The mechanism of protonolysis of phenylplatinum(II) bonds in complexes with phenyl trans to nitrogen or carbon donors[1]

Christopher M. Ong, Michael C. Jennings, and Richard J. Puddephatt

Abstract: Addition of acids of the form HX (X = Cl, BF_4, CF_3SO_3, CF_3CO_2) to complexes [$PtPh_2$(NN)] (NN = bu_2bpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine) and [PtPh(NCN)] (NCN = 2,6-$C_6H_3(CH_2NMe_2)_2$) at –78 °C gave the corresponding phenyl(hydrido)platinum(IV) complexes [PtX(H)Ph_2(NN)] and [PtX(H)Ph(NCN)], which decomposed by reductive elimination of benzene at about –20 °C to give the platinum(II) complexes [PtXPh(NN)] and [PtX(NCN)]. Further addition of HCl to [PtClPh(NN)] at low temperature gave [$PtHCl_2$Ph(NN)], which decomposed above –10 °C, to give benzene and [$PtCl_2$(NN)]. The reaction of DBF_4 in the presence of excess CD_3OD with [$PtPh_2$(NN)] led to formation of C_6H_5D and $C_6H_4D_2$ but with [PtPh(NCN)] no multiple deuterium incorporation was observed in the product benzene. The mechanisms of these reactions are discussed.

Key words: platinum, phenyl, benzene, protonolysis.

Résumé : L'addition, à –78 °C, d'acides de la forme HX (X = Cl, BF_4, CF_3SO_3, CF_3CO_2) à des complexes [$PtPh_2$(NN)] (NN = bu_2bpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine) et [PtPh(NCN)] (NCN = 2,6-$C_6H_3(CH_2NMe_2)_2$ conduit aux complexes correspondants phényl(hydrido)platine(IV) [PtX(H)Ph_2(NN)] et [PtX(H)Ph(NCN)] qui se décomposent par élimination réductrice du benzène, à environ –20 °C, pour conduire aux complexes de platine(II) [PtXPh(NN)] et [PtX(NCN)]. L'addition subséquente de HCl au complexe [PtClPh(NN)], à basse température, conduit au [$PtHCl_2$Ph(NN)] qui se décompose au-dessus de –10 °C pour donner du benzène et du [$PtCl_2$(NN)]. La réaction du DBF_4 avec du [$PtPh_2$(NN)], en présence d'un excès de CD_3OD, conduit à la formation de C_6H_5D et de $C_6H_4D_2$; toutefois, avec le [PtPh(NCN)], on n'observe aucune incorporation multiple de deutérium dans le benzène obtenu comme produit. On discute des mécanismes de ces réactions.

Mots clés : platine, phényle, benzène, protonolyse.

[Traduit par la Rédaction]

Introduction

The activation of alkanes or arenes by platinum(II) complexes is thought to involve the intermediacy of alkyl(hydrido)platinum(IV) or aryl(hydrido)platinum(IV) complexes, and so there has been much interest in such complexes (1–13). A useful synthetic route to platinum(IV) complexes [PtX(H)R_2(NN)] (NN = bidentate nitrogen-donor ligand, X = halide, R = alkyl or aryl) is by addition of acid HX to a platinum(II) complex [PtR_2(NN)] and the decomposition of these platinum(IV) complexes by reductive elimination of RH to give [PtXR(NN)], which leads to overall protonolysis of the alkyl–platinum or aryl–platinum bond, can then be studied (3–5). Hydrido(alkyl)-, hydrido(aryl)-, and hydrido(silyl)platinum complexes are proposed in several other important catalytic reactions, including the hydrosilation reactions catalyzed by platinum complexes (14). Most of the recent studies of protonolysis of platinum–carbon bonds have involved complexes [PtR_2(NN)], in which the alkyl or aryl groups are trans to nitrogen donor ligands (3–5), and it was of interest to compare complexes with mutually trans Pt—C bonded groups. This paper reports a study of the reactions of acids with the complexes *cis*-[$PtPh_2$(NN)](NN = bu_2bpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine, **1**) and [PtPh(NCN)] (NCN = 2,6-$C_6H_3(CH_2NMe_2)_2$, **2**) in which the NCN pincer ligand forces the two aryl groups to be mutually trans (15) (Chart 1).

Results

The phenylplatinum complexes 1 and 2

Complex **1** was prepared by reaction of the ligand bu_2bpy with the precursor [$PtPh_2(\mu\text{-}SMe_2)]_n$, n = 2 or 3 (16–18), in

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This article is dedicated to Dr. John Harrod for his distinguished contributions to organometallic chemistry and its applications in catalysis and materials science.

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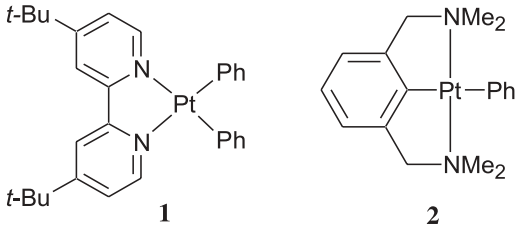
Chart 1.



diethyl ether solution, while complex **2** was prepared by a modified literature method (15).

The structures of complexes **1** and **2** are shown in Figs. 1 and 2, with selected bond distances and angles listed in Tables 1 and 2. Each complex contains a roughly square-planar platinum(II) center, but with *cis*- and *trans*-PtC_2N_2 coordination, respectively, and in each case the phenyl group lies roughly orthogonal to the square plane (79° in **1**, in which the two phenyl groups are crystallographically equivalent; 84° in **2**, Figs. 1 and 2). This conformation allows platinum–phenyl $d\pi$-$p\pi$ bonding and minimizes steric effects. The Pt—C(phenyl) bond distance is shorter in **1** (2.023(2) Å, trans to N) than in **2** (2.111(6) Å, trans to C), as expected since nitrogen has the lower trans-influence. However, the distance Pt(1)—C(1) = 1.956(6) Å in **2** is shorter than either of these Pt—C(phenyl) distances, as a result of the chelate effect. Other bond distances and angles are comparable to those reported for related complexes [$PtR_2(bu_2bpy)$] (5, 16) or [$PtX\{2,6\text{-}C_6H_3(CH_2NMe_2)_2\}$] (15).

Fig. 1. A view of the structure of complex **1**. 30% Thermal ellipsoids are shown and hydrogen atoms have been omitted for clarity.

