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Intramolecular C–H activation by dicationic Pt(II) complexes

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Abstract

The dicationic complexes [(ArN=C(Me)–C(Me)=NAr)Pt(solv)$_2$]X$_2$, (Ar = 2,6-(CH$_3$)$_2$C$_6$H$_3$; **5a**: solv = CH$_3$CN, X = CF$_3$SO$_3^-$, BF$_4^-$, SbF$_6^-$; **5b**: solv = (CH$_3$)$_2$CO, X = BF$_4^-$, SbF$_6^-$) and [(CyN=C(H)–C(H)=NCy)Pt(CH$_3$CN)$_2$]X$_2$, (Cy = C$_6$H$_{11}$, **6**: X = OTf$^-$, BF$_4^-$, PF$_6^-$, SbF$_6^-$) were synthesized from the corresponding Pt dichlorides with two equivalents of AgX. The reactions of **5a** with 1-phenylpyrazole, 2-phenylpyridine, 2-vinylpyridine, and 2-(2-thienyl)pyridine afford the cyclometalated products **11–14** via intramolecular C–H activation of an sp^2 C–H bond of the unsaturated sidegroup. Pyridines with saturated groups at the 2-position do not undergo a similar cyclometalation reaction. In trifluoroethanol-d$_3$ solution, **6** undergoes cyclometalation of one of the cyclohexyl groups, an example of sp^3 C–H bond activation. The latter reaction proceeds only partway to completion, implying that an equilibrium has been reached; in the case where X = OTf$^-$ the equilibrium favors the starting dication.

Keywords: Dicationic complexes; Activation; Cyclometalation; Platinum

1. Introduction

The "Shilov system" represents the first example of homogeneous alkane functionalization [1] in which simple (or unactivated) alkanes, including methane, are oxidized to mixtures of alcohols and alkyl chlorides in aqueous solution. The process is catalytic in [PtCl$_4$]$^{2-}$ and requires stoichiometric [PtCl$_6$]$^{2-}$ (Eq. (1)) [2–4].

$$\mathrm{R{-}H + PtCl_6^{2-} + H_2O(HCl)} \xrightarrow[\mathrm{H_2O,120\,^\circ C}]{\mathrm{PtCl_4^{2-}}} \mathrm{R{-}OH(R{-}Cl) + PtCl_4^{2-} + 2HCl} \qquad (1)$$

It is generally accepted that the C–H activation or actual cleavage of the C–H bond governs the overall rate and selectivity for this alkane functionalization reaction (Eq. (2)). Unfortunately, the instability of the resulting Pt(II) alkyl complex towards protonolyis in protic media and its tendency to disproportionate in aprotic media has precluded the direct mechanistic study of this key reaction in the actual Shilov system [5–7]. We have reported mechanistic studies on the microscopic reverse of the C–H activation reaction—the protonolysis of the Pt alkyl bond—for a series of ligand-stabilized alkyl Pt(II) complexes [8,9]. Insights gained from these studies ultimately led to the development of cationic diamine [10,11], tris(pyrazolyl)borate [12,13], and α-diimine [14] supported Pt(II) complexes capable of activating alkanes under mild conditions. Key features of

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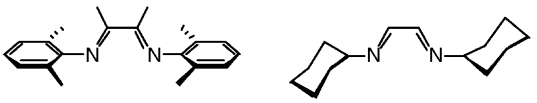


1 2

Fig. 1. Representative aryl and alkyl α-diimine ligands.

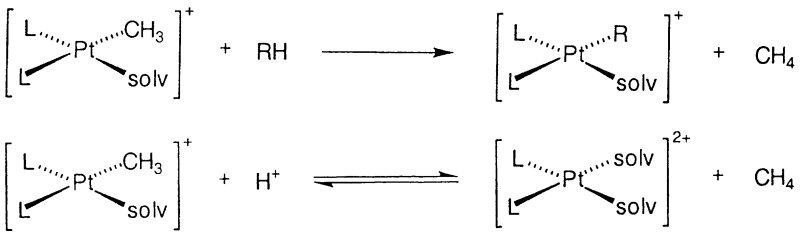
these systems include an electrophilic metal center, a non-coordinating counter-anion, a substitutionally labile fourth ligand, and the use of a non-oxidizable and extremely weakly coordinating solvent.

(2)

Cationic group 10 transition metal complexes of the general type $[(N–N)M(CH_3)(solv)]^+[WCA]^-$ (M = Ni, Pd; N–N = α-diimine; solv = Et_2O, CH_3CN; WCA = weakly coordinating anion) have been applied to a variety of important catalytic transformations [15].[2] Pt(II) complexes $[(N–N)Pt(CH_3)L]^+[BF_4]^-$ (where N–N = bis (aryl)diimine; L = CH_3CN, H_2O, CF_3CH_2OH) are thermally more robust than the corresponding Pt(II) diamine (*N*,*N*,*N*′,*N*′-tetramethylethylenediamine) complexes, probably because of the α-diimines' ability to bind to the metal both as a moderately strong σ-donor and weak π-acceptor [16,17]. Perhaps more importantly, the versatility of the α-diimine synthesis permits both the steric and electronic parameters of the ligand to be varied relatively easily [18], making these complexes well-suited for mechanistic studies aimed at elucidating the steric and electronic requirements, as well as the inherent selectivity of the Pt center in the C–H activation of alkanes under mild conditions [19,20]. Two representative α-diimine ligands are shown in Fig. 1.

[2] For a review of α-diimine ligated late transition metal olefin polymerization complexes, see [15].

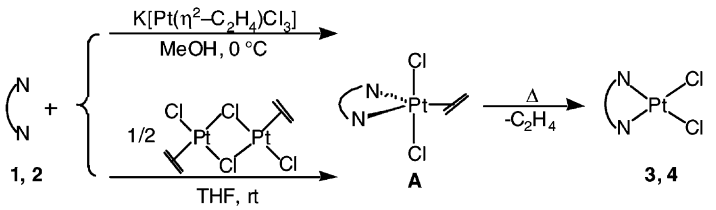
However, nearly all previous model studies involve a metathesis-like stoichiometry, in which one hydrocarbyl group replaces a methyl group which departs with the hydrogen atom as methane (Eq. (3)), We have not yet demonstrated the exact analog of Eq. (2), Pt-alkyl formation with proton loss, which is required in a functioning catalyst based on Shilov chemistry. In trying to design such a model, we noted that the methyl groups of Pt(II) cations $[L_2Pt(CH_3)(solv)]^+$ are relatively stable towards protonolysis, compared to the neutral dimethyl or chloromethyl Pt(II) complexes which are readily protonated to generate methane [21]. For example, the methyl acetonitrile cations $[(N–N)Pt(CH_3)(NCCH_3)]^+[BF_4]^-$ (N–N = **1**, **2**) can be prepared quantitatively by treating the neutral dimethyl Pt(II) complexes even using a slight excess of HBF_4 in CH_3CN [14]. More remarkably, the methyl group in the cationic Pt(II) complex $[((C_2F_5)_2PCH_2CH_2P(C_2F_5))Pt(Me)CO]^+$ resists protonolysis even in the superacid mixture SbF_5/FSO_3H [22].



(3)

(4)

It is unclear whether this reduced reactivity is primarily a kinetic or equilibrium effect. While the equilibrium shown in Eq. (4) probably lies to the right in most or all cases, we reasoned that the increased electrophilicity of a dicationic Pt(II) center, as compared to a monocationic one, would favor deprotonation, whether from a coordinated C–H bond or a subsequent Pt(IV) alkylhydride intermediate. This would lead to facile exchange of H^+ with D^+ from the solvent and overall incorporation of deuterium into the alkane substrate, which might be detected even if the equilibrium of Eq. (4) does lie well to the right. However, studies on intermolecular C–H activation of arenes such as



Scheme 1.

benzene and xylene in trifluoroethanol-d_3 were inconclusive, since we were unable to rule out competing H/D exchange catalyzed by traces of acid.

