOB(C$_6$F$_5$)$_3$}(DPK)], 4a. To a solution of complex **1a** (0.41 g, 1 mmol) in CF_3CH_2OH (30 mL) was added a solution of $B(C_6F_5)_3$ (0.54 g, 1 mmol) in CF_3CH_2OH (10 mL), followed by addition of C_6H_5OMe (30 mmol), to give a yellow-orange solution. After 4 days, the yellow precipitate of the product was separated by filtration, washed with ether (3 × 2 mL) and pentane (3 × 10 mL), and dried under vacuum. Yield: 48%. Anal. Calcd for $C_{36}H_{16}BF_{15}N_2O_3Pt$: C, 42.58; H, 1.61; N, 2.80. Found: C, 42.64; H, 1.81; N, 2.72. NMR in CD_2Cl_2: *ortho*-**4a**: $\delta(^1H)$ = 4.01 [s, 3H, OMe]; 4.81 [m, br, 1H, OH]; 6.29 [d, 1H, An H^6]; 6.39 [t, 1H, An H^5]; 6.68 [d, 1H, An H^3]; 6.90 [dt, 1H, An H^4]; 7.21−9.01 [8H, py]. $\delta(^{19}F)$ = −134.5 [br m, 6F, *o*-F]; −161.7 [t, 3F, *p*-F]; −166.9 [m, 6F, *m*-F]. *meta*-**4a**: $\delta(^1H)$ = 3.75 [s, 3H, OMe]; 3.70 [m, br, 1H, OH]; 6.51 [s, 1H, An H^2]; 6.56 [d, 1H, An H^6]; 6.83 [t, 1H, An H^5]; 6.90 [d, 1H, An H^4]; 7.25−8.97 [8H, py]. *para*-**4a**: $\delta(^1H)$ = 3.72 [s, 3H, OMe]; 3.69 [m, br, 1H, OH]; 6.44 [d, 2H, An H^{2,6}]; 6.54 [d, 2H, An H^{3,5}]; 7.3−8.9 [8H, py].

[Pt(C$_6$H$_4$OMe)(O$_3$SCF$_3$)(DPK)], 4b. This was prepared similarly but by using triflic acid. Yield: 42%. Anal. Calcd for $C_{19}H_{15}F_3N_2O_5PtS$: C, 35.91; H, 2.38; N, 4.41. Found: C, 35.55; H, 2.29; N, 4.06. NMR in CD_2Cl_2: *ortho*-**4b**: $\delta(^1H)$ = 4.04 [s, 3H, OMe]; 6.34 [d, 1H, An H^6]; 6.42 [t, 1H, An H^5]; 6.70 [d, 1H, An H^3]; 6.94 [dt, 1H, An H^4]; 7.2−9.0 [8H, py]. *meta*-**4b**: $\delta(^1H)$ = 3.77 [s, 3H, OMe]; 6.51 [s, 1H, An H^2]; 6.60 [d, 1H, An H^6]; 6.85 [t, 1H, An H^5]; 6.93 [d, 1H, An H^4]; 7.2−9.0 [8H, py]. *para*-**4b**: $\delta(^1H)$ = 3.73 [s, 3H, OMe]; 6.47 [d, 2H, An H^{2,6}]; 6.55 [d, 2H, An H^{3,5}]; 7.2−9.0 [8H, py].

[Pt(C$_6$H$_4$OMe){HOB(C$_6$F$_5$)$_3$}(DPA)], 4c. This was prepared as for **4a** but using complex **1b**. Yield: 51%. Anal. Calcd for $C_{35}H_{17}BF_{15}N_3O_2Pt$: C, 41.94; H, 1.71; N, 4.19. Found: C, 41.48; H, 1.85; N, 3.88. NMR in CD_2Cl_2: *ortho*-**4c**: $\delta(^1H)$ = 3.95 [s, 3H, OMe]; 4.73 [m, br, 1H, OH]; 6.32 [d, 1H, An H^6]; 6.35 [t, 1H, An H^5]; 6.60 [d, 1H, An H^3]; 6.83 [dt, 1H, An H^4]; 7.1−9.1 [8H, py]. $\delta(^{19}F)$ = −134.0 [br m, 6F, *o*-F]; −161.1 [t, 3F, *p*-F]; −167.2 [m, 6F, *m*-F]. *meta*-**4c**: $\delta(^1H)$ = 3.77 [s, 3H, OMe]; 6.52 [s, 1H, An H^2]; 6.58 [d, 1H, An H^6]; 6.80 [t, 1H, An H^5]; 6.90 [d, 1H, An H^4]; 7.1−9.1 [8H, py]. *para*-**4c**: $\delta(^1H)$ = 3.71 [s, 3H, OMe]; 6.42 [d, 2H, An H^{2,6}]; 6.50 [d, 2H, An H^{3,5}]; 7.1−9.1 [8H, py].