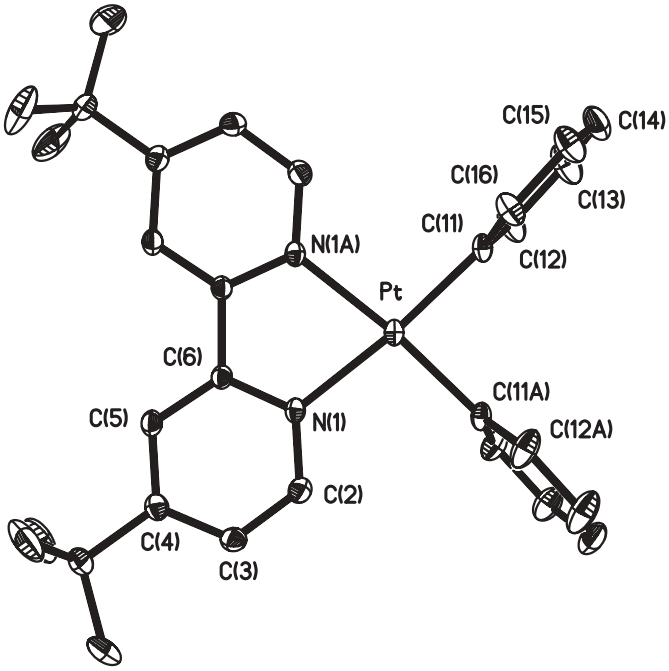


Fig. 2. A view of the structure of complex **2**. 30% Thermal ellipsoids are shown and hydrogen atoms have been omitted for clarity.

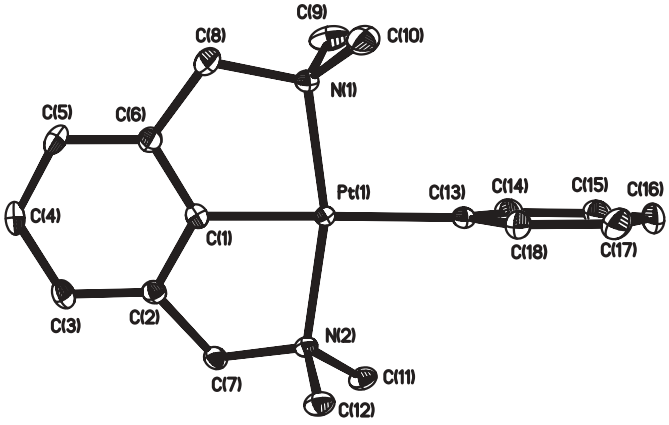


Table 1. Selected bond lengths (Å) and angles (°) for complex **1**.

Bond lengths (Å)	
Pt(1)—C(11)	2.023(2)
Pt(1)—N(1)	2.097(3)
Bond angles (°)	
N(1)-Pt(1)-N(1A)	77.1(2)
N(1A)-Pt(1)-C(11)	97.4(1)
N(1)-Pt(1)-C(11)	174.5(1)
C(11A)-Pt(1)-C(11)	88.2(2)

Reactions with acids

Complex **1** reacted with 1 equiv. of acid HX (X = Cl, CF_3CO_2, CF_3SO_3, BF_4) at room temperature to give benzene and the corresponding product [$PtXPh(bu_2bpy)$] (**3a**, X = Cl; **3b**, X = CF_3CO_2; **3c**, X = CF_3SO_3; **3d**, X = BF_4) (Scheme 1). The complexes were characterized by elemental analysis and by their ^{1}H NMR spectra, which showed the presence of nonequivalent *t*-BuC_4H_3N units and only a single phenylplatinum group.

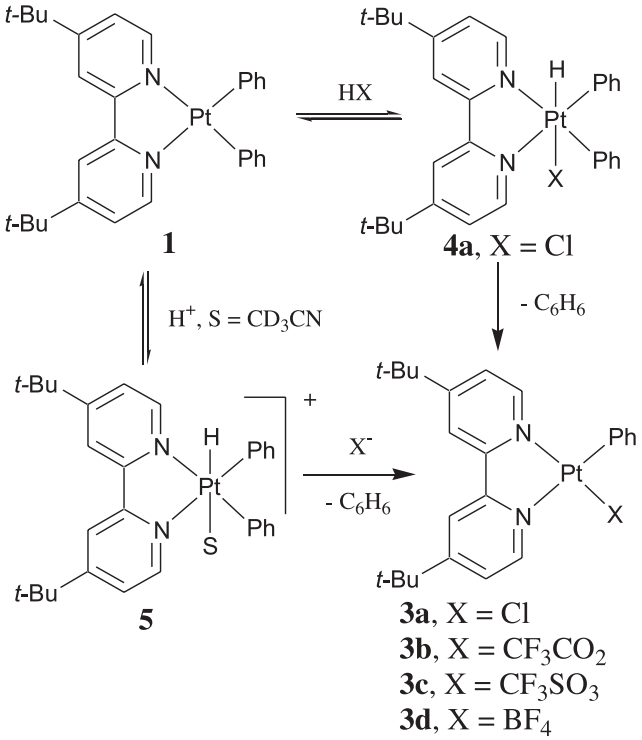
The reaction of complex **1** in $CDCl_3$ solution with HCl at –78 °C gave an intermediate hydridoplatinum(IV) complex **4a** (Scheme 1) that was identified by its ^{1}H NMR spectrum. The hydride resonance was observed at δ = –20.15 with ^1J(PtH) = 1613 Hz (Table 3). The trans oxidative addition of HCl was shown by the observation of equivalent *t*-BuC_4H_3N and phenyl groups. Complex **4a** decomposed at –20 °C by reductive elimination of benzene to yield the product [$PtClPh(bu_2bpy)$] (**3a**) and no other intermediates were observed. The similar reaction of **1** in $CDCl_3$ with the other acids failed to give detectable hydride intermediates, but the reaction with HBF_4 or CF_3SO_3H in $CDCl_3$–CD_3CN gave a hydride intermediate (**5**) characterized by δ(PtH) = –21.84, ^1J(PtH) = 1619 Hz. This is presumed to be a cationic acetonitrile complex, since the spectral properties were the same in each case and acetonitrile is a stronger ligand than either triflate or tetrafluoroborate. Complex **5** decomposed on warming the solution to –20 °C to give complex **3d**.

The complex [$PtClPh(bu_2bpy)$] (**3a**) reacted with HCl at room temperature to give benzene and [$PtCl_2(bu_2bpy)$] (5). When the reaction was carried out at –78 °C, the intermediate hydridoplatinum(IV) complex [$PtHCl_2Ph(bu_2bpy)$] (**6**)

Table 2. Selected bond lengths (Å) and angles (°) for complex **2**.

Bond lengths (Å)	
Pt(1)—C(1)	1.956(6)
Pt(1)—N(1)	2.079(5)
Pt(1)—N(2)	2.079(5)
Pt(1)—C(13)	2.111(6)
Bond angles (°)	
N(1)-Pt(1)-N(2)	164.1(2)
N(1)-Pt(1)-C(13)	97.8(2)
N(2)-Pt(1)-C(13)	97.9(2)
N(1)-Pt(1)-C(1)	82.3(2)
N(2)-Pt(1)-C(1)	81.9(2)
C(1)-Pt(1)-C(13)	177.2(2)

Scheme 1.