Accordingly, we turned our attention to intramolecular C–H activation to generate cyclometalated complexes, where the favorable entropy change of chelation would be expected to provide an additional driving force. There is ample precedent for this behavior [23,24], including related platinum complexes [25–29]. We report here C–H bond activation and deprotonation processes for Pt(II) complexes with the diimine auxiliary ligands **1** and **2**.

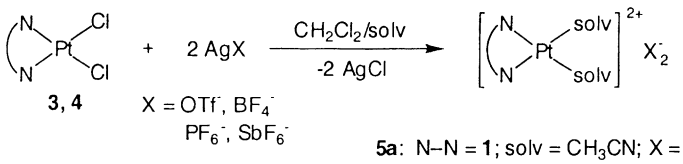
2. Results and discussion

2.1. Preparation of dicationic solvento complexes *3* and *4*

The complexes examined in this study were prepared from the corresponding (N–N)$PtCl_2$ complexes **3** (N–N = **1**) and **4** (N–N = **2**). The dichlorides are prepared by adding the appropriate α-diimine to a solution of Zeise's anion in methanol at 0 °C [30] or to a THF solution of the neutral dimer [31] (Scheme 1).

Upon addition of the ligand, the 5-coordinate, 18 e^- intermediate **A** precipitated from methanol solution. This intermediate is generally more soluble in non-polar halogenated solvents and ethers. The propensity of intermediate **A** to liberate ethylene to afford the corresponding dichloride complexes depends on the steric bulk imparted by the substituents on the imine nitrogens in the axial regions above and below the trigonal plane [32,33]. For example with the bulkier ligand ArN=C(Me)–C(Me)=NAr, Ar = 2,6-$(CH(CH_3)_2)_2C_6H_3$, the 5-coordinate olefin complex **A** was too unstable at room temperature to be isolated, whereas with ligand **2** (RN=C(H)–C(H)=NR, R = cyclohexyl), **A** was isolated exclusively. With ligand **1** (ArN=C(Me)–C(Me)=NAr, Ar = 2,6-$(CH_3)_2C_6H_3$), a mixture of **A** and **3** was obtained. Quantitative conversion to the dichlorides, **3** and **4**, can be achieved by refluxing the respective 5-coordinate olefin complexes in THF or methylene chloride. The α-diimine ligands are generally unable to displace COD (1,5-cyclooctadiene) from (COD)$PtCl_2$, NBD (norbornadiene) from (NBD)$PtCl_2$, or SMe_2 from $(SMe_2)_2PtCl_2$ [31,33]. Surprisingly, treatment of the substitutionally labile Pt(II) complex $[Pt(CH_3CN)_4][OTf]_2$ [34] in nitromethane with one equivalent of an α-diimine did not yield the expected bis-acetonitrile complex.

The bis-solvento complexes **5a**, **5b**, and **6** were synthesized by abstracting the chlorides with two equivalents of a silver salt in a mixture of CH_2Cl_2/CH_3CN or $(CH_3)_2CO$ (Eq. (5)).



5a: N–N = **1**; solv = CH_3CN; X = OTf^-, BF_4^-, SbF_6^-
5b: N–N = **1**; solv = $(CH_3)_2CO$; X = BF_4^-, SbF_6^-
6: N–N = **2**; solv = CH_3CN; X = OTf^-, BF_4^-, PF_6^-, SbF_6^- (5)

The acetonitrile and acetone adducts were isolated as yellow solids by addition of ether to the reaction mixtures after filtration to remove AgCl. In general, it was necessary to repeat the above procedure several times to remove all the AgCl. Attempts at synthesizing the bis-pentafluoropyridine or bis-tetrafluoro-4-picoline analogues in either mixtures

of CH_2Cl_2 and the fluorinated pyridines or in neat fluorinated pyridines proved unfruitful due to the insolubility of the (N–N)$PtCl_2$/AgX mixtures.

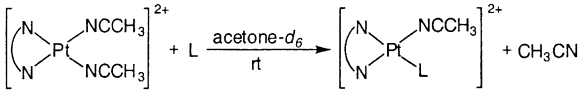
The ^{1}H NMR spectra of the bis-acetonitrile and bis-acetone complexes in weakly coordinating solvents such as CD_2Cl_2 or CF_3CD_2OD (TFE-d_3) are consistent with a single C_{2v}-symmetric species in solution in each case. In CD_2Cl_2, there is a single resonance for bound acetonitrile in **5a** (X = OTf^-, BF_4^-, SbF_6^-) at 2.13 ppm; the ^{19}F NMR spectrum of the OTf^- salt consists of a sharp singlet at −75 ppm, characteristic of non-coordinated OTf^- [35].[3] When **5a** was dissolved in more coordinating solvents such as MeOH-d_4 or D_2O, however, a mixture of products was observed, the major one being $[(N–N)Pt(CH_3CN)(solv)]^{2+}X_2$, in which one acetonitrile molecule had been replaced by a solvent molecule. In contrast, a D_2O solution of **5b** exhibits signals corresponding to two symmetric species, in an approximate 5:1 ratio, as well as free acetone. The major species is assigned as the bis-aqua complex $[(N–N)Pt(D_2O)_2]^{2+}$ which was verified by independent synthesis. The minor species is the C_{2v}-symmetric bis-acetone complex **5b**; its signal grows in intensity upon addition of acetone. The equilibrium between **5b** and the bis-aqua complex suggests that acetone has a higher affinity for the electrophilic platinum center than water. Interestingly, there was no indication of the unsymmetrical $[(N–N)Pt((CH_3)_2CO)(D_2O)]^{2+}X_2$ complex being formed under these conditions.

The acetone ligands in **5b** are more labile than the corresponding acetonitrile ligands in **5a**. In fact, clean isolation of the complex **5b** was possible only in cases where the anions were BF_4^- or SbF_6^-. Attempted isolation of **5b** with OTf^- anion invariably yielded oils that were difficult to purify. ^{1}H NMR spectra of the crude reaction mixtures in CD_2Cl_2 showed multiple products. Presumably, OTf^- anion can displace one or even both acetone molecules, affording a mixture of dicationic, monocationic, and neutral Pt species. The fact that OTf^- anion can easily replace bound acetone in **5b** but not the acetonitrile in **5a** implies that acetonitrile is a better ligand for Pt, as one might expect. On the other hand, the equilibrium between **5b** and the bis-aqua complex, and previous measurement of equilibrium constants between $[(N–N)Pt(Me)(D_2O)][BF_4]$ and $[(N–N)Pt(Me)(TFE)][BF_4]$ (TFE = trifluoroethanol) [19]. indicate that acetone has a higher affinity for the electrophilic Pt(II) center than water, which in turn is a better ligand than trifluoroethanol. Thus, a qualitative ordering of acetonitrile > acetone > water > trifluoroethanol can be obtained for the affinity of various solvents for the Pt center with ligand **1**.

With α-diimine **2**, the only solvento complex that could be isolated relatively cleanly was the bis-acetonitrile adduct **6**. Attempts to isolate the corresponding bis-acetone adducts resulted only in the formation of sticky pale yellow oils consisting of various products. Varying the counteranion from OTf^- to BF_4^- to SbF_6^- did not to help to produce any isolable products.

2.2. Substitution reactions of *5a* with 1-phenylpyrazole and 2-substituted pyridines

Addition of 1-phenylpyrazole or a 2-substituted pyridine to a clear yellow solution of **5a** results in an immediate color change to dark yellow-brown and (by ^{1}H NMR) liberation of free CH_3CN. At least 95% of the resulting Pt species can be assigned as $[(N–N)Pt(CH_3CN)(L)]^+$ (N–N = ***1***, L = 1-phenylpyrazole or 2-R-pyridine), **7**–**10** (Eq. (6)).



5a

7, L = 1-phenylpyrazole
8, L = 2-phenylpyridine
9, L = 2-vinylpyridine
10, L = 2-(2-thienyl)pyridine

(6)

Further addition of substrate (up to two equivalents) does not displace the remaining bound acetonitrile. The increased crowding at the metal center due to the 2-substituted heterocycles may be responsible for the observed substitution pattern in these cases. For example, treatment of **5a** with two equivalents of pyridine or 4-methylpicoline results in formation of

[3] Johansson et al. have observed the neutral methyl triflate complex (N–N)Pt(Me)(OTf)(N–N = 3,5-$(CF_3)_2C_6H_3$N=C(Me)–C(Me)3,5-$(CF_3)_2C_6H_3$N) in CD_2Cl_2 by ^{19}F NMR, as indicated by the ^4J(Pt–F) coupling constant of 14.4 Hz.

