Cationic Methyl(hydrido)platinum(IV) Complexes

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The new complex $[PtMe_2(BPMA)]$, **1**, BPMA = bis(2-pyridylmethyl)amine, is shown to contain bidentate BPMA with one of the pyridyl groups not coordinated to platinum. Complex **1** reacts with HX (X = Cl, BF_4) at room temperature to yield $[PtHMe_2(BPMA)][X]$, which may exist in two isomeric forms, each containing tridentate BPMA. The major initial product **2** has the hydride *trans* to a pyridyl group, but this equilibrates with isomer **3** in which the hydride is *trans* to an amine. The cationic methyl(hydrido)platinum(IV) complexes **2** and **3** are stable at room temperature for several hours, but undergo slow reductive elimination of CH_4 to yield [PtMe(BPMA)][X], **4**. Complex **1** reacts with DCl to give $[PtDMe_2(BPMA)][X]$, and deuterium incorporation at the methyl group *trans* to amine occurs slowly; the methane formed by subsequent reductive elimination is a mixture of CH_4, CH_3D, and CH_2D_2. Reaction of **1** with MeI initially yields a mixture of two compounds, $[PtMe_3(BPMA)][I]$, **5a**, and a neutral compound, $[PtIMe_3(BPMA)]$, **6**, but **6** isomerizes to **5** over a period of 2 h at room temperature. Reaction of **1** with CD_3I gives $[PtMe_2(CD_3)(BPMA)][I]$, **5a***, and $[PtIMe_2(CD_3)(BPMA)]$, **6***, with CD_3 largely *trans* to pyridyl or iodide, respectively, but equilibration gives a mixture of **5a*** and **5a****, in which CD_3 is *trans* to amine. In contrast to the reaction with MeI, oxidative addition of CF_3SO_3Me to **1** gives only $[PtMe_3(BPMA)][CF_3SO_3]$, **5b**. Reaction of **1** with allyl bromide yields a mixture of two products, $[PtMe_2(CH_2CH{=}CH_2)(BPMA)][Br]$, **7**, and $[PtBrMe_2(CH_2CH{=}CH_2)(BPMA)]$, **8**; complex **8** isomerizes rapidly to **7**. Complexes **4** and **7** have been characterized by X-ray structure determinations and are shown to contain the BPMA ligands in *fac* and *mer* coordination modes.

Introduction

There is evidence for at least two mechanisms for the cleavage of methylplatinum(II) bonds by electrophilic reagents, involving either direct attack at the M−C bond or a two-step oxidative-addition/reductive-elimination sequence (Scheme 1).[2] For complexes $[PtMe_2L_2]$, in which the ligands L are good σ-donors, it has recently been shown that dimethyl(hydrido)platinum(IV) intermediates can be detected, thus giving strong support for the oxidative-addition/reductive-elimination mechanism for such compounds.[3−7]

The reaction of HCl with $[PtMe_2(N\text{-}N)]$ (N-N = bipy = 2,2′-bipyridyl, me_2bipy = 4,4′-dimethyl-2,2′-bipyridyl, or bu_2bipy = 4,4′-di-*tert*-butyl-2,2′-bipyridyl) yields the *trans* oxidative-addition product $[PtHClMe_2(N\text{-}N)]$ at −78 °C, and as the temperature of the solutions of these complexes is increased, loss of CH_4 is observed.[3,6] The complexes $[PtHMe_2Tp]$ (Tp = tris(pyrazolyl)borate and tris(3,5-dimethylpyrazolyl)borate) are much more stable to thermolysis and do not reductively eliminate methane at room temperature.[4,5] These complexes can, therefore, be isolated in their pure form, and one derivative has been structurally characterized.[5] It has been suggested that reductive elimination occurs through a five-coordinate intermediate,[3−7] and the exceptional thermal stability of $[PtHMe_2Tp]$ arises since there is no easily dissociated ligand.[4,5]

The ligand Tp gives exceptional stability to platinum(IV) for a number of reasons, in addition to that

Scheme 1

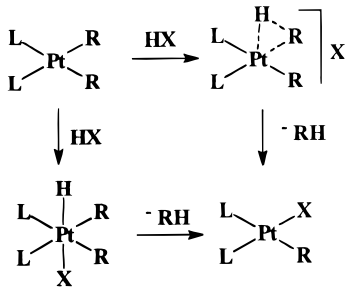

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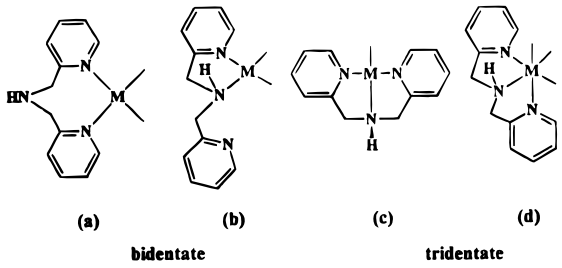
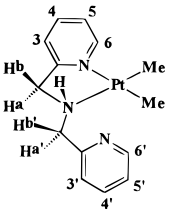
Chart 1. Binding Modes of BPMA



already discussed. It gives very strong facial binding as a tridentate ligand, but can only act as a bidentate ligand in square planar complexes. Hence, reductive elimination of platinum(IV) to platinum(II) is not favored.[4,5] In addition, the negative charge of Tp^- increases the donor strength and again stabilizes the higher oxidation state, platinum(IV). It, thus, seemed likely that a neutral, flexible, tridentate nitrogen donor ligand might give dimethyl(hydrido)platinum(IV) complexes of intermediate thermal stability suitable for mechanistic studies. The ligand bis(2-pyridylmethyl)-amine, BPMA, was chosen to test this hypothesis. First prepared by Larsen[8] to study structural and magnetic properties of dimeric chromium(III) complexes, it and related ligands have also been used in structural studies of ruthenium(II) "piano-stool" complexes[9] and in oxo-bridged complexes of manganese(III).[10] It has most recently been used on silica supports to test metal binding selectivities in wastewater treatment.[11] On the basis of these reports, BPMA appears to bind strongly to transition metals (Chart 1) and it offers an interesting comparison to the bidentate bipyridyl and tris(pyrazolyl)borate ligands studied earlier.[3−7,12,13] The results are reported below.

