Protonation of Platinum(II) Dialkyl Complexes Containing Ligands with Proximate H-Bonding Substituents

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The possibility of activating C−H bonds at a platinum(II) center that contains a ligand with a proximate H-bonding functionality, for example a NH_2 substituent, has been investigated. A series of platinum(II) dimethyl complexes [Pt(L)Me_2], where L is an unsymmetrically substituted bipyridine ligand, has been prepared. Protonation reactions in acetonitrile with 1 equiv of a strong acid generate cationic complexes of the type [Pt(L)Me(CH_3CN)]$^+$. The selectivity of the protonation reactions appears to be governed by steric effects rather than H-bonding effects. This is believed to be the result of the low basicity of the amino subsituent in 2-amino pyridines.

Introduction

Alkanes are notoriously difficult to functionalize selectively and are therefore currently underused as a chemical feedstock. With the advent of large-scale gas to liquid (GTL) processing,[1] higher alkanes are likely to become available in ever increasing amounts. The future efficient utilization of this carbon resource will depend on the development of highly active, selective, and stable catalysts that can convert these unreactive hydrocarbons into useful intermediates or products.[2−5] To this end, the activation of a C−H bond at a transition metal center is generally regarded as the first step toward alkane functionalization and has therefore received a great deal of attention during the last 20 years.[6−12]

Several modes of C−H activation have been identified and are summarized in Figure 1. Oxidative addition of a C−H bond (**A**) and σ-bond metathesis (**B**, where X is a carbon-based fragment) are classic examples of C−H activation at a single metal center. Electrophilic activation (**B**, where X is, for example, chloride) has attracted a great deal of interest in recent years because this C−H activation process constitutes the first step in the Shilov reaction and also in related reactions.[4,11,13] Other approaches such as the oxidative addition of a C−H bond across two metal centers (**C**)[14,15] or the addition across a metal−heteroatom multiple bond M=Y, where Y = CR_2 or NR (**D**), have also been explored.[16−18] In the case of Y = O in method **D**, C−H activation by high-valent metal oxo complexes has been investigated,[19,20] including studies involving non-heme iron systems.[21,22]

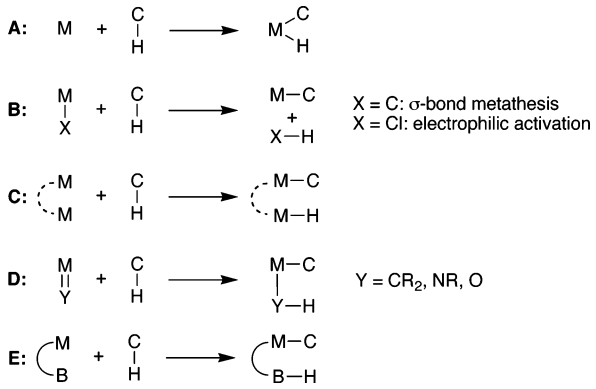

Figure 1. Various C−H activation modes.

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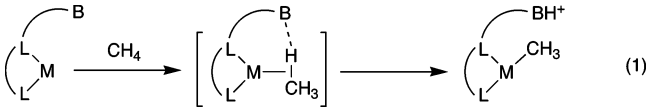
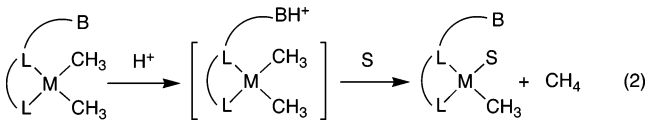
Several reports have shown that the binding of H_2 to a transition metal center containing a basic functionality in the proximity can lead to heterolytic cleavage of the H−H bond. Examples of such reactivity are the 2-aminobenzoquinolate iridium system developed by Crabtree[23] and a nickel PNP system developed by DuBois.[24] We were intrigued whether this reactivity could also be applied to alkanes, as it is known that the pK_a of an alkane (and of H_2) decreases dramatically upon coordination to a metal center,[8] and this could provide another C−H activation mode, schematically depicted as **E** in Figure 1. In this mode, which can also be viewed as a base-assisted electrophilic activation process, a basic H-bonding functionality is held in close proximity to the metal center, such that it cannot coordinate to the metal center, but it can interact with a hydrogen atom from a coordinated alkane. After C−H bond cleavage, the proton binds to the basic functionality and the metal will be left with the alkyl moiety (eq 1). An important advantage of this activation process is that only one coordination site at the metal center is occupied, leaving space for further reactivity.



(1)

The basic H-bonding functionality, for example a nitrogen base (C−H···N hydrogen bonding is well established),[25] should be more basic than the metal center, and the possibility of direct coordination to the metal center must be prevented. Energetically, this process is highly favorable, as the cost of cleaving a C−H bond (440 kJ/mol) is more than compensated by the formation of a Pt−CH_3 (251−268 kJ/mol) and a N−H^+ (343−533 kJ/mol) bond (cf. Pt−H bond enthalpies: 306−314 kJ/mol).[26,27] Very recently, the possibility of activating a C−H bond at a Pt(II) center using a basic donor (pyridine) near the metal center was elegantly demonstrated by Caulton and co-workers. An equilibrium was observed between a N−Pt^{IV}−H (the classic oxidative addition activation process **A**) and a N−H···Pt^{II} species (the base-assisted process **E**),[28,29] the latter being favored by electron-withdrawing ligands on the Pt center.