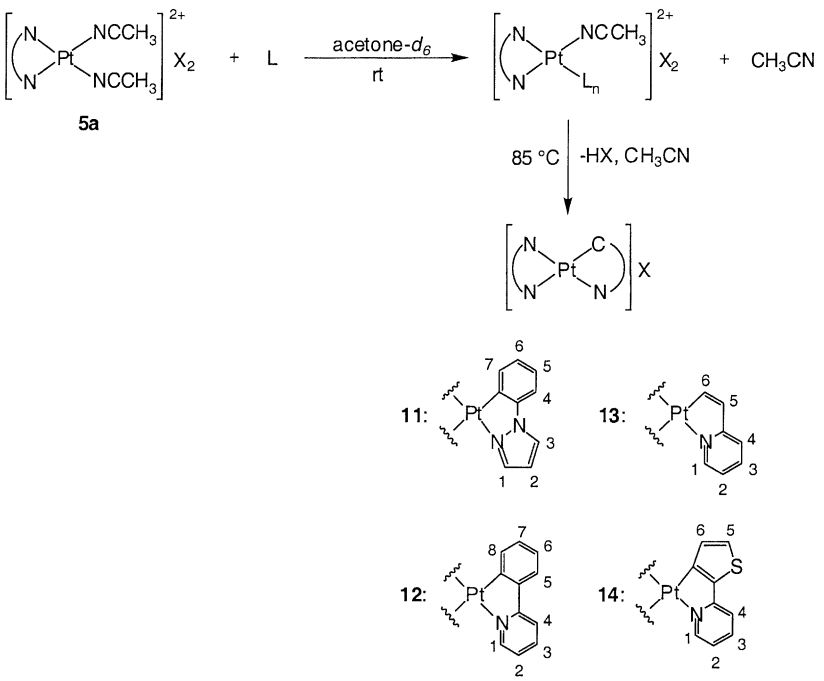
the bis-pyridine or bis-picoline adducts, while treatment of **5a** with two equivalents of 2-ethylpyridine results in only 1 pyridyl group adding to the metal center.

Displacement of acetonitrile by 2-(2-thienyl)pyridine in **5a** could potentially lead to κ^1(N)-, κ^1(S)-, or κ^2(N,S)-bound 2-(2-thienyl)pyridine. The methyl region of the ^{1}H NMR spectrum exhibits seven singlets; six for methyl groups of the diimine ligand (four on the aryl groups, two on the backbone) and one for the remaining bound acetonitrile. The latter establishes κ^1-binding—otherwise both acetonitriles would have been displaced—and is also consistent with all the diimine methyl groups being nonequivalent, assuming restricted rotation around the Pt-(2-(2-thienyl)pyridine) bond on the NMR time-scale. The substantial downfield shift of the proton a to the pyridine nitrogen, at δ 9.25 (compared to δ 8.52 for free 2-thienylpyridine) implies an N-bonded structure (compare **8**, where the proton α to the pyridine nitrogen resonates at δ 9.23).

2.3. Intramolecular C–H activation of 1-phenylpyrazole and 2-substituted pyridines by 5a

Heating reaction mixtures containing a 1:1 or a 2:1 mixture of 1-phenylpyrazole or a 2-substituted pyridine and **5a** (or **5b**) at 85 °C in acetone for 4–6 h results in deep burgundy solutions of the cyclometalated products **11**–**14** (Scheme 2). In each case the ^{1}H NMR spectrum exhibits a characteristic doublet in the region δ 5 to 6 with Pt satellites ($^3J_{Pt-H}$ = 26–33 Hz) that grows in intensity over time, assigned to the proton α to the Pt-bonded carbon. Cyclometalated phenyl- and thienylpyridine complexes of platinum with other ligands have been reported previously [36].

The unusually high upfield shift of this proton is attributed to the ring current shielding of the 2,6-xylyl groups of the diimine ligand. The *ortho*-proton of the pyridyl group is likewise shifted to higher field (~6.5–7.0 ppm) in complexes **12**–**14**. The crystal structure of **12** (X = BF_4^-), shown in Fig. 2, clearly indicates that the protons on C22 and C31 lie in the shielding regions of the arenes on the diimine



Scheme 2.

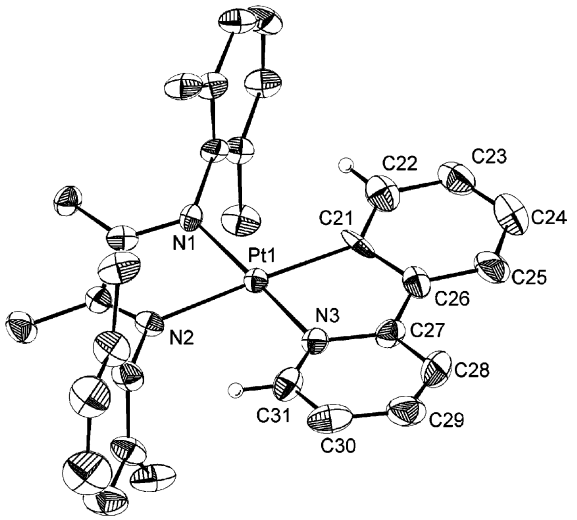


Fig. 2. Labeled diamond drawing of the cationic portion of **12** ($X = BF_4^-$) with ellipsoids at 50% probability.

ligand. Selected metrical parameters for **12** are listed in Table 1.

The X-ray structure reveals that C–H bond activation yields a five-membered ring, the common preference. The α-diimine is bound unsymmetrically to the Pt, with a moderate lengthening of the Pt–N bond *trans* to the phenyl group relative to that *trans* to the pyridyl group (2.092 Å versus 2.056 Å), presumably due to higher *trans* influence [37].

In general, cyclometalation reactions are carried out in the presence of a weak base to trap the equivalent of acid (HX) that is generated [23,38]. Here, a 2:1 molar ratio of substrate to Pt complex yields substantially cleaner reactions than without the extra equivalent of base. In principle, one should be able to replace the second equivalent of substrate with another weak base. This is indeed the case for the extremely hindered base, 2,6-di-*t*-butylpyridine; triethylamine on the other hand gives significantly lower yields. Inorganic bases such as Na_2CO_3 lead to dramatic color changes affording deep purple or green solutions, exhibiting complex ^{1}H NMR spectra.

Table 1
Selected bond lengths and bond angles for the cationic portion of **12** ($X = BF_4^-$)

Bond lengths (Å)	
Pt1–N1	2.056 (5)
Pt1–N2	2.092 (6)
Pt1–N3	2.016 (6)
Pt1–C21	2.009 (8)
Bond angles (°)	
N1–Pt1–N2	76.6 (2)
N1–Pt1–N3	176.5 (2)
N1–Pt1–C21	101.7 (3)
Pt1–N3–C31	127.2 (5)
Pt1–C21–C22	112.0 (5)
N2–Pt1–N3	101.0 (3)
N2–Pt1–C21	174.8 (3)
N3–Pt1–C21	80.9 (3)

As noted above, the reaction between **5a** and 2-(2-thienyl)pyridine could lead to a κ^2 (N,S) chelate when the second acetonitrile is displaced; but only the cyclometalated product **14** is observed, as unequivocally demonstrated by a crystal structure determination. The structure of **14** is shown in Fig. 3, with selected bond lengths and bond angles reported in Table 2.

Surprisingly, reactions of **5a** or **5b** with 2-substituted pyridines containing sp^3 C–H bonds (2-ethylpyridine, 2-*n*-propylpyridine, 2-*i*-propylpyridine, 2-*t*-butylpyridine, and 8-methylquinoline) did not yield the expected cyclometalated products. The ^{1}H NMR spectra of the reaction mixtures indicated the formation of multiple products, of which only the protonated pyridines could be identified unambiguously.