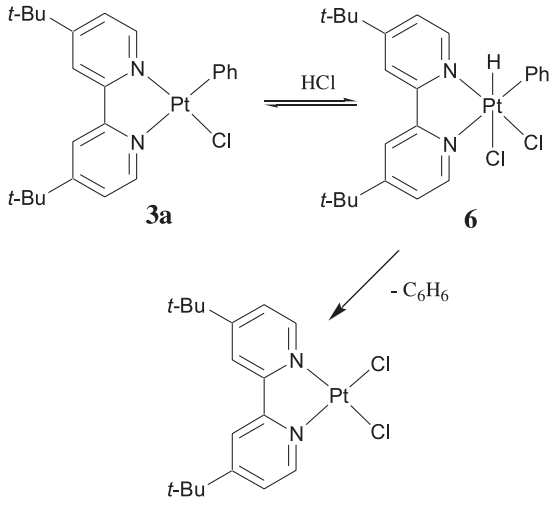
was detected. The ^{1}H NMR spectrum contained a hydride resonance at δ = –25.94 with ^1J(PtH) = 1540 Hz, in the range expected for a hydride trans to chloride (Table 3) (5). The aromatic region of the spectrum contained six resonances for the bu_2bpy ligand and three for the phenyl group, consistent with the proposed structure that arises from trans oxidative addition. The hydride complex decomposed at –20 °C to give benzene and [$PtCl_2(bu_2bpy)$] (Scheme 2).

Reaction of [PtPh{2,6-$C_6H_3(CH_2NMe_2)_2$}] (**2**) with acids HX gave benzene and the corresponding complexes [PtX{2,6-$C_6H_3(CH_2NMe_2)_2$}] (**7a**, X = Cl; **7b**, X = CF_3CO_2; **7c**, X = CF_3SO_3; **7d**, X = BF_4) (Scheme 3) (15). Reaction of complex **2** with HCl in $CDCl_3$ at –78 °C gave the hydridoplatinum(IV) complex [PtHClPh{2,6-$C_6H_3(CH_2NMe_2)_2$}] (**8**) which was characterized by a hydride resonance at δ = –21.36 with ^1J(PtH) = 1622 Hz. The hydride resonance decayed at –20 °C as reductive elimination of benzene occurred to give **7a**. Similarly, reaction of **2** in $CDCl_3$–CD_3CN at –78 °C with triflic acid or tetrafluoroboric acid gave [PtHPh(NCCD$_3$){2,6-$C_6H_3(CH_2NMe_2)_2$}]$^+$ (**9**) identified by its ^{1}H NMR spectrum (δ(PtH) = –20.47, ^1J(PtH) = 1644 Hz) and it decomposed at –20 °C to give benzene and complex **7c** or **7d**. The complexes **7** were inert to protonolysis under

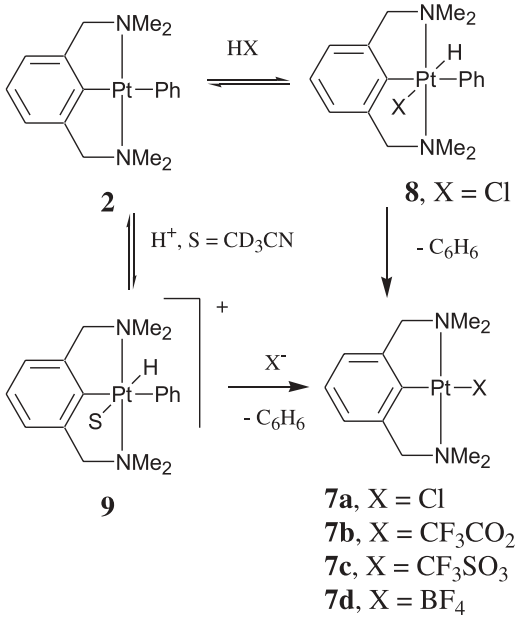
Table 3. ^{1}H NMR data for hydridoplatinum(IV) complexes.

Complex	δ (PtH)	^1J(PtH) (Hz)
[$PtHClPh_2(bu_2bpy)$] (**3a**)	–20.15	1613
[$PtHPh_2$(MeCN)(bu_2bpy)]$^+$ (**5**)	–21.84	1619
[$PtHCl_2Ph(bu_2bpy)$] (**6**)	–25.94	1540
[PtHClPh{2,6-$C_6H_3(CH_2NMe_2)_2$}] (**8**)	–21.36	1622
[PtHPh(MeCN){2,6-$C_6H_3(CH_2NMe_2)_2$}]$^+$ (**9**)	–20.47	1644

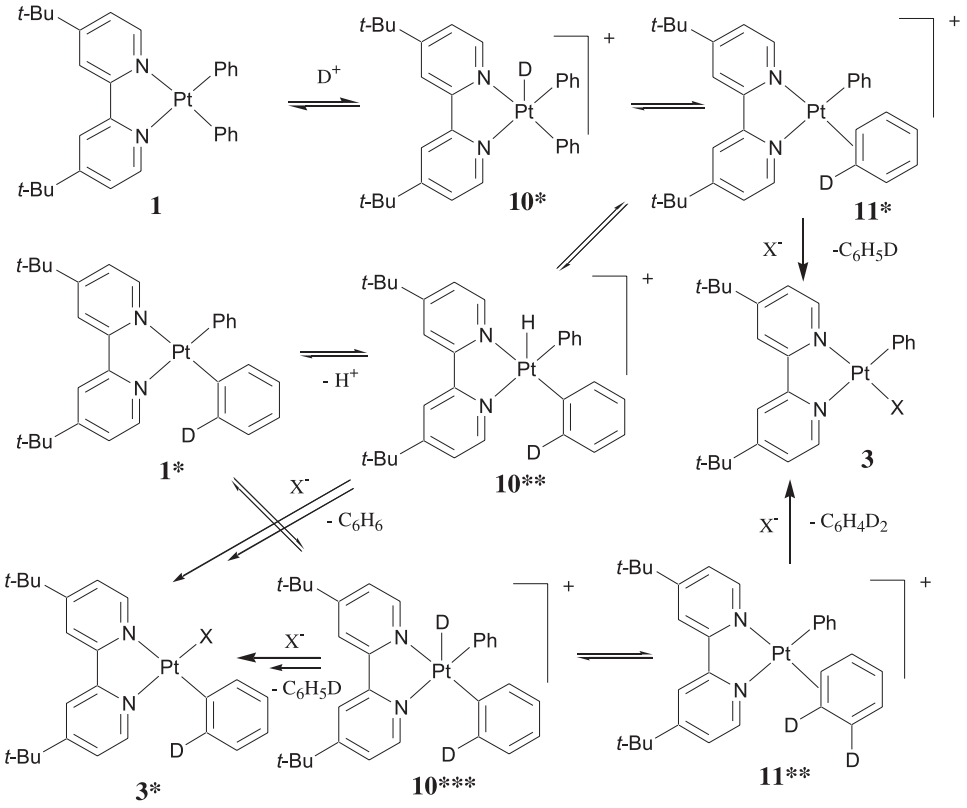
Scheme 2.



Scheme 3.



Scheme 4.



mild conditions, and there was no evidence for the addition of protons to the aryl group, though several electrophiles are known to add easily to the ipso carbon atom (15).