We started our investigations into the activation of alkanes via mode **E** with the preparation of platinum(II) complexes containing the 6-amino-substituted bipyridine ligand **1**. Surprisingly, no metal complexes containing this ligand have been reported. To determine whether the NH_2 substituent can act as a basic H-bonding functionality, we decided to investigate initially the microscopic reverse reaction, the protonation of a platinum(II) dimethyl complex.[9,12] The metal center is normally the kinetic site for protonation of platinum dimethyl complexes,[30] and in the case of a symmetrical bipyridine ligand there would be no preference for the subsequent reaction with either methyl group. However, if a basic H-bonding functionality is to assist in C−H bond cleavage, this basic H-bonding functionality may also favor the protonation of the methyl group closest to the basic group, as shown schematically in eq 2.



(2)

To distinguish between a H-bonding effect or an electronic or steric effect due to the 6-amino substituent, we also investigated variations such as **2**, **3**, and **4** (Figure 2). The phenanthroline ligand **4** was chosen to prevent the possibility of "rollover" cyclometalation as observed by Minghetti and co-workers for Pt(II) complexes containing a 6-alkyl-substituted bipyridine ligand such as **3**.[31,32]

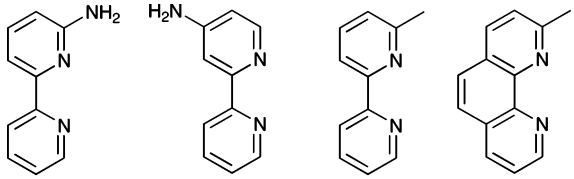
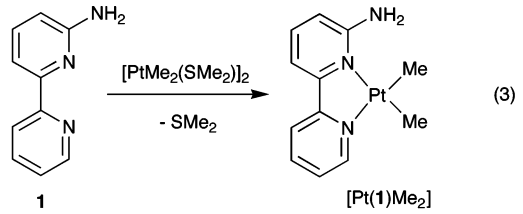


Figure 2. Functionalized ligands **1**−**4**.

Results and Discussion

Synthesis of Ligands and Complexes. Previously reported procedures for the synthesis of 6-aminobipyridine **1** by amination of 6-bromobipyridine gave only low and unreliable yields in our hands.[33,34] We therefore developed a new procedure, based on the method described by Lang et al., using 6-bromobipyridine, ammonia, and a catalytic amount of Cu_2O.[35] 6-Dimethylaminobipyridine **5** was prepared via a similar procedure using dimethylamine.

The reaction of **1**, **2**, and **4** with $[PtMe_2(SMe_2)]_2$ in toluene resulted in the clean formation of the platinum(II) dimethyl complexes [Pt(**1**)Me_2], [Pt(**2**)Me_2], and [Pt(**4**)Me_2] (eqs 3−5). The ^{1}H NMR spectra (in acetone-d_6) show the Pt-Me signals at 0.94/1.02 ppm for [Pt(**1**)Me_2], 0.78/0.85 ppm for [Pt(**2**)Me_2],



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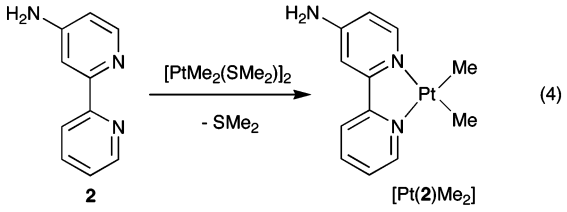

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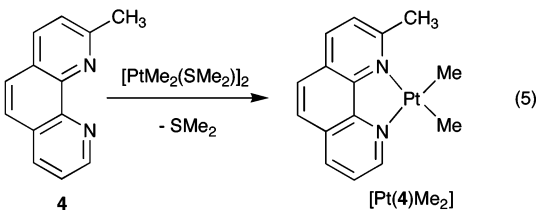

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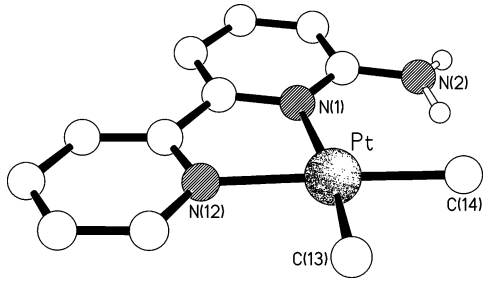
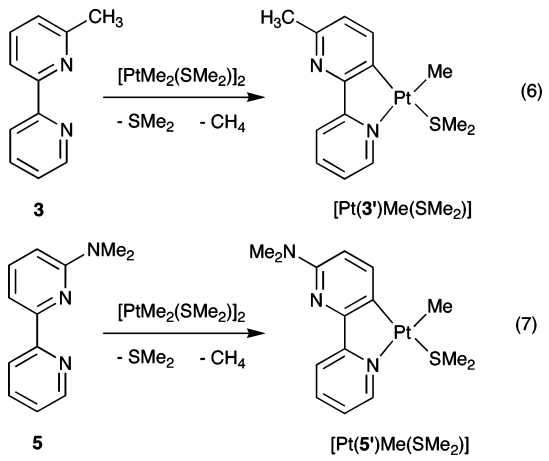


Figure 3. Molecular structure of [Pt(**1**)Me_2].

and 1.16/1.20 ppm for [Pt(**4**)Me_2] together with their characteristic Pt(II) satellites ($J_{Pt-H} \approx 85-90$ Hz).