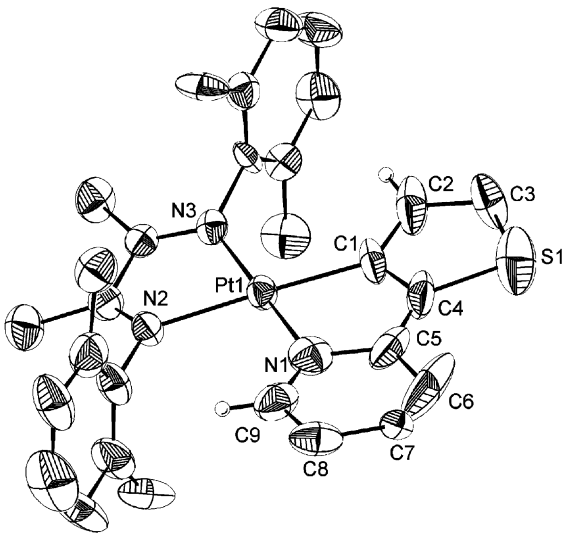


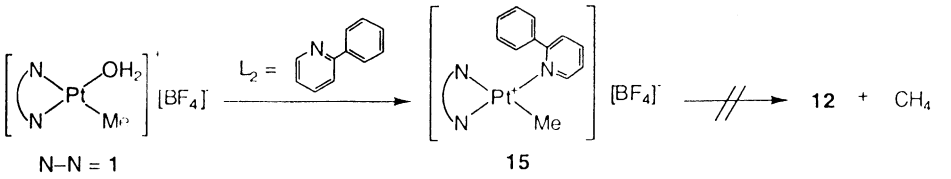
Fig. 3. Labeled diamond drawing of the cationic portion of **14** ($X = BF_4^-$) with ellipsoids at 50% probability.

Table 2
Selected bond lengths and bond angles for the cationic portion of **14** ($X = BF_4^-$).

Bond lengths (Å)	
Pt1–N1	2.013 (7)
Pt1–N2	2.095 (5)
Pt1–N3	2.009 (6)
Pt1–C1	2.006 (7)
Bond angles (°)	
N1–Pt1–N2	103.3 (3)
N1–Pt1–N3	177.9 (3)
N1–Pt1–C1	78.1 (3)
Pt1–N1–C9	128.9 (6)
Pt1–C1–C2	132.5 (7)
N2–Pt1–N3	76.1 (2)
N2–Pt1–C1	176.2 (3)
N3–Pt1–C21	102.6 (3)

Similarly, the anilines 2-*t*-butylaniline and *N*,*N*-dimethyl-*o*-toluidine yielded only deep green/black unidentifiable mixtures. Changing solvents from acetone to 2-methoxyethanol or trifluoroethanol did not affect the outcome of these reactions.

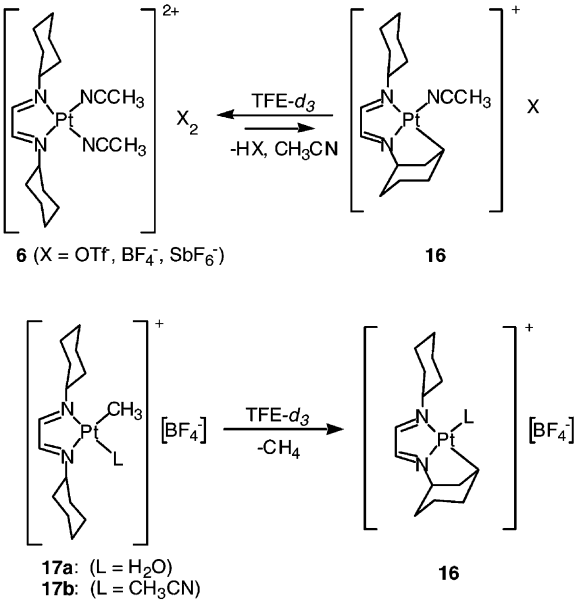
In order to compare the reactivity of the dicationic platinum complexes to that of the well-studied monocationic systems, complex **15** ([(N–N)Pt(Me)(2-$C_6H_5NC_5H_4$)][BF_4]; N–N = **1**), was synthesized by treatment of the methyl aqua cation, $[(N–N)Pt(Me)(H_2O)]^+$ (N–N = **1**) [20] with 2-phenylpyridine in acetone (Eq. (7)). Thermolysis of this complex in acetone-d_6 does not result in cyclometalation even after prolonged (2 days) heating above 85 °C.



(7)

2.4. Intramolecular cyclometalation of 6

To probe the viability of alkyl C–H bond activation by these dicationic complexes, we examined the reaction pattern of **6**, which contains a cyclohexyl moiety in its α-diimine ligand framework. Heating a solution of **6** in trifluoroethanol-d_3 at 85 °C does result in cyclometalation, albeit slowly, of one of the cyclohexyl groups on the imine nitrogens to yield **16** (Scheme 3).



Scheme 3.

16 has been previously synthesized by intramolecular C–H activation of the cationic methyl-acetonitrile complex **17b** or the methyl-aqua adduct **17a** (bottom of Scheme 3) and crystallographically characterized as its BF_4^- salt [39].

Whereas **17a** undergoes cyclometalation at ambient temperature over the course of 24 h, the acetonitrile complex **17b** and the bis-acetonitrile complex **6** must be refluxed in trifluoroethanol for the reaction to occur. Furthermore, whereas **17a** is converted quantitatively to **16** after refluxing in trifluoroethanol for 48 h, complete conversion of the dication **6** ($X = OTf^-$) to **16** is not observed. Instead, a 2.7:1 mixture of **6**:**16** was obtained after 12 h. Heating for another 24 h does not change this ratio.

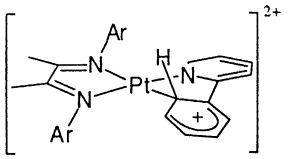
The reaction is highly solvent-dependent. Switching from TFE-d_3 to acetone-d_6 resulted in a mixture of unidentifiable products. Different anions also affect

the outcome of the reaction. Both SbF_6^- and OTf^- anions afforded considerably cleaner reaction mixtures than BF_4^-. With PF_6^- no cyclometalation product was observed, which may be attributed to the extensive decomposition of the PF_6^- anion as indicated by ^{19}F NMR spectroscopy.

2.5. Comments on intramolecular C–H activation by dicationic Pt(II)

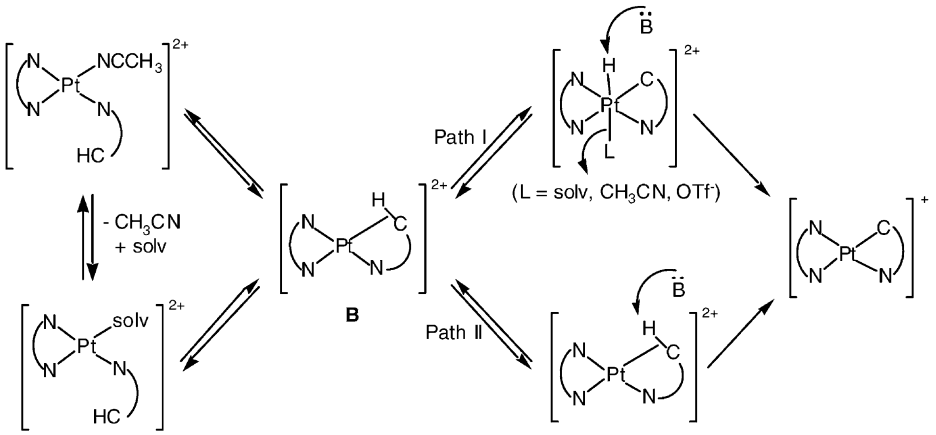
The bis-acetonitrile complex **5a** reacts readily with 2-aryl- or 2-vinylpyridines to give first substitution of one acetonitrile by pyridine and then, under relatively mild heating (85 °C), the cyclometalated products **11**–**14**. These C–H activation reactions are slower than those of monocationic $[L_2Pt(CH_3)S]^+$ complexes with benzene (Eq. (3)) where S = TFE or H_2O [14,19,20]. This trend almost surely reflects the fact that displacement of the second acetonitrile by the reacting arene C–H (or C=C) bond is more difficult than the corresponding displacement in the monocationic systems, because ligands such as TFE and water are much more weakly bonded to Pt(II) than acetonitrile, and perhaps also because the solvent-Pt(II) bond is probably stronger in a dication. Displacement of a ligand is required, as demonstrated by the fact that conversion of complex **15** to **12** with liberation of methane (Eq. (7)), a reaction that should be strongly thermodynamically favored, is not observed under comparable conditions. Formation of **11**–**14** from **5** is driven to completion by the presence of a second equivalent of base, although some conversion is observed even without extra base present.