Experimental Section

All ^{1}H, COSY, and ^{13}C{^{1}H} NMR spectra were recorded using a Varian Gemini 200 or 300 MHz spectrometer. Chemical shifts are reported in ppm relative to TMS. The ^{1}H NMR labeling scheme for BPMA is given below; assignments are given in the most detail for complex **1** and more briefly for the other compounds. IR spectra were recorded as Nujol



mulls, unless otherwise stated, by using a Perkin-Elmer 2000 FTIR spectrometer. Elemental analyses were performed by Guelph Chemical Laboratories, Guelph, Ontario, Canada. All solvents were dried and distilled under N_2; toluene and THF were dried over sodium benzophenone ketyl, and CH_2Cl_2 was dried over CaH_2. Me_3SiCl, allyl bromide, $HBF_4{\cdot}OEt_2$, 2-pyridinecarboxaldehyde, and 2-(methylamino)pyridine were purchased from Aldrich. The complexes $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$[14] and bis(2-pyridylmethyl)amine[11] (BPMA) were prepared according to literature methods. All reactions were carried out under an atmosphere of dry N_2.

[PtMe$_2$(BPMA)], 1. $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ (500 mg, 0.659 mmol) was dissolved in toluene (20 mL), and a solution of BPMA (0.25 mL, 1.32 mmol) in toluene (5 mL) was added dropwise with stirring. The colorless solution gradually changed to pale red, and within 5 min the yellow microcrystalline product began to precipitate from solution. Stirring was stopped, and the mixture was allowed to stand overnight at room temperature. The yellow microcrystalline product was filtered in air and dried *in vacuo*, yield 560 mg, 90%. Anal. Calcd for $C_{14}H_{19}N_3Pt{\cdot}H_2O$: C, 38.0; H, 4.8; N, 9.5. Found: C, 38.5; H, 4.5; N, 9.4. IR: ν(NH) = 3271 cm^{-1}. NMR (CD_2Cl_2): δ(^{1}H) 8.80 (d, 1H, $^3J(H^6H^5)$ = 5 Hz, $^3J(PtH^6)$ = 20 Hz, H^6), 8.60 (m, 1H, $^3J(H^{6'}H^{5'})$ = 5 Hz, H$^{6'}$), 7.87 (td, 1H, $^3J(H^4H^3)$ = $^3J(H^4H^5)$ = 8 Hz, $^4J(H^4H^6)$ = 2 Hz, H^4), 7.69 (td, 1H, $^3J(H^{4'}H^{3'})$ = $^3J(H^{4'}H^{5'})$ = 8 Hz, $^4J(H^{4'}H^{6'})$ = 2 Hz, H$^{4'}$), 7.25 (m, 4H, H$^{3,5,3',5'}$), 4.75 (br, NH), 4.42 (dd, 1H, $^2J(H^aH^b)$ = 15 Hz, J = 4 Hz, C*H*^{a}H^b), 4.25 (dd, 1H, $^2J(H^aH^{b'})$ = 15 Hz, J = 5 Hz, C*H*^{a}H$^{b'}$), 3.90 (dd, 1H, $^2J(H^{a'}H^{b'})$ = 15 Hz, J = 5 Hz, CH$^{a'}$*H*$^{b'}$), 3.82 (dd, 1H, $^2J(H^aH^b)$ = 15 Hz, $^3J(H^bH)$ = 10 Hz, CH^a*H*^{b}), 0.55 (s, 3H, ^2J(PtH) = 87 Hz, CH_3), 0.49 (s, 3H, ^2J(PtH) = 86 Hz, CH_3).

[PtMe$_2$(H)(BPMA)][Cl], 2a and 3a. $SiMe_3Cl$ (9 μL, 0.071 mmol) was added to a solution of H_2O (1.3 μL, 0.071 mmol) (to generate HCl) and **1** (30 mg, 0.071 mmol) in THF (3 mL), changing the color of the orange solution to yellow. Within 5 min a pale yellow precipitate formed, and after the mixture was stirred for 10 min the solvent was removed via cannula and the solid washed with THF (3 × 1 mL) to leave a mixture of pale yellow **2a** and **3a**, yield 28 mg, 86%. The complex is hygroscopic and decomposes over a period of days in the solid state, and good analytical data could not be obtained.

Alternatively, the mixture of **2a** and **3a** can be generated by the addition of excess HCl as an ether solution. Addition of HCl−ether to a solution of **1** in THF yields a pale yellow microcrystalline product. After the mixture was stirred for 2 min, THF, ether, and excess HCl are removed *in vacuo* to leave **2a** and **3a** in quantitative yield. IR (acetone): ν(PtH) 2274 cm^{-1}. NMR (CD_2Cl_2 **2a**): δ(^{1}H) 8.50 (d, 1H, ^3J(PtH) = 18 Hz, J = 6 Hz, H^6), 8.43 (d, 1H, ^3J(PtH) = 21 Hz, J = 6 Hz, H$^{6'}$), 7.80 (m, 2H, H$^{4,4'}$), 7.60 (m, 1H, J = 4 Hz, H^5), 7.57 (m, 1H, J = 4 Hz, H$^{5'}$), 7.33 (m, 2H, H$^{3,3'}$), 8.38 (br, NH), 5.08 (dd, 1H, J = 17,7 Hz, C*H*^{a}H^b), 5.01 (dd, 1H, J = 17, 7 Hz, C*H*$^{a'}$H$^{b'}$), 4.68 (d, 1H, ^4J(PtH) = 19 Hz, J = 17 Hz, CH$^{a'}$*H*$^{b'}$), 4.55 (d, 1H, ^4J(PtH) = 15 Hz, J = 17 Hz, CH^a*H*^{b}), 1.12 (s, 3H, ^2J(PtH) = 65 Hz, CH_3 *trans* to amine), 0.94 (s, 3H, ^2J(PtH) = 71 Hz, CH_3 *trans* to py), −20.03 (s, J(PtH) = 1381 Hz, Pt−H). ^{1}H NMR (CD_2Cl_2, **3a**): δ(^{1}H) 8.72 (d, 2H, ^3J(PtH) = 18 Hz, J = 7 Hz, H$^{6,6'}$), 7.96 (td, 2H, J = 2, 8 Hz, H$^{4,4'}$), 7.52 (d, 2H, J = 9 Hz, H$^{5,5'}$), 7.25 (t, 2H, J = 6 Hz, H$^{3,3'}$), 4.94 (m, 2H, CH_2), 4.52 (m, 1H, CH_2), 4.36 (m, 1H, CH_2), 0.99 (s, 6H, ^2J(PtH) =71 Hz, CH_3), −18.90 (s, J(PtH) = 1380 Hz, Pt−H].