Studies of H-D exchange

The reaction of **1** and **2** with DBF_4 in $CDCl_3$–CD_3OD was studied to observe H-D exchange and hence, to investigate reversibility of the protonation and C-H reductive elimination steps. In each case, the benzene was analyzed by GC–MS. In the reaction with **1**, the ratio of C_6H_6:C_6H_5D:$C_6H_4D_2$ was 0.1:1.0:0.2, indicating significant formation of $C_6H_4D_2$, but in the reaction of **2** the ratio was 0.1:1.0:0.01, indicating very little if any deuterium enrichment beyond C_6H_5D. Integration of the phenylplatinum resonances in the product **3a** from reaction with complex **1** indicated that there was about 10% D-incorporation, distributed equally in the ortho, meta, and para positions. In the reaction with **2** there was no detectable D-incorporation in the C_6H_3 group of the NCN ligand. It has been shown previously that electrophilic attack at the ipso carbon atom of the C_6H_3 group of the NCN ligand is easy, but of course the chelate ligand prevents scrambling if reversible addition of D occurs at this point and no direct evidence of such reactivity was found (15).

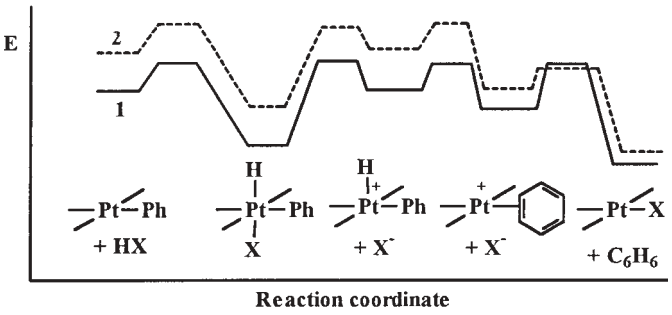
Discussion

The intermediacy of hydridoplatinum(IV) complexes in the protonolysis of metal–carbon bonds in electron-rich alkyl or aryl complexes of platinum(II) or in C-H activation by electrophilic platinum complexes, is now accepted as the general rule, though other mechanisms are possible (1–12). It is easier to detect these hydridoplatinum(IV) complex intermediates when they are generated by protonation of alkyl or aryl platinum(II) complexes and many details of their structures and energetics have been determined over recent years (1–10). Strong dependence on the nature of the hydrocarbyl group, the supporting ligands, the acid used, and the solvent medium has been demonstrated (3–5). The phenylplatinum complexes **1** and **2** are constrained to have the phenyl group(s) trans to nitrogen or carbon, respectively, and so a study of the dependence of protonolysis mechanism on stereochemistry is possible.

The chemistry shown in Schemes 1–3 illustrates that the mechanism of protonolysis of the phenylplatinum groups in **1**, **2**, and **3a** is similar in each case. Intermediate hydridoplatinum(IV) complexes are detected by low-temperature ^1H NMR in all cases. These intermediates are formed essentially quantitatively at –78 °C and they survive for several hours at this temperature, but they decompose on warming to –10 to –20 °C by reductive elimination of benzene. No other intermediates were detectable during reactions that were monitored by NMR, and there were no very dramatic differences in reactivity.

The chief difference between **1** and **2** was observed when the deuterolysis of the phenylplatinum groups was carried out in $CDCl_3$–CD_3OD solvent medium, in which there is a very large excess of exchangeable deuterium. The cleavage of the phenylplatinum groups from **1** or **2** under these conditions gave mostly C_6H_5D, as expected for simple cleavage. However, complex **1** also gave $C_6H_4D_2$ in significant yield and moderate deuterium enrichment in the residual phenylplatinum group of the product **3a**. Free benzene did

Fig. 3. Proposed reaction coordinate diagram for the protonolysis of a phenyl group from either complex **1** or **2** in $CDCl_3$–CD_3OD.



not undergo H-D exchange under the experimental conditions, so the deuterium enrichment occurred during cleavage of the phenylplatinum group to give **3**. A proposed sequence of reactions leading to H-D exchange is shown in Scheme 4. The five-coordinate complex **10*** is proposed as a key intermediate based on earlier work (4, 5); it can be formed by addition of D^+ to complex **1** or by chloride dissociation from the resting state complex [$PtDClPh_2(bu_2bpy)$] (**4a***), which is not shown in Scheme 4. Reductive elimination with C—D bond formation then leads naturally to the benzene-d_1 complex **11***, for which there are now several known precedents (4, 7, 10). Deuterium enrichment in the phenylplatinum groups requires that this reductive elimination reaction be reversible to form a hydrido(deuteriophenyl)platinum(IV) cation **10**** (Scheme 4). The complex **11*** is expected to be fluxional and to undergo rapid edge-to-edge migration of the benzene group, and so the position of the deuterium label will naturally scramble among all possible positions in **11*** and **10**** (though only one is shown in Scheme 4). Formation of $C_6H_4D_2$ requires further deuterium incorporation, likely by deprotonation of **10**** to give **1*** followed by addition of D^+ to give **10***** and C-H reductive elimination to give **11****. Dissociation or displacement of the coordinated benzene from **11** is irreversible, so free benzene cannot coordinate and hence, cannot undergo H-D exchange. In principle, the reactions of Scheme 4 can continue and give complete H-D exchange but only modest enrichment is observed. Hence, the benzene dissociation or displacement step from **11** to give **3** is competitive with the C-H oxidative addition and PtH–PtD exchange steps. Since the addition of D^+ to complex **2** gives no significant amount of $C_6H_4D_2$, in this case the C-H reductive elimination is probably irreversible.

The difference between the chemistry of complexes **1** and **2** can be understood in terms of the qualitative reaction coordinate diagram shown in Fig. 3. There is a destabilizing effect of two strong donor ligands (antisymbiosis) in organoplatinum chemistry, and so the trans-diaryl arrangement in **2** is less stable than the cis-diaryl arrangement in **1**. This relative stability is maintained through the various intermediates through to the proposed benzene complex, but is most pronounced in the trans-diaryl complexes. The six-coordinate hydridoplatinum(IV) complex is the most stable of the intermediates and so the only one that is directly observable in either case. The difference comes at the benzene loss step. The trans-ligand controls the rate of ligand loss through the trans-effect, and so the activation energy for benzene loss is much lower for **2** than for **1**. For **1** the activation energy for benzene loss from the benzene complex cation (Fig. 3) is similar to that for the reverse reactions leading to H-D exchange, whereas for **2** the benzene loss is much faster and so the back reactions are not competitive.