Based on the earlier studies of the corresponding mono-cationic systems [8,19,20], we would propose Scheme 4 to account for these observations. Replacement of the second acetonitrile ligand by a C–H bond (perhaps preceded by formation of an η^2-π-arene species [20]) may take place either by direct displacement or by a solvent-assisted pathway to give intermediate **B**. In the cyclometalation of 2-phenylpyridine, the η^1-arenenium, **B′**, species is another possible structure for **B**; such intermediates have been implicated in a number of studies involving Pt and Pd arene cyclometalation [27,40].



B´

From **B**, the actual cleavage of the C–H bond can proceed via an oxidative addition mechanism (Scheme 4, Path I) to generate a Pt(IV) hydride which is then deprotonated by a base in solution, or alternatively via direct deprotonation of the agostic complex (Scheme 4, Path II). Most of the evidence supports the formation of Pt(IV) hydrides as important intermediates in C–H activation, and we tend to favor the oxidative addition route, although it is conceivable



Scheme 4.

that the involvement of additional external base in the present case could result in a different preferred route.

No cyclometalated products were observed when the bis-solvento complexes **5a** or **5b** were treated with pyridines containing adjacent aliphatic or benzylic C–H bonds, although intermolecular alkane activations by $[L_2Pt(CH_3)(H_2O)]^+$ have been observed [14,19]. This presumably reflects the fact that displacement of acetonitrile by an sp^3 C–H bond is less favorable than by vinyl or aryl C–H bonds (vide supra). However, an example of clean intramolecular C–H activation of an sp^3 C–H bond is observed in the formation of **16** from **6**. This reaction is slower than the formation of **16** from the monocationic platinum methyl-aquo complex **17a**, but proceeds at about the same rate as monocationic platinum methyl-acetonitrile complex **17b**, again implying that (solvent) ligand displacement is a central factor in determining reactivity. Note that whereas acetone is the solvent of choice for the cyclometalations involving **5a**, no cyclometalation of **6** was observed in acetone; clean reaction to yield the cyclometalated product was observed only in trifluoroethanol-d_3.

Also, whereas formation of **16** from **17** proceeds to completion, cyclometallation of **6** only proceeds partway, to an equilibrium mixture in which the dicationic complex is favored. In principle, addition of a base stronger than solvent to take up the liberated proton should drive the reaction further; addition of the hindered base 2,6-di-*t*-butylpyridine does seem to shift the equilibrium towards the cyclometallated product **16**, but there is competing decomposition. Stronger bases such as Na_2CO_3 resulted in highly colored solutions of which the ^{1}H NMR spectra showed only decomposition products. Nonetheless, the observation of the cyclometalated product **16** implies that electrophilic C–H activation at a dicationic Pt(II) center with proton liberation is possible. The fact that the equilibrium lies in favor of the starting material and not the highly entropically favored cyclometalated species suggests that direct observation of a Pt alkyl via intermolecular C–H activation may be difficult, requiring indirect methods such as H/D exchange to access whether C–H activation has occurred, but a catalytic cycle involving such a step, driving the unfavorable equilibrium forward by coupling to a subsequent rapid reaction, is a potentially viable strategy.

3. Experimental

3.1. General considerations

All air and moisture sensitive compounds were manipulated using standard high-vacuum line, Schlenk line or cannula techniques, or in a nitrogen atmosphere glove box as previously described [41]. Solvents were dried over sodium/benzophenone ketyl (toluene, THF, Et_2O, petroleum ether), CaH_2 (CH_2Cl_2), Drierite (acetone), and 3 Å molecular sieves/$NaHCO_3$ (trifluroethanol-d_3). Zeise's salt ($K[Cl_3Pt(C_2H_4)]\cdot H_2O$) and Zeise's dimer $[(PtCl_2(C_2H_4)]_2$ were purchased from Strem Chemicals. All silver salts were purchased from Aldrich and stored in a glove box. 1-Phenylpyrazole, 2-phenylpyridine, 2-vinylpyridine, and 2-ethylpyridine were purchased from Aldrich. 2-(2-Thienyl)pyridine was purchased from Lancaster. α-Diimines **1** and **2** were prepared as previously described [42,43]. NMR spectra were recorded on a General Electric QE300 (^{1}H, 300.1 MHz), a Varian ^{UNITY}INOVA 500 (^{1}H, 499.853 MHz; ^{13}C, 125.701 MHz) or a Varian *Mercury-VX* 300 (^{1}H, 300.1 MHz; ^{19}F, 282.081 MHz; ^{13}C, 75.46 MHz) spectrometer. All ^{1}H NMR shifts are relative to the residual NMR solvent and assignments are numbered as shown below. X-ray structure determinations were performed on a Bruker SMART 1000 CCD area detector under a cold stream of N_2 gas. Data reduction was done with Bruker SAINT v6.2. All structures were solved by direct methods using SHELXS-97 and refined with SHELXL-97. Elemental Analyses were performed at the Caltech Elemental Analysis Facility or by Midwest Microlab, Indianapolis, IN.

3.2. *(ArN= C(Me)–C(Me)= NAr)PtCl$_2$, (Ar = 2,6-(CH$_3$)$_2$C$_6$H$_3$), **3***

$K[Cl_3Pt(\eta^2\text{-}C_2H_4)]\cdot H_2O$ (1.0 g, 2.71 mmol) was dissolved in methanol and cooled to 0 °C in an ice bath. To this was added ligand **1** (0.873 g, 2.98 mmol) in small portions under vigorous stirring. A dark brown-red precipitate formed immediately upon addition. As this brown-red precipitate is the 5-coordinate ethylene complex and is unstable with respect to loss of ethylene at room temperature, filtering this intermediate is unnecessary. Instead the reaction was

allowed to warm to room temperature and stirred until a color change to light brown was observed (3 h). The solid was then filtered, washed with methanol (10 ml) and Et_2O (10 ml). Drying over a water aspirator yielded a light brown powder. Yield: 1.5 g (100%). The dichloride is only sparingly soluble in most organic solvents giving rise to poorly resolved ^1H NMR spectra. ^1H NMR (DMSO-d_6, δ): 7.17 (s, 6H, 2,6-$(CH_3)_2C_6H_3$), 2.21 (s, 12H, 2,6-$(CH_3)_2C_6H_3$), 1.74 (s, 6H, N=CCH_3). Analytically calculated for $C_{20}H_{24}Cl_2N_2Pt$ (found): C, 43.02 (42.97); H, 4.33 (4.40); N, 5.02 (4.97).

3.3. *(CyN=C(H)–C(H)=NCy)PtCl$_2$, (Cy = C$_6$H$_{11}$), **4***

$K[Cl_3Pt(\eta^2\text{-}C_2H_4)]\cdot H_2O$ (0.405 g, 1.10 mmol) was dissolved in methanol and cooled to 0 °C in an ice bath. To this was added ligand **2** (0.266 g, 1.21 mmol) in small portions under vigorous stirring. A bright yellow precipitate formed upon addition. The reaction was stirred for 0.5 h, then the resulting precipitate was filtered and washed with cold methanol (5–10 ml) and dried. This solid was then dissolved in THF (30 ml) and refluxed for 1 h after which time a orange-brown solid formed. This was cooled in an ice bath, then filtered to yield a flocculent orange-brown solid. Yield: 324 mg (60%). The dichloride is only sparingly soluble in most organic solvents. ^1H NMR (CD_2Cl_2, δ): 8.40 (s, 2H, $^3J_{PtH}$ = 100 Hz, N=C*H*), 4.69 (m, 2H, NC*H*$(CH_2)_5$), 2.36 (m, 4H, Cy CH_2), 1.16–1.91 (m, 16H, overlapping Cy CH_2). Analytically calculated for $C_{20}H_{24}Cl_2N_2Pt$ (found): C, 34.57 (33.93); H, 4.97 (4.73); N, 5.76 (5.39).