[PtMe$_2$(H)(BPMA)][BF$_4$], 2b and 3b. $HBF_4{\cdot}OEt_2$ (85% solution; 20 μL, 0.118 mmol) was added to a solution of **1** (50 mg, 0.118 mmol) in THF (5 mL) via μL syringe. The orange solution immediately changed color to pale yellow, and a yellow microcrystalline precipitate formed. After the mixture was stirred for 5 min, the solvent was removed *in vacuo* to leave a pale yellow solid, a mixture of the isomers **2b** and **3b** (ratio 1.7:1) in essentially quantitative yield. Anal. Calcd for $C_{14}H_{20}N_3BF_4Pt$: C, 32.8; H, 3.9; N, 8.2. Found: C, 32.4; H, 3.9; N, 8.5. IR (acetone): ν(NH) 3271, ν(PtH) 2273 cm^{-1}. NMR (CD_2Cl_2, **2b**): δ(^{1}H) 8.52 (d, 1H, ^3J(PtH) = 18 Hz, J = 6 Hz,

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H^6), 8.47 (d, 1H, ^3J(PtH) = 21 Hz, J = 6 Hz, $H^{6'}$), 7.85 (td, 1H, J = 2, 8 Hz, H^4), 7.64 (td, 1H, J = 3, 10 Hz, $H^{4'}$), 7.52 (m, 2H, $H^{5,5'}$), 7.37 (m, 2H, $H^{3,3'}$), 5.83 (br, NH), 4.96 (dd, 2H, J = 9, 17 Hz, CH^aH^b), 4.92 (dd, 1H, J = 7, 17 Hz, C$H^{a'}$H$^{b'}$), 4.63 (d, 1H, ^4J(PtH) = 18 Hz, J = 17 Hz, CH$^{a'}H^{b'}$), 4.52 (d, 1H, ^4J(PtH) = 13 Hz, J = 17 Hz, CH$^aH^b$), 1.20 (s, 3H, ^2J(PtH) = 66 Hz, CH_3 *trans* to amine), 0.94 (s, 3H, ^2J(PtH) = 70 Hz, CH_3 *trans* to py), −20.01 (s, J(PtH) = 1384 Hz, Pt−H). ^{1}H NMR (CD_2Cl_2, **3b**): δ(^{1}H) 8.92 (d, 2H, ^3J(PtH) = 22 Hz, J = 6 Hz, $H^{6,6'}$), 7.99 (m, 2H, $H^{4,4'}$), 7.69 (m, 2H, $H^{5,5'}$), 7.44 (t, 2H, J = 6 Hz, $H^{3,3'}$), 5.02 (m, 2H, CH_2), 4.83 (m, 2H, CH_2), 0.99 (s, 6H, ^2J(PtH) = 71 Hz, CH_3), −19.01 (s, J(PtH) = 1396 Hz, Pt−H).

[PtMe(BPMA)][BF$_4$], 4b. **1** (50 mg, 0.118 mmol) was dissolved in CH_2Cl_2 (3 mL) to give an orange solution. HBF_4·OEt_2 (85% solution; 20 μL, 0.118 mmol) was added via μL syringe, and the solution changed color to bright yellow. After ca. 50 min, a pale yellow microcrystalline product began to precipitate. The mixture was filtered after standing at room temperature for 12 h. Yield 53 mg, 91%. Anal. Calcd for $C_{13}H_{16}N_3BF_4Pt$: C, 31.5; H, 3.1; N, 8.5. Found: C, 31.4; H, 3.1; N, 7.9. NMR (CD_2Cl_2): δ(^{1}H) 8.68 (d, 2H, ^3J(PtH) = 49 Hz, J = 5 Hz, $H^{6,6'}$), 7.79 (dt, 2H, J = 2, 8 Hz, $H^{4,4'}$), 7.72 (d, 2H, J = 7 Hz, $H^{5,5'}$), 7.56 (td, 2H, J = 2, 5 Hz, $H^{3,3'}$), 6.28 (br, NH), 4.96 (dd, 2H, ^4J(PtH) = 32 Hz, J = 6, 16 Hz, CH^aH^b), 4.77 (dd, 2H, J = 10, 16 Hz, CH$^aH^b$), 0.79 (s, 3H, ^2J(PtH) = 78 Hz, CH_3). NMR data for **4a** are essentially the same.