The reaction of 6-methylbipyridine **3** with $[PtMe_2(SMe_2)]_2$ resulted in rollover cyclometalation, as previously observed by Minghetti for similar complexes (eq 6). In an attempt to increase the basicity of the 6-amino substituent, we also prepared the 6-dimethylamino derivative **5**. However, the reaction of this ligand with the platinum(II) precursor did not give the expected dimethyl platinum complex [Pt(**5**)Me_2] but the cyclometalated monomethyl product [Pt(**5′**)Me(SMe_2)] (eq 7). The increased size of the dimethylamino group compared to a simple NH_2 group apparently does not allow direct coordination, and a rotation followed by C−H activation and elimination of CH_4 occurs instead. The conformation of [Pt(**5′**)Me(SMe_2)] with the methyl group *trans* to the pyridine donor was confirmed by NOESY spectroscopy (see Figure S3).



Solid-State Structure. The molecular structure of complex [Pt(**1**)Me_2], as determined by X-ray crystallography, is depicted in Figure 3. The geometry of the complex was shown to be only slightly distorted from planarity with N(2) and C(13) ca. +0.14 and −0.14 Å out of the plane of the remaining non-hydrogen atoms, which are coplanar to within ca. 0.06 Å. The *cis* angles range from 77.34(16)° to 104.0(2)°, the most acute angle being associated with the bite of the bipyridyl ligand; the *trans* angles are 171.3(2)° and 178.4(2)° (Table 1). It is notable that the Pt−N distance to the N(1) pyridyl ring [2.180(4) Å] (the one that bears the NH_2 substituent) is ca. 0.1 Å longer than

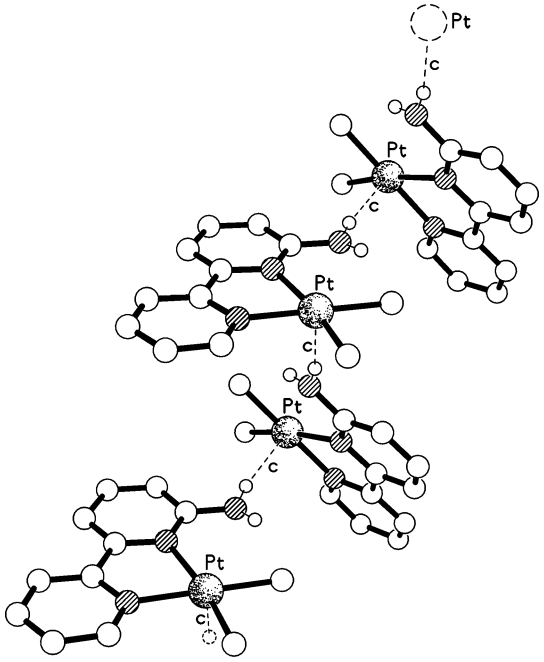


Figure 4. Molecular structure of [Pt(**1**)Me_2]. The N−H···Pt hydrogen bond (c) has N···Pt = 3.406(5) Å, H···Pt = 2.52 Å, and N−H···Pt = 170°.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for [Pt(1)Me_2].

Pt−N(1)	2.180(4)	Pt−N(12)	2.092(4)
Pt−C(13)	2.025(6)	Pt−C(14)	2.055(6)
N(1)−Pt−N(12)	77.34(16)	N(1)−Pt−C(13)	171.3(2)
N(1)−Pt−C(14)	104.0(2)	N(12)−Pt−C(13)	94.1(2)
N(12)−Pt−C(14)	178.4(2)	C(13)−Pt−C(14)	84.6(3)

that to N(12) [2.092(4) Å]. Since the bond lengths within the two pyridine rings are comparable, this is likely to be a steric rather than an electronic effect; the intramolecular N(2)···C(14) separation is only 3.026(9) Å. The two Pt−C distances are the same within statistical significance. Other than this lengthening of the Pt−N(1) bond, the coordination distances are comparable to those seen in the closely related complex [Pt(bipy)Me_2].[36] Likewise, the $C_{(py)}-NH_2$ bond length [1.351(8) Å] is comparable to those seen in other 2-aminopyridine compounds.[37] The NH_2 protons were located in the structure (see Experimental Section) and found to be coplanar with the adjacent pyridyl ring, giving a trigonal planar arrangement around the parent nitrogen, which suggests a significant degree of delocalization of the amine nitrogen lone pair into the aromatic ring.

The amino group is also involved in an intermolecular hydrogen-bonding interaction to the platinum center of a neighboring molecule (see Figure 4), with N···Pt and H··Pt distances of 3.406(5) and 2.52 Å and an N−H···Pt angle of 170°; the H···Pt vector is inclined by ca. 71° to the platinum coordination plane. This interaction is probably an indication of the basic character of the platinum center.