3.4. *[(ArN=C(Me)–C(Me)=NAr)Pt(CH$_3$CN)$_2$]X$_2$, (Ar = 2,6-(CH$_3$)$_2$C$_6$H$_3$; X = CF$_3$SO$_3^-$, BF$_4^-$, SbF$_6^-$), **5a***

To a stirred suspension of **3** (1.04 g, 1.86 mmol) in CH_2Cl_2 (75 ml) containing CH_3CN (2 ml) was added AgOTf (0.978 g, 3.81 mmol). As the reaction proceeded, the color of the suspended solids slowly turned light yellow. The mixture was stirred while protected from light at room temperature for 12 h, after which time a dull yellow precipitate formed. The entire mixture was then evaporated to dryness. Acetone (10 ml) and acetonitrile (1 ml) were then added to this residue and filtered through a pad of Celite to yield a yellow-orange solution. The solvent was removed in vacuo. Redissolving in acetone and acetonitrile followed by filtering through Celite was repeated until all the AgCl was removed. Precipitation with Et_2O of a 10:1 acetone:acetonitrile solution afforded the product as a bright yellow powder. Yield: 1.01 g (63%). ^1H NMR (CD_2Cl_2, δ): 7.35 (t, 2H, $^3J_{HH}$ = 6.00 Hz, *p*-H 2,6-$(CH_3)_2C_6H_3$), 7.31 (d, 4H, $^3J_{HH}$ = 6.00 Hz, *m*-H 2,6-$(CH_3)_2C_6H_3$), 2.45 (s, 6H, N=CCH_3), 2.44 (s, 12H, 2,6-$(CH_3)_2C_6H_3$). ^{13}C $\{^1H\}$ NMR (CD_2Cl_2, δ): 188.4, 141.4, 130.9, 130.7, 129.6, 120.7, 20.6, 18.2, 3.5, (*C*$F_3SO_3^-$ not found). ^{19}F $\{^1H\}$ NMR (CD_2Cl_2, δ) −79.1. Analytically calculated for $C_{26}H_{30}F_6N_4O_6PtS_2$ (found): C, 35.99 (36.58); H, 3.48 (3.63); N, 6.46 (6.35). Analogous procedures were used for X = BF_4^- and SbF_6^-. For X = BF_4^-, **3** (0.300 g, 0.357 mmol) was combined with $AgBF_4$ (0.214 g, 1.10 mmol). Workup afforded a yellow powder. Yield: 0.334 g (83.7%). ^1H NMR in CD_2Cl_2 is the same as for theX = OTf^-. ^{19}F $\{^1H\}$ NMR (CD_2Cl_2, δ) −152.3. Analytically calculated for $C_{24}H_{30}B_2F_8N_4Pt$ (found): C, 38.79 (39.01); H, 4.07 (3.9); N, 7.54 (7.08). For X = SbF_6^-, **3** (0.100 g, 0.179 mmol) was combined with $AgSbF_6$ (0.123 g, 0.367 mmol). Workup afforded a bright yellow powder. Yield: 143 mg (66%). ^1H NMR ($(CD_3)_2CO$, δ): 7.43 (br m, 6H, 2,6-$(CH_3)_2C_6H_3$), 2.60 (s, 6H, N=CCH_3), 2.50 (s, 12H, 2,6-$(CH_3)_2C_6H_3$), 2.34 (s, 6H, CH_3CN). Analytically calculated for $C_{24}H_{30}F_{12}N_4PtSb_2$ (found): C, 27.69 (27.66); H, 2.90 (3.01); N, 5.38 (5.25).

3.5. *[(ArN=C(Me)–C(Me)=NAr)Pt(Me$_2$CO)$_2$]X$_2$, (Ar = 2,6-(CH$_3$)$_2$C$_6$H$_3$; X = BF$_4^-$, SbF$_6^-$), **5b***

A solution of **3** (100 mg, 0.179 mmol) and $AgSbF_6$ (123 mg, 0.367 mmol) in dry acetone (7 ml) was stirred at room temperature while protected from light for 3 h. The resulting mixture was filtered through a pad of Celite and the solvent removed in vacuo to afford a red-orange oil. This was redissolved in dry acetone (5 ml) and filtered through a pad of Celite followed by removal of solvent in vacuo. The above procedure was repeated at least one more time until all the AgCl was removed. The crude product was purified by repeated precipitation of acetone (2 ml) solutions with Et_2O under vigorous stirring. Drying

in vacuo afforded a bright yellow solid. Product is very hygroscopic. Yield 68 mg (35.2%). ^{1}H NMR ($(CD_3)_2CO$, δ): 7.46 (t, 2H, $^3J_{HH}$ = 6.28 Hz, *p*-H 2,6-$(CH_3)_2C_6H_3$), 7.40 (d, 3H, $^3J_{HH}$ = 6.28 Hz, *m*-H 2,6-$(CH_3)_2C_6H_3$) 2.61 (s, 6H, N=CCH_3), 2.57 (s, 12H, 2,6-$(CH_3)_2C_6H_3$). Analytically calculated for $C_{26}H_{36}F_{12}N_2O_2PtSb_2$ (found): C, 29.04 (27.78); H, 3.37 (3.38); N, 2.61 (2.45). For X = BF_4^-, **3** (200 mg, 0.358 mmol) was combined with $AgBF_4$ (143 mg, 0.734 mmol) in dry acetone (15 ml). Workup as above afforded a bright yellow powder. Yield 132 mg (47.4%). ^{1}H NMR appears to be consistent with the formation of the bis-acetone complex, however, the product is again extremely hygroscopic and yielded poor analysis.

3.6. *[(CyN=C(H)–C(H)=NCy)Pt(CH_3CN)$_2$]X_2, (Cy = C_6H_{11}, X = OTf^-, BF_4^-, PF_6^-, SbF_6^-), **6***

The solids **4** (135 mg, 0.278 mmol) and AgOTf (149.6 mg, 0.583 mmol) were suspended in a mixture of CH_2Cl_2 (10 ml) and CH_3CN (0.5 ml) and stirred for 3 h at room temperature while protected from light. The resulting mixture was filtered through a pad of Celite and the solvent removed in vacuo. The yellow-orange oil was dissolved in acetone and a small amount of CH_3CN, filtered and solvent again was removed in vacuo. Addition of Et_2O to a concentrated acetone solution of this mixture yields a viscous, yellow-orange oil. All attempts to recrystallize or precipitate a solid resulted in the formation of this oil. Redissolving the oil in acetone, followed by removal of the solvent in vacuo a number of times afforded a foam that could be triturated with Et_2O to yield a very sticky slightly yellow solid. Prolonged exposure to air results in the solid turning to an orange oil. Yield: 66 mg (30%) ^{1}H NMR (TFE-d_3 δ): 8.25 (s, 2H, $^3J_{PtH}$ = 106.4 Hz, N=C*H*), 3.77 (m, 2H, *ipso* H on CyN), 2.73 (s, 6H, Pt(NC*Me*)$_2$), 2.31–1.23 (m, 20H, CH_2 on CyN). ^{13}C $\{^1H\}$ NMR (CD_3CN, δ): 172.85, 71.02, 32.95, 25.78, 25.71. Analytically calculated for $C_{20}H_{30}F_6N_40_6PtS_2$ (found): C, 30.19 (29.27); H, 3.80 (3.78); N, 7.04 (6.38). Isolation of the BF_4^- salt was similarly complicated by the product precipitating as a viscous oil. This occurred to a lesser extent with SbF_6^- as the counteranion, while with PF_6^- the final product precipitated as a nice off-white solid.