H/D Exchange Experiments. The reaction of **1** with anisole-d_8 was carried out in a way similar to the synthesis of complex **4a**, but using the perdeuterated arene. The extent of H/D exchange at each position of the aryl group of the product complex was determined by integration of the corresponding resonance in the ^{1}H NMR spectrum, using an adjacent pyridyl resonance for calibration. In a separate experiment, the complex **4a** was dissolved in deuterated alcohol in an NMR tube, but negligible H/D exchange was observed over several days at room temperature under these conditions. The isotope effect was determined by carrying out the synthesis as for **4a** but using equimolar amounts of anisole and anisole-d_8. The product was isolated followed by analysis by using ^{1}H NMR. Aliquots were taken during the course of the reaction, evaporated, and analyzed as a cross-check.

Me$_3$Sn-4-C$_6$H$_4$OMe. This was prepared by the literature method.[15] NMR in $CDCl_3$: $\delta(^1H)$ = 0.26 [s, 9H, $^2J_{SnH}$ = 54 Hz, Sn*Me*]; 3.80 [s, 3H, O*Me*]; 6.91 [d, 2H, $^3J_{HH}$ = 8 Hz, *H*^{3}]; 7.40 [d, 2H, $^3J_{HH}$ = 8 Hz, $^3J_{SnH}$ = 43 Hz, *H*^{2}].

***trans*-[PtCl(4-C$_6$H$_4$OMe)(SMe$_2$)$_2$], 5.** A mixture of *cis*/*trans*-$[PtCl_2(SMe_2)_2]$ (1.10 g, 2.82 mmol) and Me$_3$Sn-4-C$_6$H$_4$OMe (0.840 g, 3.10 mmol) in acetone (25 mL) was warmed to 50 °C with stirring for 3 days. The resulting solution was allowed to cool to room temperature and filtered, and the solvent was evaporated under vacuum. The product was purified by crystallization from CH_2Cl_2/pentane. Yield: 1.03 g, 79%. NMR in CD_2Cl_2: $\delta(^1H)$ = 2.31 [s, 12H, $^3J_{PtH}$ = 57 Hz, S*Me*]; 3.72 [s, 3H, OMe]; 6.64 [d, 2H, $^3J_{HH}$ = 9 Hz, *H*^{m}]; 7.20 [d, 2H, $^3J_{HH}$ = 9 Hz, $^3J_{PtH}$ = 45 Hz, *H*^{o}].

[PtCl(4-C$_6$H$_4$OMe)(bipy)], 6c. A mixture of *trans*-[PtCl(*p*-anisyl)-$(SMe_2)_2$] (100 mg, 0.216 mmol) and bipy (33.8 mg, 0.216 mmol) in benzene (10 mL) was warmed to 50 °C for 2 days. The solvent was evaporated, and the orange product was purified by recrystallization from CH_2Cl_2/pentane. Yield: 105 mg, 98%. Anal. Calcd for $C_{17}H_{15}ClN_2OPt$: C, 41.35; H, 3.06; N, 5.67. Found: C, 40.89; H, 2.77; N, 5.27. NMR in CD_2Cl_2: $\delta(^1H)$ = 3.80 [s, 3H, O*Me*]; 6.75 [d, 2H, $^3J_{HH}$ = 8 Hz, *H*^{m}]; 7.27 [d, 2H, $^3J_{HH}$ = 8 Hz, $^3J_{PtH}$ = 38 Hz, *H*^{o}]; 7.33 [t, 1H, H$^{5'}$]; 7.73 [t, 1H, H^5]; 8.05 [d, 1H, H$^{3'}$]; 8.10−8.20 [m, 3H, H^3,H^4,H$^{4'}$]; 8.69 [d, 1H, $^3J_{PtH}$ = 56 Hz, H$^{6'}$]; 9.59 [d, 1H, $^3J_{PtH}$ = 15 Hz, H^6]. EI-MS: *m*/*z* = 494.0 [M$^+$].