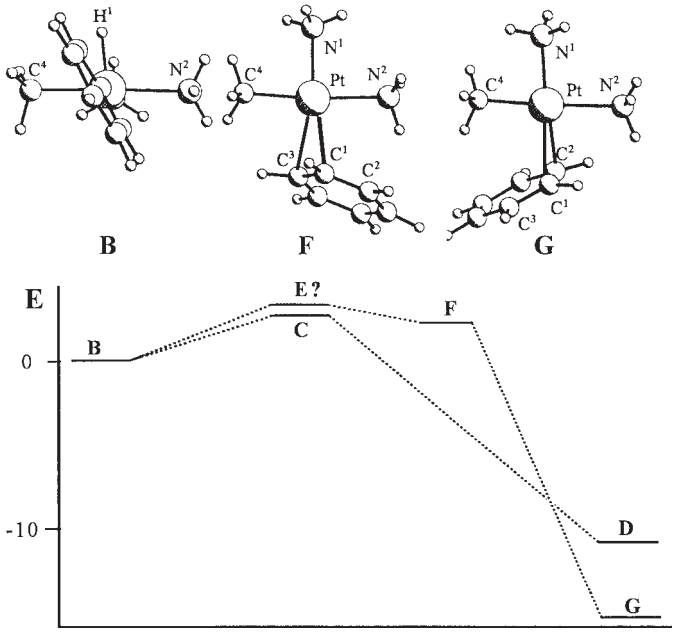
Table 4. Relative energies and bond distances as predicted by the DFT calculations.

Complex	B	C	D	F	G	H
E (kcal mol^{-1})	0	3.1	–10.0	2.5	–16.9	–17.0
Distances (Å)						
PtH^1	1.53	1.87	1.91	2.91	2.69	2.69
PtH^2	2.66	2.64	2.43	2.68	2.64	2.65
PtC^4	2.07	2.55	2.52	2.08	2.06	2.07
PtC^1	2.03	2.03	2.03	2.57	2.37	2.35
PtC^2	3.06	3.00	3.00	3.45	2.38	2.35
PtC^3	2.93	2.99	3.00	2.35	3.27	3.23
PtN^1	2.28	2.28	2.27	2.10	2.11	2.11
PtN^2	2.28	2.07	2.07	2.26	2.30	2.26

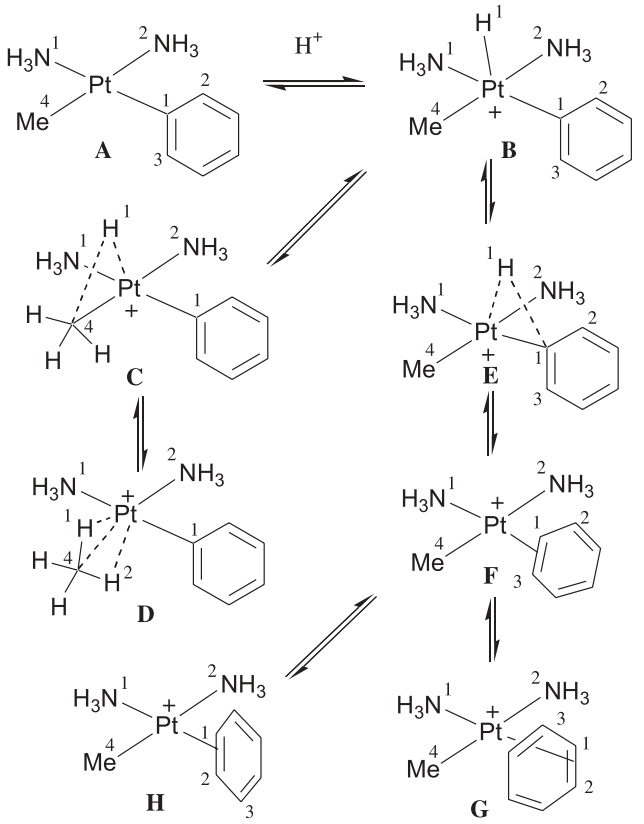
The relevance to C—H bond activation is also clear from Fig. 3. The trans-aryl group in [PtX(NCN)] will labilise the group X^- and so facilitate benzene coordination, but the overall energetics for oxidative addition of the C—H bond will be less favorable than in the case of [PtXPh(NN)]. It is interesting that a platinum(II) complex with a pincer ligand, which has a nitrogen-donor amide rather than a carbon-donor aryl group at the center, is capable of activating benzene to give a phenylplatinum(II) derivative (17).

The mechanism by which the five-coordinate hydrido(phenyl)platinum(IV) intermediate might be transformed to the benzene complex was examined by using density functional theory (DFT) on the model complex [$PtHMePh(NH_3)_2$]$^+$, chosen so as to give a reasonable model for the complex [$PtHPh_2(bu_2bpy)$]$^+$ (**10**). This model is also useful since it allows a comparison of the Me···H and Ph···H reductive elimination pathways. Some data are given in Table 4 and summarized in Fig. 4, while the proposed mechanism is summarized in Scheme 5. The five-coordinate complex **B** (Fig. 4, Scheme 5) has square-pyramidal stereochemistry. The hydride is slightly displaced towards the methyl group (HPtC = 85°) and the phenyl group rotates away from the position in which it is orthogonal to the C_2PtN_2 plane to avoid steric effects between the hydride and the ortho hydrogen atom of the phenyl group (Fig. 4). Complex **B** can decompose by C-H reductive elimination to give either a phenyl(methane)platinum(II) complex **D** or a methyl(benzene)platinum(II) complex **G** (Scheme 5). The formation of **D** (Scheme 5) occurs in a very similar way to that found earlier for methane reductive elimination from methyl(hydrido)platinum(IV) complexes (9), with a late transition state **C** (Scheme 5) and the activation energy was calculated as 3.1 kcal mol^{-1} (Table 4). The reductive elimination from **B** by coupling of the hydride and phenyl groups proved more difficult to define by DFT. The final state is predicted to be **G** (Scheme 5, Fig. 4) in which the benzene ligand is η^2-bonded, with the C-C axis perpendicular to the plane of the platinum(II) and with the benzene oriented towards the methyl group. The orientation of the benzene in **G**

Fig. 4. The predicted structures of the complexes $[PtHMePh(NH_3)_2]^+$ (**B**) and $[PtMe(C_6H_6)(NH_3)_2]^+$ (**F** and **G**) and below the calculated energies (kcal mol^{-1}) of the complexes **B**–**G**.