3.7. *[(ArN=C(Me)–C(Me)=NAr)Pt(κ^2-(C,N)-1-$C_6H_4N_2C_3H_3$)]X, (Ar = 2,6-$(CH_3)_2C_6H_3$; X = OTf^-), **11***

A solution of **5a** (X = OTf^-) (153 mg, 177 mmol) and 1-phenylpyrazole (46.7 μl, 353 mmol) in acetone (70 ml) was refluxed for 6 h, at which point the solution was deep red. The solvent was removed in vacuo to yield a red-orange residue. This was dissolved in CH_2Cl_2 (40 ml) and washed with aqueous HOTf (0.1 M, 2× 20 ml), water (20 ml), and then dried over Na_2SO_4. Solvent was removed in vacuo and the crude product was purified by repeated precipitation of concentrated acetone (2 ml) solutions with Et_2O to afford a red-brown powder. Yield 66 mg (48%). ^{1}H NMR ($(CD_3)_2CO$, δ): 8.54 (d, 1H, $^3J_{HH}$ = 2.90 Hz, H^3 on $N_2C_3H_3$), 7.49–7.47 (br m, 5H, 2,6-$(CH_3)_2C_6H_3$ and H^4 on C_6H_4), 7.03 (t, 1H, $^3J_{HH}$ = 8.8 Hz, H^5 on C_6H_4), 6.61 (t, 1H, $^3J_{HH}$ = 8.7 Hz, H^6 on C_6H_4), 6.51 (t, 1H, $^3J_{HH}$ = 2.90 Hz, H^2 on $N_2C_3H_3$), 5.40 (d, 1H, $^3J_{HH}$ = 2.90 Hz, H^1 on $N_2C_3H_3$), 5.18 (dd, 1H, $^3J_{HH}$ = 2.90 Hz, $^3J_{PtH}$ = 30 Hz, H^7 on C_6H_4). ^{13}C $\{^1H\}$ NMR ($(CD_3)_2CO$, δ): 184.5, 180.6, 145.5, 145.2, 145.1, 139.3, 132.5, 132.3, 131.6, 130.0, 129.7, 127.3, 125.7, 123.8, 122.4 (q, $^1J_{CF}$ = 323 Hz), 112.2, 108.7, 21.2, 20.0, 17.83, 17.82, (was not able to detect ^{195}Pt coupling to C bonded to Pt). Analytically calculated for $C_{30}H_{31}F_3N_4O_3PtS$ (found): C, 46.21 (46.01); H, 4.01 (4.09); N, 7.19 (6.96).

3.8. *[(ArN=C(Me)–C(Me)=NAr)Pt(κ^2-(C,N)-1-$C_6H_4NC_5H_4$)]X, (Ar = 2,6-$(CH_3)_2C_6H_3$; X = OTf^-), **12***

A solution of **5a** (X=OTf^-) (63 mg, 0.073 mmol) and 2-phenylpyridine (20.5 ml, 0.146 mmol) in acetone (10 ml) was heated at 85 °C overnight in a re-sealable Schlenk tube. The resulting dark red solution was diluted with water (30 ml), extracted with CH_2Cl_2 (2× 10 ml), then dried over Na_2SO_4. The solvent was removed in vacuo and the crude product was purified by repeated precipitation of concentrated acetone (2 ml) solutions with Et_2O at −20 °C to afford an orange-brown powder. Yield: 24 mg (41%). ^{1}H NMR ($(CD_3)_2CO$, δ): 7.96–8.05 (overlapping m, 2H, H^3 and H^4 on NC_5H_4), 7.61 (d, 1H, $^3J_{HH}$ = 7.61 Hz, H^5 on C_6H_4), 7.40–7.47 (br m, 6H,

2,6-$(CH_3)_2C_6H_3$), 7.00 (t, 1H, $^3J_{HH}$ = 7.61 Hz, H^6 on C_6H_4), 6.87 (dd, 1H, $^3J_{HH}$ = 6.3 Hz, $^3J_{PtH}$ = 34 Hz, H^1 on NC_5H_4), 6.81 (t, 1H, $^3J_{HH}$ = 6.3 Hz, H^2 on NC_5H_4), 6.65 (t, 1H, $^3J_{HH}$ = 7.54 Hz, H^7 on C_6H_4), 5.27 (dd, 1H, J_{HH} = 8.1 Hz, $^3J_{PtH}$ = 39 Hz, H^8 on C_6H_4), 2.44 (s, 3H, N=CCH_3), 2.36 (s, 6H, 2,6-(CH_3)$_2C_6H_3$), 2.34 (s, 3H, N=CCH_3), 2.28 (s, 6H, 2,6-(CH_3)$_2C_6H_3$). ^{13}C {^{1}H} NMR ($(CD_3)_2CO$, δ): 184.14, 180.47, 168.17, 148.68, 147.10, 145.58, 144.61, 142.13, 138.66, 132.16, 132.02, 131.31, 130.33, 129.97, 129.78, 129.72, 129.21, 126.81, 124.55, 122.77, 120.41, 21.44, 20.67, 17.96, 17.92. Analytically calculated for $C_{32}H_{32}F_3N_3O_3PtS$ (found): C, 48.6 (47.13); H, 4.08 (4.10); N, 5.31 (5.08).

3.9. [(ArN=C(Me)–C(Me)=NAr)Pt(κ^2-(C,N)-(2-$C_2H_2NC_5H_4$)]X, (Ar = 2,6-$(CH_3)_2C_6H_3$; X = OTf^-), ***13***

A solution of **5a** (X = OTf^-) (100 mg, 0.115 mmol) and 2-vinylpyridine (27.4 μl, 0.230 mmol) in acetone (40 ml) was heated to reflux for 4 h. The solvent was then removed in vacuo to 1/4 the volume. This was diluted with CH_2Cl_2 (30 ml), washed with aqueous HOTf (0.1 M, 2× 20 ml), water (20 ml), and then dried over Na_2SO_4. Solvent was removed in vacuo and the crude product was purified by repeated precipitation of concentrated acetone (2 ml) solutions with Et_2O/hexanes to afford a rust-colored powder. Yield: 44 mg (52%) ^{1}H NMR ($(CD_3)_2CO$, δ): 7.84 (t, 1H, $^3J_{HH}$ = 7.7 Hz, H^3 on NC_5H_4), 7.45–7.34 (br m, 6H, 2,6-(CH_3)$_2C_6H_3$), 7.30 (d, 1H, $^3J_{HH}$ = 7.5 Hz, H^4 on NC_5H_4), 6.78 (t, 1H, $^3J_{HH}$ = 7.8 Hz, H^2 on NC_5H_4), 6.32 (dd, 1H, $^3J_{HH}$ = 5.9 Hz, $^3J_{PtH}$ = 30 Hz, H^1 on NC_5H_4), 6.30 (dd, 1H, $^3J_{HH}$ = 7.9 Hz, $^3J_{PtH}$ = 89 Hz, H^6 on C_2H_2), 5.84 (dd, 1H, $^3J_{HH}$ = 7.9 Hz, $^3J_{PtH}$ = 82 Hz, H^5 on C_2H_2), 2.48 (s, 3H, N=CCH_3), 2.35 (s, 6H, 2,6-(CH_3)$_2C_6H_3$), 2.33 (s, 6H, 2,6-(CH_3)$_2C_6H_3$), 2.31 (s, 3H, N=CCH_3). ^{13}C {^{1}H} NMR ($(CD_3)_2CO$, δ): 182.59, 180.57, 171.88, 156.84 (d, $^1J_{PtC}$ = 1041 Hz), 148.47, 145.07, 144.73, 143.02, 142.85, 139.50, 130.89, 130.66, 130.13, 129.73, 129.41, 122.4 (q, $^1J_{CF}$ = 323 Hz), 121.67, 121.39, 20.50, 2014, 17.94, 17.85. Analytically calculated for $C_{28}H_{30}F_3O_3PtS$ (found): C, 45.40 (45.17); H, 4.08 (4.15); N, 5.67 (5.45).