[PtCl(4-C$_6$H$_4$OMe)(DPK)], 6a. This was prepared similarly but using DPK. Yield: 74%. Anal. Calcd for $C_{18}H_{15}ClN_2O_2Pt$: C, 41.43; H, 2.90; N, 5.59. Found: C, 40.96; H, 2.79; N, 5.20. NMR in CD_2Cl_2: $\delta(^1H)$ = 3.74 [s, 3H, O*Me*]; 6.60 [d, 2H, $^3J_{HH}$ = 8 Hz, H^m]; 6.94 [d, 2H, $^3J_{HH}$ = 8 Hz, $^3J_{PtH}$ = 41 Hz, H^o]; 7.31 [t, 1H, H$^{5'}$]; 7.74 [t, 1H, H^5]; 8.03 [d, 1H, H$^{3'}$]; 8.10−8.17 [m, 3H, H^3, H^4, H$^{4'}$]; 8.39 [d, 1H, $^3J_{PtH}$ = 60 Hz, H$^{6'}$]; 9.38 [d, 1H, $^3J_{PtH}$ = 16 Hz, H^6]. EI-MS: *m*/*z* = 521.0 [M$^+$]. IR (CH_2Cl_2): ν(CO) 1690 cm^{-1}.

[PtCl(4-C$_6$H$_4$OMe)(DPA)], 6b. This was prepared similarly but using DPA. Yield: 65%. Anal. Calcd for $C_{17}H_{16}ClN_3OPt$: C, 40.13; H, 3.17; N, 8.26. Found: C, 40.08; H, 3.48; N, 7.92. NMR in CD_2Cl_2: $\delta(^1H)$ = 3.72 [s, 3H, O*Me*]; 6.56 [d, 2H, $^3J_{HH}$ = 8 Hz, H^m]; 6.95 [d, 2H, $^3J_{HH}$ = 8 Hz, H^o]; 6.6 [t, 1H, H$^{5'}$]; 6.95 [t, 1H, H^5]; 7.17 [d, 1H, H$^{3'}$]; 7.29 [d, 1H, H^3]; 7.56 [t, 1H, H$^{5'}$]; 7.62 [t, 1H, H^5]; 7.94 [d, 1H, $^3J_{PtH}$ = 68 Hz, H$^{6'}$]; 8.98 [d, 1H, $^3J_{PtH}$ = 15 Hz, H^6]; 9.17 [s, 1H, N-*H*]. ESI-MS: *m*/*z* = 507.1 [M$^+$].

[Pt(O$_3$SCF$_3$)(4-C$_6$H$_4$OMe)(bipy)], 7b. To a solution of complex **6c** (100 mg, 0.20 mmol) in thf (10 mL) was added AgO_3SCF_3 (52 mg, 0.20 mmol). The mixture was stirred for 30 min at 0 °C and filtered through Celite, and the solvent evaporated. The product was extracted with benzene, the volume was reduced, and pentane was added to precipitate the product as a yellow powder. Yield: 38%. Anal. Calcd for $C_{19}H_{15}F_3N_2O_4PtS$: C, 36.84; H, 2.44; N, 4.52. Found: C, 37.17; H, 2.87; N, 4.29. NMR in CD_2Cl_2: $\delta(^1H)$ = 3.80 [s, 3H, O*Me*]; 6.83 [d, 2H, $^3J_{HH}$ = 8 Hz, *H*^{m}]; 7.38 [d, 2H, $^3J_{HH}$ = 8 Hz, *H*^{o}]; 7.88 [t, 1H, H$^{5'}$]; 8.22 [t, 1H, H^5]; 8.3−8.5 [m, 4H, H^3, H$^{3'}$,H^4,H$^{4'}$]; 8.48 [d, 1H, H$^{6'}$]; 8.77 [d, 1H, H^6].