Scheme 5.



is very similar to that found experimentally in the hydrido(benzene)platinum(II) complex $[PtH(C_6H_6)\{\kappa^2\text{-}(Hpz^*)BHpz^*_2\}]^+$, in which benzene is oriented towards the hydride (10). There is a conformer of **G** in which the benzene is oriented towards the ammine (**H**) and it is very close in energy, presumably because the steric effects of CH_3 and

NH_3 are essentially the same (Table 4), but **H** will certainly be less favored in complexes with bulkier amine or imine ligands. The hydrogen atoms C^1H^1 and C^2H^2 in **G** and **H** are bent away from the platinum by about 10° but otherwise the benzene molecule is like free benzene. The transition state was expected to resemble **E** (Scheme 5), with the hydride bridging between platinum and the ipso carbon in an analogous way as in **C**, but no such transition state could be located. The only transition state found was **F** in which the Pt—H bond is completely broken (PtH^1 = 2.91 Å) and the C—H bond completely formed (C^1H^1 = 1.09 Å) (Scheme 5, Fig. 4). Complex **F** is another η^2-bonded benzene complex of platinum(II) but with atom H^1 still oriented roughly perpendicular to the plane of platinum(II) and so with the coordinated C-C axis in a less favorable orientation than in **G** or **H** for binding to platinum. The benzene is oriented towards the ammine ligand in **F** (Fig. 4). It is possible that the reaction proceeds in two steps, with a first transition state on the way to C-H reductive elimination (**E**) but this could not be defined and is probably close in energy to **F**; the transition from **F** to **G** just requires rocking about the Pt-C^1 axis. The benzene complex **G** is more stable than the methane complex **C**, as expected from the relative ligating abilities of benzene and methane. Since the transition state for C-H reductive elimination was not found, the relative energies of the transition states **C** and **E** are not known. Complex **E** is placed slightly higher than **C** or **F** in Fig. 4, based on the known selectivity for methane elimination in methyl(phenyl)platinum(II) complexes with nitrogen-donor ligands (4). The activation energy for the benzene C-H oxidative addition step, as measured by the energy difference between **G** and **F**, is calculated as 19 kcal mol^{-1}, which can be compared to experimental activation energies of ΔG = 13 to 14 kcal mol^{-1} for transformation of the benzene complex $[PtH(C_6H_6)\{\kappa^2\text{-}(Hpz^*)BHpz^*_2\}]^+$ and similar arene complexes, to the corresponding hydrido(phenyl)platinum(IV) complexes, such as $[PtH_2Ph\{\kappa^2\text{-}(Hpz^*)BHpz^*_2\}]^+$ (10).

Although there are still some questions about the detailed mechanism of the reductive elimination step to form benzene from complex **B**, it seems that the initial C···H bond formation occurs by movement of the hydride parallel to the Pt-C axis, but then a major sideways motion of the phenyl group occurs so as to allow side-on η^2-coordination of the forming benzene group. The activation of benzene by oxidative addition (4, 7, 10, 17) is then expected to follow the microscopic reverse of this sequence.

Experimental section

Syntheses were carried out using a nitrogen atmosphere, employing either Schlenk or glovebox techniques. Solvents were dried and distilled under N_2 prior to use. ^1H and ^{13}C NMR spectra were recorded using Varian Inova 400 and 600 MHz spectrometers. Chemical shifts are reported relative to $SiMe_4$. GC–MS experiments were carried out using a Finnigan Mat 8200 spectrometer; samples were prepared using CD_2Cl_2–CD_3OD solutions followed by direct injection to the GC coupled to the MS and isotopic composition of benzene was determined by simulation, based on spectra of authentic samples. The phenylplatinum(II) complexes were stable in CD_2Cl_2–CD_3OD solution in the absence of added acid, as shown by NMR. The complexes $[\{PtPh_2(\mu\text{-}SMe_2)\}_n]$, bu_2bpy, and $[PtCl\{2,6\text{-}C_6H_3(CH_2NMe_2)_2\}]$ were prepared according to literature methods (15, 18). Solutions containing HCl or DCl were prepared by reaction of a known amount of acetyl chloride with MeOH or CD_3OD, respectively. The DFT calculations were carried out at the B3LYP level employing a LANL2DZ basis set, which uses a relativistic effective core potential for platinum. The program used was the Gaussian-94 software package (19) and the methods used were as described and justified previously (9).

[$PtPh_2(bu_2bpy)$] (1)

To a solution of $[\{PtPh_2(\mu\text{-}SMe_2)\}_n]$ (0.494 g, 1.04 mmol) in Et_2O was added bu_2bpy (0.280 g, 1.04 mmol). The solution immediately turned orange in color. After 12 h, the orange precipitate that formed was filtered off, washed with Et_2O, and dried under vacuum. Yield: 54%. ^1H NMR ($CDCl_3$) δ: 8.45 (d, 2H, J_{HH} = 6Hz), 7.94 (s, 2H), 7.45 (d, 4H, J_{HH} = 8Hz, H_o(Ph)), 7.35 (d, 2H, J_{HH} = 7 Hz), 7.01 (t, 4H, J_{HH} = 7 Hz, H_m(Ph)), 6.88 (t, 2H, J_{HH} = 7 Hz, H_p(Ph)), 1.37 (s, 18H, *t*-Bu). Anal. calcd. for $C_{30}H_{34}N_2Pt$ (%): C 58.33, H 5.55; found: C 58.11, H 5.56.

[$PtClPh(bu_2bpy)$] (3a)

To a solution of **1** (0.062 g, 0.099 mmol) in CH_2Cl_2 (0.5 mL) was added HCl (0.099 mmol). The orange precipitate of the product was filtered off, washed with Et_2O, and dried under vacuum. Yield: 73%. ^1H NMR (acetone-d_6) δ: 9.31 (d, 1H, J_{HH} = 6 Hz), 8.40 (s, 1H), 8.38 (d, 1H, J_{HH} = 6 Hz), 8.33 (s, 1H), 7.79 (d, 1H, J_{HH} = 6 Hz), 7.42 (d, 1H, J_{HH} = 6 Hz), 7.32 (m, 2H, H_o(Ph)), 6.98 (t, 2H, J_{HH} = 7 Hz, H_m(Ph)), 6.87 (t, 1H, J_{HH} = 7 Hz, H_p(Ph)), 1.44 (s, 9H, *t*-Bu), 1.38 (s, 9H, *t*-Bu). Anal. calcd. for $C_{24}H_{29}ClN_2Pt$ (%): C 50.04, H 5.07; found: C 49.56, H 4.94.

[$PtPh(O_2CCF_3)(bu_2bpy)$] (3b)

To a solution of **1** (0.068 g, 0.11 mmol) in CH_2Cl_2 was added CF_3CO_2H (9 μL, 0.11 mmol). The reaction mixture was stirred for 12 h and the solvent was removed under vacuum to yield the product as an orange powder. Yield: 56%. ^1H NMR (acetone-d_6) δ: 8.85 (d, 1H, J_{HH} = 6 Hz), 8.53 (s, 1H), 8.46 (s, 1H), 8.17 (d, 1H, J_{PtH} = 60 Hz, J_{HH} = 6Hz), 7.82 (d, 1H, J_{HH} = 6 Hz), 7.53 (d, 1H, J_{HH} = 6 Hz), 7.37 (d, 2H, J_{HH} = 7 Hz, H_o(Ph)), 7.13 (t, 2H, J_{HH} = 7 Hz, H_m(Ph)), 7.08 (t, 1H, J_{HH} = 7 Hz, H_p(Ph)), 1.46 (s, 9H, *t*-Bu), 1.39 (s, 9H, *t*-Bu). Anal. calcd. for $C_{26}H_{29}F_3N_2O_2Pt_1$(%): C 47.78, H 4.47; found: C 47.49, H 4.41.