Protonation Studies. The reaction between [Pt(**1**)Me_2] and 1 equiv of the acid $[H(Et_2O)_2][BAr^F]$ (where $BAr^F = B(3,5-(CF_3)_2C_6H_3)_4$) was carried out at −20 °C in acetonitrile solution. After warming to room temperature, the product was isolated

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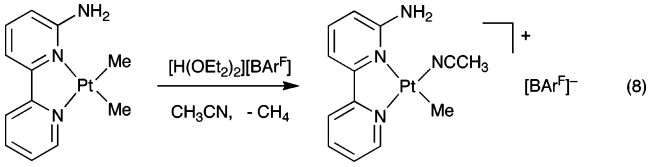
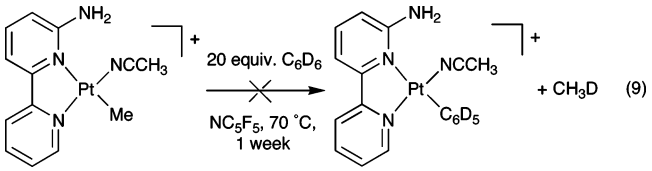
and characterized by ^{1}H and ^{13}C NMR spectroscopy. The protonation reaction resulted in the immediate loss of methane and the formation of a single product, [Pt(**1**)Me(CH$_3$CN)][BAr^F], containing a coordinated acetonitrile ligand (eq 8). The coordination of the acetonitrile ligand *cis* to the aminopyridine moiety was unambiguously confirmed by NOESY spectroscopy (see Figure S4). A strong interaction between the amine and acetonitrile protons, as well as between the Pt-methyl and the proton in the 6′-position of the unsubstituted pyridine ring, was observed.



(8)

[Pt(**1**)Me$_2$] [Pt(**1**)Me(CH$_3$CN)][BAr^F]

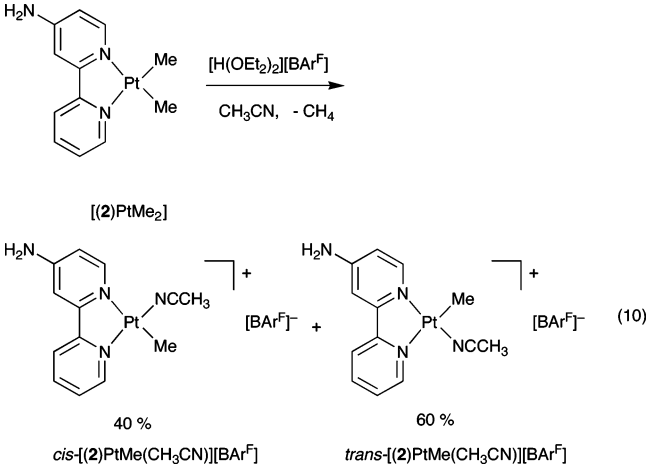
Attempts to activate C−H bonds were made, by reacting 20 equiv of benzene-d_6 with the complex [Pt(**1**)Me(CH$_3$CN)][BAr^F] in pentafluoropyridine for one week at 70 °C, but no reaction was observed (eq 9). C−H activation reactions at cationic Pt(II) complexes generally require a labile ligand in the coordination sphere of the platinum center.[9] Presumably the acetonitrile ligand is bound too strongly and inhibits substitution by the arene. Further attempts to generate cationic complexes of the type [Pt(**1**)Me(L)][BAr^F], where L is a more weakly coordinating ligand such as pentafluoropyridine or trifluoroethanol, were unsuccessful. In the case of pentafluoropyridine the resulting cationic complex was found to be unstable and rapidly decomposed (probably due to steric congestion), whereas in the case of trifluoroethanol, an immediate reaction occurred upon dissolution of [Pt(**1**)Me$_2$] in trifluoroethanol, resulting in several unidentifiable species.



(9)

The remarkable selectivity of the protonation reaction (eq 8) could be due to an electronic or steric effect (or both) or perhaps, and which is the purpose of these studies, a H-bonding effect as shown in eq 2. To distinguish between these three possible effects, we have carried out similar protonation reactions with complexes [Pt(**2**)Me$_2$] and [Pt(**4**)Me$_2$]. The 4-amino substituent in complex [Pt(**2**)Me$_2$] should provide an electronic effect on the pyridine nitrogen donor similar to that of a 2-amino substituent, and therefore a similar selectivity would be expected if the protonation reaction was simply governed by an electronic effect due to the amino substituent. Protonation of [Pt(**2**)Me$_2$] under the same conditions as for [Pt(**1**)Me$_2$] resulted in a mixture of two isomeric products, *cis*- and *trans*-[Pt(**2**)Me(CH$_3$CN)]-[BAr^F], in a 40/60 ratio (eq 10). The identity of each complex was unambiguously confirmed by NMR, including NOESY (Figure S5), but the two isomers could not be separated and characterized individually.

The 40/60 ratio observed is close to the 50/50 ratio expected for the protonation of [Pt(bipy)Me$_2$], which indicates that the contribution of an electronic effect due to an amino substituent in the 4-position is small. A similar weak electronic effect can be expected from the 2-amino substituent in [Pt(**1**)Me$_2$], and the selectivity seen in eq 8 is therefore more likely due to another



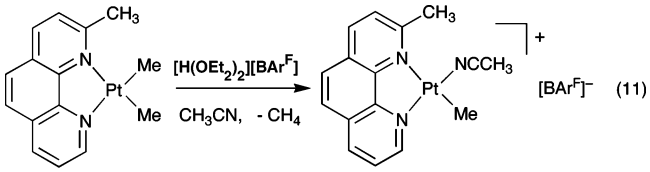
[(**2**)PtMe$_2$]

cis-[(**2**)PtMe(CH$_3$CN)][BAr^F] *trans*-[(**2**)PtMe(CH$_3$CN)][BAr^F]

(10)

effect. In addition, the 4-amino substitution favors the protonation of the *trans* methyl group, resulting in an excess of the opposite isomer as observed in the case of [Pt(**1**)Me$_2$]. This is most likely due to the stronger *trans* effect of the substituted pyridine donor weakening this particular Pt−methyl bond.