[PtMe$_3$(BPMA)][I], 5, and [PtIMe$_3$(BPMA)], 6. MeI (7 μL, 0.118 mmol) in CH_2Cl_2 (3 mL) was added to solid **1** (50 mg, 0.118 mmol), and the resultant yellow solution was stirred for 15 min. Stirring was stopped, and *n*-pentane (3 mL) was layered on top of the CH_2Cl_2 solution. After the mixture was allowed to stand for 2 days, pale yellow **5** formed as needles. Yield 59 mg, 88%. Anal. Calcd for $C_{15}H_{22}N_3IPt$·CD_2Cl_2: C, 29.5; H, 3.7; N, 6.4. Found: C, 28.2; H, 3.2; N, 6.5. IR: ν(NH) 3078 cm^{-1}. NMR (CD_2Cl_2, **5**): δ(^{1}H) 8.47 (d, 2H, ^3J(PtH) = 16 Hz, J = 5 Hz, $H^{6,6'}$), 7.83 (td, 2H, J = 2, 8 Hz, $H^{4,4'}$), 7.56 (d, 2H, J = 8 Hz, $H^{5,5'}$), 7.35 (t, 2H, J = 6 Hz, $H^{3,3'}$), 7.47 (br, NH), 5.05 (dd, 2H, J = 7, 17 Hz, CH^aH^b), 4.50 (d, 2H, ^4J(PtH) = 14 Hz, J =17 Hz, CH$^aH^b$), 1.05 (s, 3H, ^2J(PtH) = 68 Hz, CH_3 *trans* to NH), 0.89 (s, 6H, ^2J(PtH) = 72 Hz, CH_3 *trans* to py). ^{13}C NMR (CD_2Cl_2): δ(^{13}C) = 161.00 (J(PtC) = 9 Hz), 145.37 (J(PtC) = 15 Hz), 139.24, 124.96 (J(PtC) = 11 Hz), 123.47 (J(PtC) = 9 Hz), 60.49 (CH_2), −2.27 (J(PtC) = 686 Hz, MePt *trans* to NH), −11.36 (J(PtC) = 658 Hz, MePt *trans* to py). ^{1}H NMR (CD_2Cl_2, **6**): δ(^{1}H) = 8.73 (d, 1H, ^3J(PtH) = 18 Hz, J = 1, 5 Hz, H^6), 8.66 (dm, 1H, $H^{6'}$), 7.76 (td, 2H, $H^{4,4'}$), 7.30 (m, 4H, $H^{3,5,3',5'}$), 4.57 (dd, 1H, J = 5, 15 Hz, CH_2), 4.40 (dd, 1H, J = 3, 15 Hz, CH_2), 4.02 (dd, 1H, J = 10, 15 Hz, CH_2), 3.84 (dd, 1H, ^4J(PtH) = 7 Hz, J = 11, 15 Hz, CH_2), 1.39 (s, 3H, ^2J(PtH) = 71 Hz, CH_3), 1.24 (s, 3H, ^2J(PtH) = 71 Hz, CH_3), 0.94 (s, 3H, ^2J(PtH) = 73 Hz, CH_3).

[PtMe$_3$(BPMA)][CF$_3$SO$_3$], 5b. CF_3SO_3Me (4.5 μL, 0.47 mmol) was added to a solution of **1** (22 mg, 0.47 mmol) in CD_2Cl_2 (0.5 mL) in an NMR tube under N_2. The orange solution immediately lost color. The ^{1}H NMR spectrum was recorded, and after the solution was allowed to stand at room temperature for 10 h, the product precipitated from solution as a finely divided solid in quantitative yield. Anal. Calcd for $C_{16}H_{22}N_3F_3O_3SPt$: C, 32.6; H, 3.8; N, 7.1. Found: C, 32.5; H, 3.5; N, 6.7. IR: ν(NH) 3215 cm^{-1}. NMR (CD_2Cl_2): δ(^{1}H) 8.48 (d, 2H, J = 5 Hz, $H^{6,6'}$), 7.84 (t, 2H, J = 8 Hz, $H^{4,4'}$); 7.50 (d, 2H, J = 8 Hz, $H^{5,5'}$), 7.36 (t, 2H, J = 6 Hz, $H^{3,3'}$), 6.33 (br, NH), 4.98 (dd, 2H, J = 8, 17 Hz, CH^aH^b), 4.46 (d, 2H, ^4J(PtH) = 14 Hz, J = 17 Hz, CH$^aH^b$), 1.09 (s, 3H, ^2J(PtH) = 67 Hz, CH_3 *trans* to NH), 0.84 (s, 6H, ^2J(PtH) = 72 Hz, CH_3 *trans* to py).