[Pt(O$_3$SCF$_3$)(4-C$_6$H$_4$OMe)(bipy)], 7a. This was prepared similarly from complex **6a**. Yield: 41%. Anal. Calcd for $C_{20}H_{15}F_3N_2O_5PtS$: C, 37.10; H, 2.34; N, 4.33. Found: C, 37.21; H, 2.74; N, 4.15. NMR in CD_2Cl_2: $\delta(^1H)$ = 3.67 [s, 3H, O*Me*]; 6.53 [d, 2H, $^3J_{HH}$ = 8 Hz, *H*^{m}]; 6.71 [d, 2H, $^3J_{HH}$ = 8 Hz, *H*^{o}]; 7.35 [t, 1H, H$^{5'}$]; 7.80 [t, 1H, H^5]; 8.15−8.30 [m, 4H, H^3, H$^{3'}$,H^4,H$^{4'}$]; 8.08 [d, 1H, H$^{6'}$]; 9.04 [d, 1H, H^6].

[PtMe(4-C$_6$H$_4$OMe)(bipy)], 8b. To a solution of *trans*-[PtCl-(4-C$_6$H$_4$OMe)$(SMe_2)_2$] (100 mg, 0.216 mmol) in Me$_2$S (4 mL) at −78 °C was added MeLi (0.27 mL, 1.6 M in diethyl ether, 0.433 mmol). The mixture was stirred at −78 °C for 30 min, then allowed to warm to 0 °C. Ten drops of a cold solution of saturated, aqueous NH_4Cl was added, followed by the addition of bipy (33.8 mg, 0.216 mmol) in benzene (4 mL). The mixture was stirred at room temperature for 8 h, the solvent was evaporated under vacuum, and the orange product was recrystallized from CH_2Cl_2/pentane. Yield: 65 mg, 63%. Anal. Calcd for $C_{18}H_{18}N_2OPt$: C, 45.67; H, 3.83; N, 5.92. Found: C, 45.50; H, 3.61; N, 5.64. NMR in CD_2Cl_2: $\delta(^1H)$ = 1.03 [s, 3H, $^2J_{PtH}$ = 86 Hz, PtMe]; 3.78 [s, 3H, OMe]; 6.73 [d, 2H, $^3J_{H-H}$ = 8 Hz, H^m]; δ 7.27 [d, 2H, $^3J_{HH}$ = 8 Hz, $^3J_{PtH}$ = 65 Hz, H^o]; 7.40 [t, 1H]; 7.59 [t, 1H]; 8.06−8.18 [m, 4H]; 8.69 [d, 1H, $^3J_{PH}$ = 21 Hz]; 9.20 [d, 1H, $^3J_{PtH}$ = 20 Hz]. EI-MS: *m*/*z* = 472.9.

[PtMe(4-C$_6$H$_4$OMe)(DPK)], 8a. This was prepared in a similar way but using DPK as ligand. Yield: 45%. Anal. Calcd for $C_{19}H_{18}N_2O_2Pt$: C, 45.51; H, 3.62; N, 5.59. Found: C, 45.49; H, 3.48; N, 5.31. NMR in CD_2Cl_2: $\delta(^1H)$ = 0.88 [s, 3H, $^2J_{PtH}$ = 84 Hz, PtMe]; 3.75 [s, 3H, OMe]; 6.60 [d, 2H, $^3J_{HH}$ = 8 Hz, H^m]; 6.96 [d, 2H, $^3J_{HH}$ = 8 Hz, $^3J_{PtH}$ = 65 Hz, H^o]; 7.32 [t, 1H, H$^{5'}$]; 7.39 [t, 1H, H^5]; 8.04−8.15 [m, 4H, H^3, H^4, H$^{3'}$, H$^{4'}$]; 8.62 [d, 1H, $^3J_{PtH}$ = 21 Hz, H$^{6'}$]; 8.80 [d, 1H, $^3J_{PtH}$ = 20 Hz, H^6]. EI-MS: *m*/*z* = 500.9.