The possibility of sterics governing the protonation of complex [Pt(**1**)Me$_2$] was investigated by substituting the NH$_2$ for a CH$_3$ group. Protonation of complex [Pt(**4**)Me$_2$] under the same conditions as above afforded a single product, [Pt(**4**)Me-(CH$_3$CN)][BAr^F], which was isolated and confirmed by NOESY spectroscopy (Figure S6) to be the isomer with a coordinated acetonitrile ligand *cis* to the methyl-substituted side of the ligand (eq 11).



(11)

[(**4**)PtMe$_2$] [(**4**)PtMe(CH$_3$CN)][BAr^F]

From these studies we can conclude that the protonation of complex [Pt(**4**)Me$_2$] and therefore also of [Pt(**1**)Me$_2$] is predominantly governed by steric effects. The clash between the amino or methyl group in the 6-position of the pyridine donor and the Pt-methyl group in *cis* position weakens this Pt−N bond, consistent with the bond distances observed in the molecular structure of complex [Pt(**1**)Me$_2$].

Protonation of the 2-amino substituent in [Pt(**1**)Me$_2$] was never observed, even at low temperature. In addition, the protonation of [Pt(**1**)Cl$_2$] at room temperature led to decomposition, and again no protonation on the amino substituent was observed, probably due to the reduced basicity. The lone pair on the amino nitrogen atom in 2-aminopyridines such as **1** is tied up in the delocalized π-system, resulting in a planar sp^2-hybridized nitrogen atom as seen in the solid-state structure of [Pt(**1**)Me$_2$], and this lone pair is therefore not available for protonation. Indeed, the pK_a value of the conjugate acid of 2-aminopyridinium is only −7.6.[38] It thus appears that our initial choice of ligand containing a basic functionality in the proximity of the metal center was not suitable, and we are currently investigating other ligand types. However, the valuable lessons learned and described here may inspire new directions in the development of C−H activating systems.

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Experimental Section

All moisture-sensitive compounds were manipulated using standard vacuum line, Schlenk, or cannula techniques or in a conventional nitrogen-filled glovebox. NMR spectra were recorded on either a Bruker AC-250 or a DRX-400 spectrometer; chemical shifts for ^{1}H and ^{13}C NMR are referenced to the residual protio impurity and to the ^{13}C NMR signal of the deuterated solvent. Mass spectra were recorded on either a VG Autospec or a VG Platform II spectrometer. Elemental analyses were performed by the Science Technical Support Unit at the London Metropolitan University.

Solvents and Reagents. Toluene and pentane were dried by passing through a column, filled with commercially available Q-5 reagent (13 wt % CuO on alumina) and activated alumina (pellets, 3 mm). Diethyl ether and tetrahydrofuran were dried over potassium metal with a benzophenone ketyl indicator, whereas dichloromethane and acetonitrile were dried over CaH_2. The following compounds were prepared according to literature procedures: 6-bromo-2,2′-bipyridine,[39] 4-amino-2,2′-bipyridine (**2**),[40] 2-methyl-1,10-phenanthroline (**4**),[41] $[PtCl_2(SMe_2)_2]$,[42] $[PtMe_2(SMe_2)]_2$,[42] and $[H(Et_2O)_2][BAr^F{}_4]$[43] (where $BAr^F{}_4 = B(3,5\text{-}(CF_3)_2C_6H_3)_4$). 4-Amino-2,2′-bipyridine (**2**) was purified by sublimation (140 °C, 0.5 mbar), as was 2-methyl-1,10-phenanthroline (**4**) (135 °C, 0.1 mbar). Pentafluoropyridine and trifluoroethanol were purchased from Apollo and distilled over 4 Å molecular sieves prior to use.

Synthesis of Ligands and Complexes. 6-Amino-2,2′-bipyridine (1). An autoclave was loaded with 0.52 g (2.2 mmols) of 6-bromo-2,2′-bipyridine and dissolved in 15 mL of ethylene glycol, to which 2.5 mg of copper(I) oxide was added. This was cooled to −40 °C, and 10 mL of liquid ammonia was added to the solid mixture. The autoclave was sealed and allowed to warm to room temperature and then heated to 110 °C for 16 h. After the autoclave had cooled and vented, the resultant red solution was poured from the autoclave into a beaker and the autoclave then flushed with 15 mL of water, which was added to the red solution. A further 20 mL of water was added to the mixture such that it turned brown. The basic aqueous solution was then extracted with 3 × 25 mL portions of dichloromethane. The combined extracts were washed with 2 × 15 mL potions of water and saturated brine solution, dried over magnesium sulfate, and evaporated under reduced pressure. The resultant brown solid was recrystallized from hot hexane. Yield: 0.24 g (63%). ^{1}H NMR ($CDCl_3$): 4.49 (br, 2H, N*H*$_2$), 6.55 (d, 1H, J = 8.0 Hz, Ar−*H*), 7.26 (m, 1H, Ar−*H*), 7.57 (t, 1H, J = 7.9 Hz, Ar−*H*), 7.75 (m, 2H, Ar−*H*), 8.26 (d, 1H, J = 8.0 Hz, Ar−*H*), 8.66 (d, 1H, J = 4.7 Hz, Ar−*H*). ^{13}C NMR ($CDCl_3$): 158.0, 156.3, 154.5, 149.1, 138.6, 136.7, 123.3, 121.0, 111.6, 109.0. MS (CI, *m*/*z* (%)): 172 (100).