[PtMe$_2$(CH$_2$CH=CH$_2$)(BPMA)][Br], 7, and [PtMe$_3$-(CH$_2$CH=CH$_2$)(BPMA)(Br), 8. Allyl bromide (11 μL, 0.120 mmol) in CH_2Cl_2 (3 mL) was added to solid **1** (50 mg, 0.118 mmol), and the resultant yellow solution was stirred for 15 min. Stirring was stopped, and *n*-pentane (3 mL) was layered on top of the CH_2Cl_2 solution. After the mixture was allowed to stand for 2 days, colorless **7** formed as prisms. Yield 60 mg, 93%. Anal. Calcd for $C_{17}H_{24}N_3BrPt$·H_2O: C, 36.2; H, 4.6; N, 7.5. Found: C, 35.7; H, 4.3; N, 7.3. IR: ν(NH) 3100 cm^{-1}. NMR (CD_2Cl_2 **7**): δ(^{1}H) 8.44 (overlapping d, 2H, J = 6.3 Hz, $H^{6,6'}$), 7.82 (overlapping td, 2H, $H^{4,4'}$), 7.58 (d, 1H, J = 8 Hz, H^5), 7.47 (d, 1H, J = 8 Hz, $H^{5'}$), 7.32 (t, 2H, J = 7 Hz, $H^{3,3'}$), 7.66 (br, NH), 5.81 (m, 1H, CH_2CH=CH_2), 5.14 (dd, 1H, J = 8, 18 Hz, CH^aH^b), 4.98 (dd, 1H, J = 7, 17 Hz, C$H^{a'}$H$^{b'}$), 3.90 (m, 2H, CH$^aH^b$, CH$^{a'}H^{b'}$), 4.79 (dd, 1H, ^4J(PtH) = 20 Hz, J = 1 Hz, 19 Hz, CH_2CHCH_2), 4.44 (dd, 1H, ^4J(PtH) = 12 Hz, J = 1, 11 Hz, CH_2CH=CH_2), 2.88 (t, 1H, ^2J(PtH) = 84 Hz, J = 1 Hz, 10 Hz, PtCH_2), 2.32 (t, 1H, ^4J(PtH) = 84 Hz, PtCH_2), 1.07 (s, 3H, ^2J(PtH) = 68 Hz, CH_3 *trans* to amine), 0.93 (s, 3H, ^2J(PtH) = 72 Hz, CH_3 *trans* to py). ^{13}C NMR (CD_2Cl_2): δ(^{13}C) 162.20 (J(PtC) = 8 Hz), 161.47 (J(PtC) = 10 Hz), 145.78 (J(PtC) = 7 Hz), 145.36 (J(PtC) = 7 Hz), 139.67, 139.38, 125.26, 125.05, 124.28 (J(PtC) = 4 Hz), 123.76 (J(PtC) = 6 Hz), 61.20, 60.90, −0.23 (J(PtC) = 696 Hz), −9.84 (J(PtC) = 660 Hz), 143.48 (J(PtC) = 60 Hz), 111.53 (J(PtC) = 45 Hz), 12.82 (J(PtC) = 590 Hz). ^{1}H NMR (CD_2Cl_2, **8**): δ(^{1}H) 8.57 (d, 1H, ^3J(PtH) = 17 Hz, J = 5 Hz, H^6), 7.73 (td, 1H, J = 2, 8 Hz, H^4), 7.54 (m, py), 7.43 (d, 1H, J = 7 Hz, H^3), 7.28 (m, py), 5.61 (m, 1H, CH_2CH=CH_2), 1.21 (s, 3H, ^2J(PtH) = 70 Hz, CH_3), 1.06 (s, 3H, ^2J(PtH) = 66 Hz, CH_3).

Reaction of 1 with DCl. Method A. $SiMe_3Cl$ (9 μL, 0.071 mmol) was added to a solution of D_2O (1.0 μL, 0.071 mmol) (to generate DCl) and **1** (30 mg, 0.071 mmol) in CD_2Cl_2 (0.5 mL), changing the color of the orange solution to yellow. The ^{1}H NMR spectrum of the solution was monitored at room temperature over the course of 10 h.

Method B. CH_3COCl (3.5 μL, 0.049 mmol) was added to a CD_2Cl_2 (0.25 mL) solution of CD_3OD (20 μL, 0.49 mmol) to generate DCl. An orange solution of **1** (21 mg, 0.049 mmol) in CD_2Cl_2 (0.5 mL) was added, and the solution immediately changed color to pale yellow. The ^{1}H NMR spectrum of this solution was recorded within 5 min of mixing and then subsequently over the next 4 h. The resonances due to CH_4 (s), CH_3D (1:1:1, t) and CH_2D_2 (quintet) were observed at δ = 0.18, 0.17, and 0.16, respectively, and that due to CH_2D_2 grew with time. The methylplatinum resonances were initially the same as for **2a**, but a second methylplatinum resonance grew in with time at δ = 1.11 (s, ^2J(PtMe) = 65 Hz), to slightly lower frequency than that of the original resonance for the methylplatinum group *trans* to NH (δ = 1.12); this is attributed to $PtCH_2D$ *trans* to NH. No such peak grew in for the resonance of the methylplatinum group *trans* to pyridyl.

Reaction of 2a/3a or 2b/3b with Et$_3$N. A mixture of **2a** and **3a** (20 mg, 0.039 mmol) was suspended in THF (5 mL), and Et_3N (9 μL, 0.039 mmol) was added. The mixture immediately changed color to pale green. After the mixture was stirred for 2 h, the solvent was removed via cannula and the solid was washed with THF (3 × 3 mL). Further washing with Et_2O gave **1**, which was identified by ^{1}H NMR (CD_2Cl_2).

Reaction of 1 with CD$_3$I. CD_3I (4.5 μL, 0.071 mmol) in CD_2Cl_2 (0.5 mL) was added to **1** (30 mg, 0.071 mmol) in an NMR tube under N_2. The ^{1}H NMR spectrum of the resultant compound was recorded at intervals over the course of 3 days to measure CH_3-CD_3 isomerization.

Reaction of 7 with LDA. Complex **7** (30 mg, 0.55 mmol) was suspended in THF (5 mL) at 0 °C. LDA (27 μL of a 2.0 M solution) was added via μL syringe. A color change to red and then pale yellow was observed over 3 h. The solvent was removed *in vacuo*, and the ^{1}H NMR (CD_2Cl_2) spectrum indicated that only **7** was present. Thus, the platinum(IV) complex is resistant to attack by strong base.

Crystallographic Structure Determinations. Pale yellow crystals of [PtMe(BPMA)]Cl, **4a**, and [$PtMe_2$(CH_2CH=CH_2)-(BPMA)]Br·$^3/_4H_2O$, **7**·$^3/_4H_2O$, were grown from saturated CD_2Cl_2 solutions of each complex. Data were collected by using a Siemens P4 diffractometer equipped with a CCD detector. The crystal data and refinement parameters are summarized in Table 1. Selected interatomic distances and angles are shown

Table 1. Crystal Data and Structure Refinement for [PtMe(BPMA)]Cl, 4a, and [PtMe$_2$(CH$_2$CH=CH$_2$)(BPMA)]Br·$^3/_4$H$_2$O, 7