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Reactions with Acids. In a typical reaction, to a solution of complex **8b** (10 mg, 0.021 mmol) in CD_2Cl_2 (1 g) in an NMR tube cooled to −78 °C was added a solution of HCl in CD_2Cl_2 (80 μL, 0.788 M, 0.063 mmol). An immediate color change from orange to yellow was observed. The tube was inserted into the NMR probe cooled to −80 °C, and NMR spectra were recorded at 20 °C intervals as the probe was warmed slowly to room temperature. Reactions with deuterated acids were carried out similarly but using a 1:1 CD_2Cl_2/CD_3OD solvent mixture.

[Pt(OTf)Me$_2$(SiMe$_3$)(bipy)], 13. To a solution of Me_3SiOTf (50 μL, 0.32 mmol) in CD_2Cl_2 (0.5 g) in an NMR tube cooled to −78 °C was added a solution of [$PtMe_2$(bipy)], **12** (0.025 g, 0.064 mmol), in CD_2Cl_2 (1 g). An immediate color change from red to green was observed. The tube was inserted into the NMR probe cooled to −80 °C, and NMR spectra were recorded at 20 °C intervals as the probe was warmed slowly to room temperature. NMR in CD_2Cl_2: $\delta(^1H)$ = −0.16 [s, 9H, ^3J(PtH) = 21 Hz, MeSi]; 1.23 [s, 6H, ^2J(PtH) = 62 Hz, MePt]; 7.74 [m, 2H, H^5]; 8.20 [m, 2H, H^4]; 8.23 [m, 2H, H^3]; 8.84 [d, 2H, H6]. When the NMR tube was stored at 0 °C, crystals of [$Pt(O_3SCF_3)_2$(bipy)], **11b**, were deposited.

[Pt(bipy)(H$_2$O)$_2$](O$_3$SCF$_3$)$_2$·(H$_2$O)$_2$, ***14.*** To a stirred solution of Me_3SiOTf (250 μL, 1.6 mmol) in CH_2Cl_2 (3 g) at room temperature was added CD_3OD (64 μL, 1.6 mmol). The reaction mixture was then cooled to −78 °C, and a solution of [$PtMe_2$(bipy)], **12** (0.125 g, 0.32 mmol), in CH_2Cl_2 (5 g) was added dropwise. An immediate color change from red to green was observed. The reaction mixture was warmed slowly to room temperature. The color changed from green to colorless with development of a white precipitate. The solvent was decanted, and the solid was washed with CH_2Cl_2 twice and dried under vacuum. Yield: 78%. NMR in $(CD_3)_2CO$: $\delta(^1H)$ = 7.86−8.07 [br m, 2H, H^5]; 8.47 − 8.64 [br m, 4H, H^3, H^4]; 8.66−8.79 [br m, 2H, H^6]; $\delta(^{19}F)$ = −79.0 [s, 6F, CF_3]. The product was crystallized from CH_2Cl_2/pentane.

X-ray Structure Determinations. Data were collected by using a Nonius Kappa-CCD or a Bruker APEX-II diffractometer. Details of the data collections and structure refinements are given in the CIF files. In a typical procedure, the subject crystal was mounted and placed in the dry N_2 cold stream of the low-temperature apparatus attached to the diffractometer. The data were collected at 150 K using APEX2 software on a Bruker APEX-II CCD diffractometer with Mo Kα radiation (λ = 0.71073 Å).[32a] Multiscan absorption correction was performed using SADABS.[32b] The structure was solved by direct methods and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for the nondisordered heavy atoms using the SHELXL-97 software package.[32c,d]

Complex **11b** was disordered in two positions with the minor component at only 1.6%; only the platinum atom of the minor component was clearly resolved, and restraints were applied for the bipy atoms of this minor component. The disorder led to approximate inversion of the Pt(bipy) units. In complex **14**, the hydrogen atoms of the water molecules were not located, and so both the free and coordinated water molecules were treated as O atoms only.

DFT Calculations. Calculations were made using the Amsterdam Density Functional program based on the Becke−Perdew functional, with first-order scalar relativistic corrections. Transition-state structures were located using a linear transit scan.[33]

■ ASSOCIATED CONTENT

Supporting Information

Crystallographic data in electronic CIF form is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: pudd@uwo.ca.

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