6-(Dimethylamino)-2,2′-bipyridine (5). 6-(Dimethylamino)-2,2′-bipy was prepared by the same procedure as for 6-aminobipyridine, from 6-bromo-2,2′-bipy and dimethylamine (33% in EtOH), and the crude product was purified by vacuum distillation (100 °C, 0.1 mbar) to give a yellow oil. Yield: 55%. ^{1}H NMR ($CDCl_3$): 3.16 (s, 6H, N(C*H*$_3$)$_2$), 6.56 (dd, 1H, J = 0.8, 8.2 Hz, Ar−*H*), 7.24 (ddd, 1H, J = 1.2, 4.8, 7.4 Hz, Ar−*H*), 7.63 (m, 2H, Ar−*H*), 7.77 (td, 1H, J = 1.8, 7.6 Hz, Ar−*H*), 8.42 (dt, 1H, J = 1.0, 8.0 Hz, Ar−*H*), 8.64 (ddd, 1H, J = 0.8, 1.8, 4.8 Hz, Ar−*H*). ^{13}C NMR ($CDCl_3$): 158.8, 157.1, 153.7, 148.8, 138.0, 136.6, 123.1, 120.9, 108.7, 106.1, 38.0. MS (CI, *m*/*z* (%)): 200 (100).

6-Amino-2,2′-bipyridineplatinum(II) Dichloride [Pt(1)Cl$_2$]. A 25 mL round-bottom flask was loaded with $Pt(SMe_2)_2Cl_2$ (0.390 g, 1 mmol) and 6-amino-2,2′-bipyridine (1) (0.171 g 1 mmol), after which 10 mL of $CHCl_3$ was added. Once dissolution was complete, the clear yellow solution was refluxed for 3 h, during which time a yellow solid had formed. The solid was filtered and washed with 3 × 5 mL of cold $CHCl_3$ and subsequently dried under vacuum. Yield: 0.372 g (0.85 mmol, 85%). ^{1}H NMR ($(CD_3)_2SO$): 6.80 (d, 1H, J = 1.2, 8.5 Hz), 7.60−7.68 (m, 2H), 7.74 (t, 1H), 8.26 (t, 1H), 8.33 (d, 1H, J = 7.1 Hz), 8.42 (br, NH_2), 9.65 (d, 1H). ^{13}C NMR ($(CD_3)_2SO$): 112.0, 116.7, 123.2, 126.0, 138.3, 140.0, 147.8, 153.4, 158.7, 162.9.

6-Amino-2,2′-bipyridineplatinum(II) Dimethyl [Pt(1)Me$_2$]. A 50 mL Schlenk tube was loaded with $[PtMe_2(SMe_2)]_2$ (0.239 g 0.41 mmol) and 6-amino-2,2′-bipyridine (**1**) (0.142 g, 0.82 mmol), to which was added 10 mL of dry toluene. The toluene immediately turned yellow, and an orange precipitate began to form. The suspension was allowed to stir for 24 h, after which time the toluene solution was heavy with an orange precipitate. The volume was reduced to approximately 2 mL and the resulting suspension washed with 3 × 15 mL of dry pentane. The product was dried under vacuum, yielding a yellow solid. Yield: 0.23 g, (69%). ^{1}H NMR ($(CD_3)_2CO$): 0.94 (s, 3H, $^2J_{PtH}$ = 87.1 Hz, PtMe), 1.02 (s, 3H, $^2J_{PtH}$ = 85.3 Hz, PtMe), 6.62 (br, NH_2), 6.91 (t, 1H, Ar−*H*), 7.51−7.60 (m, 2H, Ar−*H*), 8.15−8.25 (m, 2H, Ar−*H*), 9.08 (d, 1H, $^3J_{PtH}$ = 25.5 Hz, Ar−*H*). ^{13}C NMR ($(CD_3)_2CO$): −22.1 (Pt−*C*), −12.8 (Pt−*C*), 111.9, 113.2, 123.8, 126.7, 137.1, 138.1 146.7, 155.8, 158.8, 161.3. MS (FAB, *m*/*z* (%)): 396 (50), 381 (60), 366 (55). Anal. Calcd for $C_{12}H_{15}N_3Pt$: C, 36.36; H, 3.81; N, 10.60. Found: C, 36.16; H, 3.77; N, 10.66. Crystals of [Pt(**1**)Me$_2$] were grown by cooling a saturated acetone solution to −30 °C for 1 week. Crystal data for [Pt(**1**)Me$_2$]: $C_{12}H_{15}N_3Pt$, M = 396.36, orthorhombic, *Pbca* (no. 61), a = 16.8836(5) Å, b = 7.7972(3) Å, c = 17.9120(6) Å, V = 2358.02(14) Å^3, Z = 8, D_c = 2.233 g cm^{-3}, μ(Mo Kα) = 11.876 mm^{-1}, T = 173 K, yellow plates, Oxford Diffraction Xcalibur 3 diffractometer; 4052 independent measured reflections, F^2 refinement, R_1 = 0.047, wR_2 = 0.123, 3987 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max}$ = 66°], 155 parameters. The NH_2 protons were located from a ΔF map and refined subject to a distance constraint. CCDC 288812.