	4	**7**
empirical formula	$C_{13}H_{16}ClN_3Pt$	$C_{17}H_{25.5}BrN_3O_{0.75}Pt$
fw	444.83	558.90
temperature, K	298(2)	293(2)
wavelength, Å	0.710 73	0.710 73
space group	*Pnna*	*C*2/*c*
a, Å	14.977(1)	16.161(2)
b, Å	11.968(1)	18.850(2)
c, Å	7.6941(7)	14.837(1)
β, deg		118.447(1)
Z, Å^3	1379.1(2)	3974.1(6)
ρ (calcd), mg/m^3	2.142	1.868
μ, mm^{-1}	10.353	9.078
F(000)	840	2140
T_{max}/T_{min}	2.12	1.89
R(*F*), %[a]	5.15	5.71
R(w*F*^{2}), %[a]	12.22	10.65

[a] $R = \sum\Delta/\sum(F_o)$, $\Delta = |(F_o - F_c|$; $R(wF^2) = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[(wF_o^2]^2\}^{1/2}$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for [PtMe(BPMA)][Cl], 4[a]

Pt−N(2)	1.993(6)	Pt−C(7)	2.04(2)
Pt−N(1)	2.11(2)	C(5)−C(6)	1.48(2)
C(6)−N(1)	1.46(3)	N(1)−C(6A)	1.42(3)
N(2)−Pt−N(1)	83.7(6)	C(7)−Pt−N(1)	174(1)
N(2)−Pt−C(7)	97(1)	N(2A)−Pt−N(1)	82.7(9)
N(2A)−Pt−C(7)	96(1)	N(2)−Pt−N(2A)	166.1(8)
C(4)−C(5)−C(6)	123.8(8)	N(2)−C(5)−C(6)	116.2(8)
C(5)−N(2)−Pt	112.7(4)	C(1)−N(2)−Pt	127.3(4)
N(1)−C(6)−C(5)	114(1)	C(6A)−N(1)−C(6)	122(2)
C(6A)−N(1)−Pt	107(1)	C(6)−N(1)−Pt	105(1)

[a] Symmetry transformations used to generate equivalent atoms: A; $x,-y+^1/_2,-z+^1/_2$.

in Tables 2 and 3, while atomic coordinates are given as Supporting Material.

Unit-cell parameters were calculated from reflections obtained from 60 data frames collected at different sections of the Ewald sphere. The systematic absences in the diffraction data and the determined unit-cell parameters defined the space group in **4a** and were consistent for either space group *Cc* or *C*2/*c* for **7**·$^3/_4$H$_2$O. The acentric option was explored for **7**·$^3/_4$H$_2$O but all solutions obtained were unreasonable, while the solution in *C*2/*c* yielded chemically reasonable and computationally stable results. Semiempirical absorption corrections were applied, using redundant data at several effective azimuthal angles with $I/\sigma > 5$.

The cation is located on a 2-fold axis in **4a**, while the anion is located on an inversion center. Atoms C(7) and N(1) were found near but not on the crystallographic axis and, thus, were rotationally disordered over two positions with equal occupancies.

In **7**·$^3/_4$H$_2$O, two independent water molecules, one of which was found at a refined site occupancy of 25%, were each located at a 2-fold axis, with a net ratio water:**7** of 3:4. The allyl group and methyl group *trans* to pyridyl were disordered, with a refined 50/50 site occupancy. This ligand disorder suggested that a crystallographically imposed mirror plane might be present, but close scrutiny of the possible monoclinic space groups with mirror planes yielded no viable solutions, and the absence of significant (>0.6) matrix correlations between the disordered contributions is consistent with the space group assigned. Analogous interatomic separations within the disordered contributions were restrained to be equal.

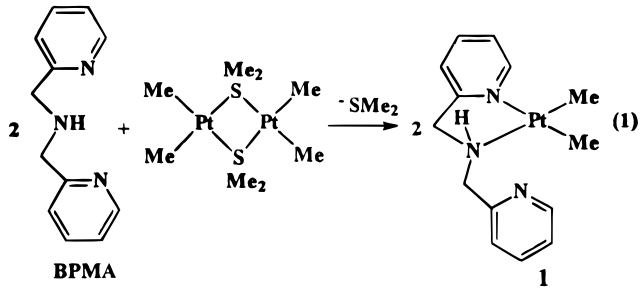
In both structures, the pyridyl groups were treated as rigid, idealized hexagons. All non-hydrogen atoms except those atoms displaying disorder were refined with anisotropic displacement coefficients. All disordered carbon and nitrogen atoms were refined isotropically. All hydrogen atoms, except those which were ignored on atoms C(6) and N(1) in **4a**, were treated as idealized contributions. Features of the final difference maps showed peaks in chemically unreasonable positions and were considered to be noise.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for [PtMe$_2$(CH$_2$CH=CH$_2$)(BPMA)][Br], 7

Pt−N(1)	2.140(7)	Pt−N(2)	2.145(5)
Pt−N(3)	2.166(7)	Pt−C(13)	2.21(2)
Pt−C(14)	1.92(2)	Pt−C(17)	2.045(9)
C(6)−N(3)	1.46(1)	C(5)−C(6)	1.49(1)
C(12)−N(3)	1.47(1)	C(11)−C(12)	1.479(9)
C(14)−C(15)	1.50(2)	C(15)−C(16)	1.33(3)
N(1)−Pt−N(2)	85.9(2)	N(1)−Pt−N(3)	80.0(4)
N(2)−Pt−N(3)	78.3(3)	N(1)−Pt−C(13)	168.5(6)
C(14)−Pt−N(1)	105.5(7)	C(17)−Pt−N(1)	99.4(5)
N(2)−Pt−C(13)	84.6(6)	C(14)−Pt−N(2)	167.4(6)
C(17)−Pt−N(2)	97.4(4)	N(3)−Pt−C(13)	91.7(6)
C(14)−Pt−N(3)	98.2(7)	C(17)−Pt−N(3)	175.7(4)
C(14)−Pt−C(13)	83.4(8)	C(17)−Pt−C(13)	88.2(6)
C(14)−Pt−C(17)	86.1(8)	C(1)−N(1)−Pt	125.7(9)
C(5)−N(1)−Pt	114.3(9)	C(7)−N(2)−Pt	125.7(5)
C(11)−N(2)−Pt	114.0(5)	C(6)−N(3)−Pt	109.3(7)
C(12)−N(3)−Pt	110.5(6)	C(15)−C(14)−Pt	108(1)
N(1)−C(5)−C(6)	116(1)	N(2)−C(11)−C(12)	116.6(6)
N(3)−C(6)−C(5)	116(1)	N(3)−C(12)−C(11)	111.2(7)
C(6)−N(3)−C(12)	113.8(8)	C(4)−C(5)−C(6)	124(1)
C(10)−C(11)−C(12)	123.1(6)	C(16)−C(15)−C(14)	114(2)