[$PtPh(CF_3SO_3)(bu_2bpy)$] (3c)

This was prepared similarly by using CF_3SO_3H. Yield: 64%. ^1H NMR (acetone-d_6) δ: 8.88 (d, 1H, J_{HH} = 6 Hz), 8.53 (s, 1H), 8.46 (s, 1H), 8.16 (d, 1H, J_{PtH} = 58 Hz, J_{HH} = 6 Hz), 7.84 (d, 1H, J_{HH} = 6 Hz), 7.54 (d, 1H, J_{HH} = 6 Hz), 7.35 (d, 2H, J_{HH} = 7 Hz, H_o(Ph)), 6.98 (t, 2H, J_{HH} = 7 Hz, H_m(Ph)), 6.87 (t, 1H, J_{HH} = 7 Hz, H_p(Ph)), 1.46 (s, 9H, *t*-Bu), 1.40 (s, 9H, *t*-Bu). Anal. calcd. for $C_{25}H_{29}F_3N_2O_3SPt$ (%): C 43.54, H 4.24; found: C 43.56, H 4.31.

[PtPh(BF_4)(bu_2bpy)] (3d)

This was prepared similarly by using HBF_4. Yield: 48%. ^{1}H NMR (acetone-d_6) δ: 8.89 (d, 1H, J_{HH} = 6 Hz), 8.55 (s, 1H), 8.47 (s, 1H), 8.19 (d, 1H, J_{HH} = 6 Hz), 7.85 (d, 1H, J_{HH} = 6 Hz), 7.55 (d, 1H, J_{HH} = 6 Hz), 7.37 (d, 2H, J_{HH} = 7 Hz, H_o(Ph)), 7.13 (m, 2H, H_m(Ph)), 7.05 (m, 1H, H_p(Ph)), 1.46 (s, 9H, *t*-Bu), 1.40 (s, 9H, *t*-Bu). Anal. calcd. for $C_{24}H_{29}BF_4N_2Pt$ (%): C 45.95, H 4.66; found: C 45.47, H 4.80.

[PtHClPh$_2$(bu_2bpy)] (4a)

To an NMR tube charged with a solution of **1** (0.052 g, 0.085 mmol) in $CDCl_3$ (0.5 mL) at –78 °C was added HCl (0.085 mmol). ^{1}H NMR in $CDCl_3$ at –80 °C δ: 8.18 (s, 2H), 8.06 (d, 2H, J_{HH} = 6 Hz), 7.86 (d, 2H, J_{HH} = 7 Hz), 7.29 (d, 4H, J_{HH} = 7 Hz, H_o(Ph)), 6.76 (t, 4H, J_{HH} = 7 Hz, H_m(Ph)), 6.67 (t, 2H, J_{HH} = 7 Hz, H_p(Ph)), 1.19 (s, 18H, *t*-Bu), –20.15 (s, 1H, J_{PtH} = 1613 Hz, Pt-H). Compound **2** was indefinitely stable at –78 °C but decomposed rapidly at –20 °C to give C_6H_6 and [PtClPh(bu_2bpy)] (**3a**) as monitored by NMR.

[PtH(NCCD$_3$)Ph$_2$(bu_2bpy)][BF_4] (7)

This was prepared similarly in $CDCl_3$–CD_3CN (1.0 mL) by using HBF_4. ^{1}H NMR ($CDCl_3$–CD_3CN) δ: 8.45 (s, 2H), 8.10 (d, 2H, J_{HH} = 6 Hz), 7.52 (d, 2H, J_{HH} = 6 Hz), 7.18 (d, 4H, J_{HH} = 7 Hz, H_o(Ph)), 6.99 (t, 4H, J_{HH} = 7 Hz, H_m(Ph)), 6.89 (t, 2H, J_{HH} = 7 Hz, H_p(Ph)), 1.36 (s, 18H, *t*-Bu), –21.84 (s, 1H, J_{PtH} = 1619 Hz, Pt-H). Compound **7** was indefinitely stable at –78 °C but decomposed rapidly at –20 °C to give C_6H_6 and [Pt(BF_4)(C_6H_5)(tbu_2bpy)] (**3d**).

[PtHCl$_2$Ph(bu_2bpy)] (6)

To an NMR tube charged with a solution of **3a** (0.016 g, 0.028 mmol) in $CDCl_3$ (0.6 mL) at –78 °C was added HCl (0.028 mmol). ^{1}H NMR ($CDCl_3$) δ: 9.17 (s, 1H), 8.25 (s, 1H), 7.99 (s, 1H), 7.94 (s, 1H), 7.52 (s, 1H), 7.22 (d, 2H, J_{HH} = 6.8Hz, H_o(Ph)), 7.15 (s, 1H), 6.89 (t, 2H, J_{HH} = 7 Hz, H_m(Ph)), 6.76 (t, 1H, J_{HH} = 7 Hz, H_p(Ph)), 1.28 (s, 9H, *t*-Bu), 1.22 (s, 9H, *t*-Bu), –25.94 (s, 1H, J_{PtH} = 1540 Hz, Pt-H). Compound **6** was indefinitely stable at –78 °C but decomposed rapidly at –10 °C to give C_6H_6 and [PtCl$_2$(bu_2bpy)].

[PtPh{2,6-C_6H_3(CH_2NMe_2)$_2$}] (2)

To a solution of [PtCl(C_6H_3(CH_2NMe_2)$_2$)] (0.357 g, 0.78 mmol) in ether (10 mL) at 0 °C was added PhLi (0.43 mL, 0.78 mmol). The mixture was stirred at 0 °C for 5 min, then for 1 h at room temperature. The beige precipitate that had formed was filtered off, washed with pentane, and recrystallized from CH_2Cl_2–pentane to yield colorless crystals of the product (15). Yield: 56%. ^{1}H NMR ($CDCl_3$) δ: 7.67 (d, 2H, J_{HH} = 6 Hz), 7.11 (t, 1H, J_{HH} = 7 Hz), 6.97 (d, 2H, J_{HH} = 7 Hz), 6.92 (m, 2H), 6.87 (t, 1H, J_{HH} = 7 Hz), 4.11 (s, 4H, J_{PtH} = 42 Hz, N-CH_2), 2.89 (s, 12H, J_{PtH} = 44 Hz, NMe_2). ^{13}C NMR ($CDCl_3$) δ: 145.54, 139.59, 126.84, 123.19, 122.63, 119.25, 81.22, 54.36.

[PtCl{2,6-C_6H_3(CH_2NMe_2)$_2$}] (7a)

To a solution of **2** (0.052 g, 0.105 mmol) in a THF:Et_2O (50:50) mixture was added HCl (0.105 mmol). The reaction mixture was stirred for 2 h at which time the beige precipitate was filtered off and washed with ether. Yield: 61%. ^{1}H NMR ($CDCl_3$) δ: 6.97 (t, 1H, J_{HH} = 7 Hz), 6.79 (d, 2H, J_{HH} = 7 Hz), 4.00 (s, 4H, J_{PtH} = 45 Hz, N-CH_2), 3.06 (s, 12H, J_{PtH} = 36 Hz, NMe_2). Anal. calcd. for $C_{12}H_{19}ClN_2Pt$ (%): C 34.17, H 4.54; found: C 34.01, H 4.62.