4-Amino-2,2′-bipyridineplatinum(II) Dimethyl [Pt(2)Me$_2$]. This was prepared by the same procedure as for **1a** as a light yellow solid. Yield: 0.27 g, (72%). ^{1}H NMR ($(CD_3)_2CO$): 0.78 (s, 3H, $^2J_{PtH}$ = 86.1 Hz, PtMe), 0.85 (s, 3H, $^2J_{PtH}$ = 86.4 Hz, PtMe), 6.18 (br, NH_2), 6.86 (dd, 1H, J = 2.4, 6.4 Hz, Ar−*H*), 7.56 (m, 2H, Ar−*H*), 8.09 (d, 1H, J = 7.9 Hz, Ar−*H*), 8.23 (td, 1H, J = 1.5, 7.6 Hz, Ar−*H*), 8.55 (d, 1H, $^3J_{PtH}$ = 21.1 Hz, J = 6.4 Hz, Ar−*H*), 9.11 (d, 1H, $^3J_{PtH}$ = 27.3 Hz, J = 5.5 Hz, Ar−*H*). ^{13}C NMR ($(CD_3)_2CO$): −17.0 (Pt−*C*, $^1J_{PtC}$ = 828 Hz), −16.8 (Pt−*C*, $^1J_{PtC}$ = 826 Hz), 108.3, 111.5, 123.2, 127.5, 136.9, 146.9, 147.2, 155.9, 157.5, 157.9. MS (FAB, *m*/*z* (%)): 396 (40), 381 (100), 366 (80). Anal. Calcd for $C_{12}H_{15}N_3Pt$: C, 36.36; H, 3.81; N, 10.60. Found: C, 36.29; H, 3.70; N, 10.75.

2-Methylphenanthrolineplatinum(II) Dimethyl [Pt(4)Me$_2$]. A 50 mL Schlenk tube was loaded with $[PtMe_2(SMe_2)]_2$ (0.162 g, 0.28 mmol) and 2-methyl-1,10-phenanthroline (**4**) (0.099 g, 0.510 mmol) to which was added 10 mL of dry toluene to form a red solution. After several minutes of stirring, an orange precipitate began to form. The suspension was allowed to stir overnight. The red toluene solution was filtered, and the resulting orange-yellow solid was washed with two further portions of toluene (15 mL in total). The solid was washed with three portions of pentane (60 mL in total) and dried under vacuum. Yield: 0.11 g (52%). ^{1}H NMR ($(CD_3)_2CO$): 1.16 (s, 3H, $^2J_{PtH}$ = 87 Hz, PtMe), 1.20 (s, 3H, $^2J_{PtH}$ = 89 Hz, PtMe), 3.03 (s, 3H, C−C*H*$_3$), 7.90 (m, 2H, Ar−*H*), 8.02 (s, 2H, Ar−*H*), 8.65 (d, 1H, J = 8.24 Hz, Ar−*H*), 8.85 (dd, 1H, J = 1.5, 8.2 Hz, Ar−*H*), 9.50 (dd, 1H, $^3J_{PtH}$ = 23.8

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Hz, Ar−*H*). ^{13}C NMR ((CD$_3$)$_2$CO): −17.9 (Pt−*C*, $^1J_{PtC}$ = 832 Hz), −14.2 (Pt−*C*, $^1J_{PtC}$ = 858 Hz), 27.5 (C−*C*H$_3$), 126.2 (J_{PtC} = 21 Hz), 126.9, 128.2, 128.5, 129.3, 131.9, 136.3, 137.1, 146.5 (J_{PtC} = 34 Hz), 148.6, 149.3, 164.4 (Ar *C*, J_{PtC} = 31 Hz). MS (FAB, *m*/*z* (%)): 419 (50), 404 (65), 388 (100). Anal. Calcd for $C_{15}H_{16}N_2Pt$: C, 42.96; H, 3.85; N, 6.68. Found: C, 42.89; H, 3.87; N, 6.58.

(6-Dimethylaminobipyridine)(dimethyl sulfide)platinum Methyl [Pt(5′)Me(SMe$_2$)]. A 50 mL Schlenk tube was loaded with [PtMe$_2$(SMe$_2$)]$_2$ (0.239 g, 0.41 mmol) to which was added 10 mL of dry diethyl ether. A 25 mL Schlenk was loaded with 6-(dimethylamino)-2,2′-bipyridine (**5**) which was dissolved in 10 mL of dry diethyl ether and added via cannula to the suspension of [PtMe$_2$(SMe$_2$)]$_2$. Upon addition, the ether suspension turned opaque red and was allowed to stir for 10 min. Subsequently, all volatiles were removed, leaving a sticky red solid. The solid was redissolved in 10 mL of diethyl ether and filtered, and subsequently pentane was added to precipitate a yellow solid. The solid was filtered and washed with two further portions of pentane, then dried in vacuo. Yield: 0.22 g (75%). ^{1}H NMR ((CD$_3$)$_2$CO): 0.87 (s, 3H, ^2JPt−H = 84.0 Hz, Pt−CH$_3$), 2.47 (s, 6H, ^3JPt−H = 26.7 Hz, S(CH$_3$)$_2$), 3.06 (s, 6H, N(CH$_3$)$_2$) 6.60 (d, 1H, J = 8.3 Hz, ^4JPt−H = 15.8 Hz), 7.40 (m, 1H), 7.76 (d, 1H, J = 8.4 Hz, ^3JPt−H = 55.2 Hz), 8.03 (td, 1H, J = 1.6, 7.5 Hz), 8.16 (d, 1H, J = 7.9 Hz), 8.85 (d, 1H, J = 5.3 Hz, ^3JPt−H = 16.4 Hz). ^{13}C NMR ((CD$_3$)$_2$CO): −15.52 (Pt−CH$_3$), 19.87 (S(CH$_3$)$_2$), 38.28 (N(CH$_3$)$_2$), 108.3, 121.7, 124.9, 135.2, 138.6 141.8, 146.2, 155.5, 157.5, 165.0.