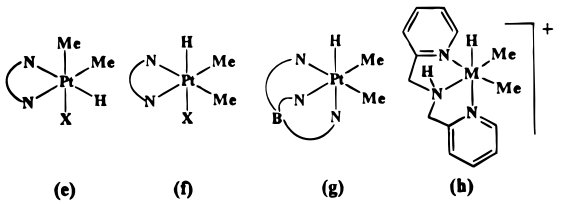
Results and Discussion

The Complex [PtMe$_2$(BPMA)]. The potentially tridentate ligand bis(2-pyridylmethyl)amine (BPMA), which should be capable of either bidentate or tridentate binding modes, is a very useful ligand in the study of oxidative-addition reactions to platinum(II), and its synthesis and characterization are reported below. The complex [PtMe$_2$(BPMA)], **1**, is easily prepared by displacement of the Me$_2$S ligands in [Pt$_2$Me$_4$(μ-SMe$_2$)$_2$] by the ligand BPMA in toluene solution; the yellow microcrystalline product **1** precipitates from the resultant solution, and therefore, it is easily isolated (eq 1).



Complex **1** is air stable, although it is somewhat deliquescent and should be stored in a desiccator. It is soluble in chlorinated solvents and in tetrahydrofuran, and it is only slightly soluble in acetone and acetonitrile. The ^{1}H NMR spectrum of **1** in CD_2Cl_2 indicates that only one of the pyridine arms of the ligand is bound to platinum, as shown, for example, by observation of the *ortho* coupling ^3J(PtH) for only one of the pyridyl groups. There are two overlapping "AB" resonances for the two CH_2 groups of the ligand at $\delta = 4.43$ and 3.85, again indicating asymmetry of the bound ligand BPMA. The

Chart 2

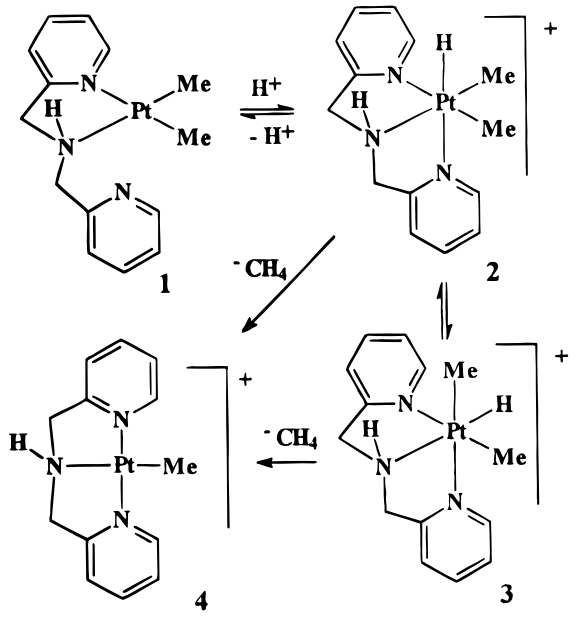


COSY spectrum indicates that the proton *anti*[15] to the Pt−NH bond of the CH_2 group couples to the amine proton, the resonance for which appears at $\delta = 4.75$. Finally, the Me resonances for **1** occur at $\delta = 0.55$ and 0.49, with $^2J(PtH) = 88$ and 86 Hz respectively, in the expected range for methyl groups *trans* to nitrogen in platinum(II) complexes.[16] The ligand, therefore, adopts the coordination mode **b**, Chart 1, with one pyridyl and the amine group coordinated, rather than the more symmetrical bidentate coordination mode **a**, Chart 1, with both pyridyl groups coordinated. In the cases where tris(pyrazolyl)borate (Tp) ligands have been employed to stabilize methyl(hydrido)platinum(IV) complexes, the dimethylplatinum(II) precursors were not isolable, perhaps in part because the anionic ligand is not flexible enough to allow bidentate coordination.[17−19] Canty has, however, isolated $[PtPh_2\{(py)_3(COH)\}]$ from the reaction of $[Pt_2Ph_4(\mu\text{-}SMe_2)_2]$ and $[(py)_3(COH)]$ ($[(py)_3(COH)]$ = tris(pyridin-2-yl)methanol),[18] but in this case, the ligand is more flexible and, in a similar way as BPMA, it chelates in a bidentate manner.

[PtHMe$_2$(BPMA)][X]. Dimethyl(hydrido)platinum(IV) complexes have recently been reported by several research groups.[3−7] Although the first reported example was the product of a *cis* oxidative addition of HX,[7] this was attributed to the sterically demanding dmphen (2,9-dimethyl-1,10-phenanthroline) ligand in $[PtXHR_2(dmphen)]$, and all other examples have been formed by *trans* oxidative-addition.[3,6] For both the *cis* and *trans* oxidative addition products (**e** and **f**, Chart 2), eventual loss of CH_4 occurred by reductive elimination. The stable complexes **g**, Chart 2, contain the strongly binding *fac*-tridentate Tp ligands (BN_3), and these compounds do not reductively eliminate CH_4 except under forcing conditions.[4,5] The new compounds **h**, Chart 2, are cationic but are still much more stable than **e** and **f**, though less stable than **g**.