[Pt(CF_3CO_2){2,6-C_6H_3(CH_2NMe_2)$_2$}] (7b)

This was prepared similarly using CF_3CO_2H. Yield: 48%. ^{1}H NMR (CD_2Cl_2) δ: 6.81 (t, 1H, J_{HH} = 6 Hz), 6.79 (d, 2H, J_{HH} = 4 Hz), 4.01 (s, 4H, J_{PtH} = 48 Hz, N-CH_2), 2.95 (s, 12H, J_{PtH} = 36 Hz, NMe_2). Anal. calcd. for $C_{14}H_{19}F_3O_2N_2Pt$ (%): C 33.67, H 3.83; found: C 33.59, H 3.72.

[Pt(CF_3SO_3){2,6-C_6H_3(CH_2NMe_2)$_2$}] (7c)

This was prepared similarly using CF_3SO_3H. Yield: 36%. ^{1}H NMR (CD_2Cl_2) δ: 6.92 (t, 1H, J_{HH} = 7 Hz), 6.76 (d, 2H, J_{HH} = 7 Hz), 3.98 (s, 4H, J_{PtH} = 41 Hz, N-CH_2), 2.99 (s, 12H, J_{PtH} = 37 Hz, NMe_2). Anal. calcd. for $C_{13}H_{19}F_3N_2O_3PtS$ (%): C 29.16, H 3.58; found: C 29.42, H 3.73.

[Pt(BF_4){2,6-C_6H_3(CH_2NMe_2)$_2$}] (7d)

This was prepared similarly using HBF_4. Yield: 57%. ^{1}H NMR (acetone-d_6) δ: 6.72 (t, 1H, J_{HH} = 7 Hz), 6.55 (d, 2H, J_{HH} = 7 Hz), 3.78 (s, 4H, J_{PtH} = 48 Hz, N-CH_2), 2.76 (s, 12H, J_{PtH} = 38 Hz, NMe_2). Anal. calcd. for $C_{12}H_{19}BF_4N_2Pt$ (%): C 30.46, H 4.05; found: C 30.42, H 4.11.

[PtHClPh{2,6-C_6H_3(CH_2NMe_2)$_2$}] (8)

To an NMR tube charged with a solution of **2** (0.046 g, 0.091 mmol) in $CDCl_3$ at –78 °C was added HCl (0.091 mmol). ^{1}H NMR ($CDCl_3$) δ: 7.70 (d, 2H, J_{HH} = 6 Hz), 7.16 (t, 1H, J_{HH} = 7 Hz), 6.98 (d, 2H, J_{HH} = 7 Hz, H_o(Ph)), 6.96 (m, 2H, H_m(Ph)), 6.94 (t, 1H, J_{HH} = 7 Hz, H_p(Ph)), 4.15 (s, 4H, N-CH_2), 2.89 (s, 12H, NMe_2), –21.36 (s, 1H, J_{PtH} = 1622 Hz, Pt-H). Compound **8** was indefinitely stable at –78 °C but decomposed rapidly at –20 °C to give C_6H_6 and [PtCl{C_6H_3(CH_2NMe_2)$_2$}] (**7a**).

[PtHPh(NCCD$_3$){2,6-C_6H_3(CH_2NMe_2)$_2$}][CF_3SO_3] (9)

This was prepared similarly in $CDCl_3$–CD_3CN solution at –78 °C by using CF_3SO_3H. ^{1}H NMR ($CDCl_3$–CD_3CN) δ: 7.92 (t, 1H, J_{HH} = 8 Hz), 7.46 (d, 2H, J_{HH} = 8 Hz), 6.98 (m, 2H, H_o(Ph)), 6.87 (t, 2H, J_{HH} = 7 Hz, H_m(Ph)), 6.75 (t, 1H, J_{HH} = 7 Hz, H_p(Ph)), 4.10 (s, 4H, N-CH_2), 2.86 (s, 12H, NMe_2), –20.47 (s, 1H, J_{PtH} = 1644 Hz, Pt-H). Compound **9** was indefinitely stable at –78 °C but decomposed rapidly at –20 °C to give C_6H_6 and [Pt(CF_3SO_3){C_6H_3(CH_2NMe_2)$_2$}] (**7c**).

X-ray structure determinations

Crystals of **1** and **2** were grown from acetone and chloroform solution, respectively. Crystals were mounted on glass fibres. Data were collected by using a Nonius Kappa-CCD diffractometer with COLLECT (20) software. Crystal data and refinement parameters are listed in Table 5. Data were scaled using SCALEPACK (21), and empirical absorption corrections were applied using redundant data and XPREP (SHELXTL 5.03). Full-matrix least-squares refinement on

Table 5. Crystal data and structure refinement for complexes **1** and **2**.

Complex	**1**·2Me$_2$CO	**2**
Formula, fw	$C_{36}H_{46}N_2O_2Pt$, 733.84	$C_{18}H_{24}N_2Pt$, 463.09
Temperature (K)	200(2)	293(2)
Wavelength (Å)	0.71073	0.71070
Crystal system	Monoclinic	Monoclinic
Space group	*P*2/*c*	*P*2(1)/*n*
Cell dimensions	*a* = 12.7265(3) Å	*a* = 9.3780(19) Å
	b = 14.2079(2) Å	*b* = 14.663(3) Å
	c = 10.0711(2) Å	*c* = 12.650(3) Å
	β = 69.0990(3)°	β = 107.35(3)°
Volume (Å^3), *Z*	1701.2(6), 2	1660.2(6), 4
Density (calcd.) (Mg m^{-3})	1.433	1.856
Abs. coeff. (mm^{-1})	4.156	2.112
F(000)	740	224
θ Range (°)	2.60–27.48	2.67–24.99
No. of reflns collected	17 452	5665
Data/restraints/param.	3897/0/203	2918/0/190
Goodness-of fit on F^2	1.029	0.961
Final *R* indices ($I > 2\sigma(I)$)	*R*1 = 0.0309	*R*1 = 0.0321
	*wR*2 = 0.0732	*wR*2 = 0.081
R indices (all data)	*R*1 = 0.0361	*R*1 = 0.0395
	*wR*2 = 0.0752	*wR*2 = 0.0852

F^2 was performed after solving using Patterson methods and the solution package SHELXTL 5.03 (22). Complex **1** contained two molecules of acetone of solvation.[3]

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[3] Supplementary data may be purchased from the Directory of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0S2, Canada (http://www/nrc.ca/cisti/irm/unpub_e.shtml for information on ordering electronically). CCDC 200608 and 200609 contain tables of crystallographic data for **1** and **2** in CIF format. These data can be obtained, free of charge, via ww.ccdc.cam.ac.uk/conts/retreiving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax +44 1223 336033; or deposit@ccdc.cam.ac.uk).

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