[(6-Amino-2,2′-bipyridine)(acetonitrile)platinum(II)methyl][BAr^F] [Pt(1)Me(CH$_3$CN)][BAr^F]. Two Schlenk flasks were loaded, one with [Pt(**1**)Me$_2$] (21.3 mg, 0.054 mmol) and the other with [H(Et$_2$O)$_2$][BAr$^F_4$] (53.7 mg, 0.053 mmol). Subsequently, ca. 20 mL of dry acetonitrile was added to [Pt(**1**)Me$_2$] and the suspension stirred until as much of the solid had dissolved as possible. [H(Et$_2$O)$_2$][BAr$^F_4$] was dissolved in approximately 10 mL of dry acetonitrile. The yellow suspension of [Pt(**1**)Me$_2$] was then cooled to −20 °C, and the acetonitrile solution of [H(Et$_2$O)$_2$][BAr$^F_4$] was added dropwise over the course of an hour, via cannula, over which time the yellow suspension turned to an orange solution. The solution was allowed to warm to room temperature, during which time no further changes were apparent. All volatiles were subsequently removed to yield a sticky solid. ^{1}H NMR ((CD$_3$)$_2$CO): 1.03 (s, 3H, $^2J_{PtH}$ = 77.3 Hz PtMe), 2.82 (s, 3H, $^4J_{PtH}$ = 14.9 Hz C*H*$_3$CN), 6.08 (br, NH$_2$), 7.19 (d, 1H, Ar−*H*), 7.71−7.80 (m, 2H, Ar−*H*), 7.89 (t, 1H, Ar−*H*), 8.34 (td, 1H, Ar−*H*), 8.41 (td, 1H, Ar−*H*), 8.91 (d, 1H, $^3J_{PtH}$ = 61.2 Hz, Ar−*H*). ^{13}C NMR ((CD$_3$)$_2$CO): −10.4 (Pt−*C*), 4.7 (NC*C*H$_3$), 113.3, 115.0, 118.0 (B*p*-*Ar*^{F}), 119.0, 123.8, 125 (q, BAr−*C*F$_3$, J_{CF} = 271 Hz), 126.8, 129.3 (q, B*m*-*Ar*^{F}, J_{CF} = 31 Hz), 131.0, 135.2 (B*o*-*Ar*^{F}), 140.4, 149.0, 151.5, 159.4, 160.2, 162.2 (q, B−*C*, J_{CB} = 50 Hz).

[(4-Amino-2,2′-bipyridine)(acetonitrile)platinum(II)methyl][BAr^F] [Pt(2)Me(CH$_3$CN)][BAr^F]. This was prepared by the same procedure as for [Pt(**1**)Me(CH$_3$CN)][BAr^F] as a mixture of two isomers. ^{1}H NMR ((CD$_3$)$_2$CO): 0.83 (s, $^2J_{PtH}$ = 75.1 Hz, PtMe), 0.86 (s, $^2J_{PtH}$ = 76.9 Hz, PtMe), 2.81 (s, $^4J_{PtH}$ = 14.6 Hz, C*H*$_3$CN), 2.84 (s, $^4J_{PtH}$ = 14.6 Hz, C*H*$_3$CN), 6.69 (br, N*H*$_2$) 6.90−6.99 (m), 8.25−8.39 (m), 8.93−9.00 (m). Further assignment of isomers was by NOESY spectroscopy (see Figure S5).

[(2-Methylphenanthroline)(acetonitrile)platinum(II)methyl][BAr^F] [Pt(4)Me(CH$_3$CN)][BAr^F]. This was prepared by the same procedure as for [Pt(**1**)Me(CH$_3$CN)][BAr^F]. ^{1}H NMR ((CD$_3$)$_2$CO): 1.23 (s, 3H, $^2J_{PtH}$ = 76.6 Hz, PtMe), 2.93 (s, 3H, $^4J_{PtH}$ = 15.3 Hz, C*H*$_3$CN), 3.10 (s, 3H, C−C*H*$_3$), 7.67 (s, 4H, B*Ar*^{f}), 7.78 (s, 8H, B*Ar*^{f}), 8.10 (m, 2H, Ar−*H*), 8.21 (m, 2H, Ar−*H*), 8.82 (d, 1H, J = 8.5 Hz, Ar−*H*), 9.00 (dd, 1H, J = 8.2, 1.2 Hz, Ar−*H*), 9.34 (dd, 1H J = 5.5, 1.2 Hz, $^3J_{PtH}$ = 62.9 Hz, Ar−*H*). ^{13}C NMR ((CD$_3$)$_2$CO): −11.8 (Pt−*C*), 4.0 (NC*C*H$_3$), 26.9 (2-*C*H$_3$), 118.4 (B*p*-*Ar*^{F}), 125 (q, BAr−*C*F$_3$, J_{CF} = 272 Hz), 126.5, 127.6 129.1, 129.7, 130.0 (q, B*m*-*Ar*^{F}, J_{CF} = 47 Hz), 132.1, 135.5 (B*o*-*Ar*^{F}), 140.2, 141.2, 150.3, 162.5 (q, B−*C*, J_{CB} = 50 Hz), 164.0.

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Supporting Information Available: Crystallographic information as well as an ORTEP diagram for [Pt(**1**)Me$_2$] and NOESY NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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