3.10. [(ArN=C(Me)–C(Me)=NAr)Pt(κ^2-(C,N)-(2-C_4H_2S)NC_5H_4)]X, (Ar = 2,6-$(CH_3)_2C_6H_3$; X = OTf^-), ***14***

A solution of **5a** (X = OTf^-) (100 mg, 0.115 mmol) and 2-(2-thienyl)pyridine (37.2 mg, 0.230 mmol) in acetone (25 ml) was heated to reflux for 4 h. The solvent was then removed. The resulting dark red residue was dissolved in CH_2Cl_2 (50 ml), washed with aqueous HOTf (0.1 M, 2 ml), water (10 ml), and then dried over Na_2SO_4. Solvent was removed in vacuo and the crude product was purified by repeated precipitation of concentrated CH_2Cl_2 (2 ml) solutions with Et_2O/hexanes to afford a maroon solid. Yield: 48.3 mg (52%) ^{1}H NMR ($(CD_3)_2CO$, δ): 7.88 (t, 1H, $^3J_{HH}$ = 7.6 Hz, H^3 on NC_5H_4), 7.53–7.40 (overlapping, 7H, 2,6-(CH_3)$_2C_6H_3$ and H^3 on NC_5H_4), 7.24 (d, 1H, $^3J_{HH}$ = 5.0 Hz, H^5 on C_4H_2S), 6.68 (t, 1H, $^3J_{HH}$ = 6.9 Hz, H^2 on NC_5H_4), 6.52 (dd, 1H, $^3J_{HH}$ = 6.0 Hz, $^3J_{PtH}$ = 37 Hz, H^1 on NC_5H_4), 5.57 (dd, 1H, $^3J_{HH}$ = 5.0 Hz, $^3J_{PtH}$ = 13.3 Hz, H^6 on C_4H_2S) 2.44 (s, 3H, N=CCH_3), 2.39 (s, 6H, 2,6-(CH_3)$_2C_6H_3$), 2.33 (s, 6H, 2,6-(CH_3)$_2C_6H_3$), 2.31 (s, 3H, N=CCH_3). ^{13}C {^{1}H} NMR ($(CD_3)_2CO$, δ): 184.06, 181.07, 163.57, 148.09, 146.46, 144.75, 143.94, 143.08, 142.74, 132.08, 131.58, 131.20, 130.36, 130.04, 129.95, 127.83, 127.69, 122.4 (q, $^1J_{CF}$ = 323 Hz), 120.71, 119.01, 20.86, 20.62, 17.95, 17.85. Analytically calculated for $C_{30}H_{30}F_3N_3O_3PtS_2$ (found): C, 45.22 (44.99); H, 3.80 (3.89); N, 5.27 (5.09).

3.11. [(ArN=C(Me)–C(Me)=NAr)Pt(CH_3)(2-$C_6H_5NC_5H_4$)][BF_4], (Ar = 2,6-$(CH_3)_2C_6H_3$) ***15***

To a solution of (ArN=C(Me)–C(Me)=NAr)Pt-Me_2 (Ar = 2,6-$(CH_3)_2C_6H_3$) (100 mg, 0.193 mmol) in acetone (15 ml), cooled to −20 °C, was added HBF_4(aq) (48%, 25.2 μl, 0.193 mmol). Upon addition of the acid the color of the solution turned yellow-orange from dark red. The reaction was stirred for 15 min, after which 2-phenylpyridine (55.2 ml, 0.386 mmol) was added. The reaction was allowed to stir for 2 h. while warming to room temperature. Solvent was then removed under vacuo and resulting red-orange residue was precipitated from acetone with Et_2O. Recrystallization from CH_2Cl_2 and Et_2O afforded

an orange solid. Yield: 45 mg (31%) ^{1}H NMR (CD_2Cl_2, δ): 8.64 (dd, 1H, $^3J_{HH}$ = 5.1 Hz, $^3J_{PtH}$ = 49 Hz, α-H on NC_5H_4), 7.8–7.7 (m overlapping, 3H, $C_6H_4NC_5H_4$), 7.54–7.42 (m overlapping, 3H, $C_6H_4NC_5H_4$), 7.30–7.17 (m overlapping, 5H, 2,6-$(CH_3)_2C_6H_3$), 7.0–6.95 (m overlapping, 2H, 1H from $C_6H_4NC_5H_4$ and 1H from 2,6-$(CH_3)_2C_6H_3$), 2.30 (s, 3H, N=CCH_3), 2.20 (s, 3H, N=CCH_3), 2.18 (s, 3H, 2,6-(CH_3)$_2$C$_6$H$_3$), 1.84 (s, 3H, 2,6-(CH_3)$_2$C$_6$H$_3$), 1.83 (s, 3H, 2,6-(CH_3)$_2$C$_6$H$_3$) 1.17 (s, 3H, 2,6-(CH_3)$_2$C$_6$H$_3$), 0.67 (3H, $^2J_{PtH}$ = 77.1 Hz, Pt(CH_3)). Analytically calculated for $C_{32}H_{36}BF_4N_3Pt$ (found): C, 51.62 (50.05); H, 4.87 (4.80); N, 5.64 (5.31).

3.12. X-ray structure determinations of **12** and **14**

Dark red crystals of **12** and **14** suitable for X-ray structure determinations were grown by layering concentrated solutions of **12** (CH_2Cl_2) and **14** (acetone) with Et_2O at −40 °C. The position of the Pt atom in **12** was located with a Patterson map. The presence of the Pt atom creates a pseudo-mirror plane perpendicular to the b-axis and passing through the Pt position. The positions of the remaining atoms in the difference Fourier maps were complicated by this pseudo-mirror but it was possible to distinguish actual peaks from ghost peaks. Numerous absorption correction schemes were tried but all resulted in unsatisfactory refinement

Table 3
X-ray crystallographic data for **12** and **14**[a]

Complex	**12**	**14**
Empirical formula	$C_{31}H_{32}N_3PtBF_4$	$C_{29}H_{29}N_3SPtBF_4$
Formula weight	728.50	733.51
Crystal habit	Plate	Plate
Crystal size	0.22 mm × 0.14 mm × 0.04 mm	0.26 mm × 0.19 mm × 0.07 mm
Crystal color	Brown/yellow	Red
Diffractometer	CCD area detector	CCD area detector
Wavelength	0.71073 Mo Kα	0.71073 Mo Kα
Temperature	98 K	98 K
Unit cell dimensions	a = 0.5686(14) Å	a = 10.6141(19) Å
	b = 11.8223 (15) Å	b = 11.884(2) Å
	c = 11.9120(16) Å	c = 11.927(2) Å
	α = 90°	α = 90°
	β = 106.1992(2)°	β = 105.081(3)°
	γ = 90°	γ = 90°
Volume	1429.3(3) Å^3	1452.6(4) Å^3
Z	2	2
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1$	$P2_1$
Density (calculated)	1.693 g/cm^3	1.677 Mg/m^3
Theta range	1.78–28.45°	1.77–28.48°
h (min, max)	−13, 13	−13, 14
k (min, max)	−15, 15	−15, 15
l (min, max)	−15, 15	−15, 15
Reflections collected	27944	21549
Independent reflections	6691	6740
R_{int}	0.1045	0.0597
GOF on F^2	1.448	1.308
Final R indices [$I > 2\sigma(I)$][b]	0.0393	0.0396
Final weighted R [F_o^2][c]	0.0489	0.0564

[a] SADABS absorption correction applied.
[b] $R(F) = \left(\sum ||F_c| - |F_o||\right) / \sum |F_o|$.
[c] $R_w(F^2) = \left[\sum w(F_o^2 - F_c^2)_2 / \sum w(F_o^2)\right]^{1/2}$.

results, therefore the uncorrected data was used in the final refinement. All large peaks in the final difference Fourier map are near the Pt atom. Crystallographic data are shown in Table 3.

4. Supplementary material

X-ray crystallographic data for all new structures, including complete listings of fractional coordinates, displacement parameters, distances and angles, and structure factors, have been deposited at the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (e-mail: software@chemcrys.cam.ac.uk). Copies can be obtained on request free of charge, by quoting the publication citation and the deposition numbers, which are: **12**, deposition number 166553; **14**, deposition number 149652.

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