The reaction of **1** with HX ($X^- = Cl^-$ or BF_4^-) in either CD_2Cl_2 or acetone-d_6 at room temperature yields the deliquescent complexes **2a** (X = Cl) or **2b** (X = BF_4), shown in Scheme 2. Complex **2** is formed cleanly in the initial reaction and can be characterized by ^{1}H NMR in solution. The ^{1}H NMR spectra of **2a** and **2b** are similar, and only that of **2a** will be discussed. Complex **2a** gives

Scheme 2



two sets of pyridyl resonances and both displays $^{195}Pt^1H$ coupling to the *ortho* proton, showing that both pyridyl groups are now coordinated. The observation of different environments for the two pyridyl groups indicates that one is *trans* to methyl while the other is *trans* to hydride (the complex has C_1 symmetry). This conclusion is reinforced by the observation of two different methylplatinum resonances, one being *trans* to pyridyl and the other *trans* to amine. These MePt resonances occur at $\delta = 0.94$ and 1.12, with $^2J(PtH) = 71$ and 65 Hz, respectively, in the normal range for methylplatinum(IV) complexes.[16] The Pt−H resonance is observed at $\delta = -20.03$, with $^1J(PtH) = 1381$ Hz, similar to the coupling observed for related platinum(IV) hydrides.[3−6] The CH_2 groups of the BPMA ligand give four resonances, with each CH^aH^b group giving rise to an AB pattern in the ^{1}H NMR spectrum. The NH resonance is shifted downfield to $\delta = 8.38$, indicating the presence of N−H···Cl hydrogen bonding. The only significant difference in the spectrum of the BF_4^- salt **2b** is the resonance due to the NH proton, which appears at $\delta = 5.83$, indicating the absence of significant hydrogen bonding in this case.

The dimethyl(hydrido)platinum(IV) complexes **2a** and **2b** are stable in solution at −10 °C, but undergo further reactions at room temperature. The first reaction observed is the equilibration of the isomers **2** and **3**, Scheme 2, which appears complete in several hours at room temperature and gives a ratio of **2**:**3** of about 3:2 in CD_2Cl_2 and about 1:3 in acetone-d_6. Complex **3** gives only one set of pyridyl resonances and one methylplatinum resonance, indicating the more symmetrical structure of C_s symmetry with both methylplatinum groups *trans* to pyridyl and hydride *trans* to amine. The methylplatinum resonance for **3a** occurs at $\delta = 0.99$, with $^2J(PtH) = 71$ Hz. Since the coupling is close to the higher value for **2a**, it could be argued that the amine group has a slightly higher *trans* influence than the pyridyl group. However, the values of $^1J(PtH)$ for **2a** and **3a** are almost identical, indicating very similar *trans* influences of the pyridyl and amine groups. In both **2** and **3**, the ligand BPMA is in the *fac*-tridentate bonding mode **d**, Chart 1. The changes in the hydride

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(17) Normally, for five-coordinate species, a chelating ligand and a strong π-acceptor molecule occupy the equatorial positions of the trigonal bipyramidal framework, see: Ferrara, M. L.; Orabona, I.; Ruffo, F.; De Felice, V. *J. Organomet. Chem.* **1996**, *519*, 75.
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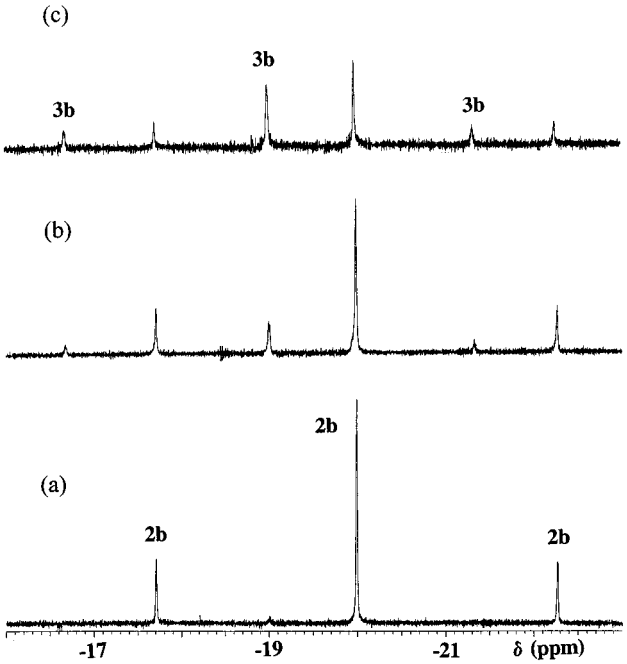


Figure 1. ^{1}H NMR spectra (300 MHz) in the PtH region for the mixture of **2b** and **3b** in acetone-d_6 solution, recorded after the following times after addition of HBF_4 to **1**: (a) 5 min, product is very largely **2b**; (b) 30 min, new peaks are due to **3b**; (c) 10 h, equilibrium mixture of **2b** with **3b**. The same number of transients was collected in each case, and the reduction in intensity with time is due to concurrent reductive elimination of methane to give **4b** along with the isomerization of **2b** to **3b**.

region of the ^{1}H NMR spectrum as **2b** equilibrates with **3b** are shown in Figure 1.

Concurrent with, but slower than, the equilibration of the isomers **2** and **3** is a second reaction involving the reductive elimination of methane with formation of $[PtMe(BPMA)]^+$, **4**, Scheme 2, whose characterization is described below. This reaction is complete in about 1 day at room temperature, as monitored by ^{1}H NMR.

The pure dimethyl(hydrido)platinum(IV) complexes, as a mixture of isomers **2** and **3**, are most easily isolated by allowing **1** to react with HX in tetrahydrofuran. A pale yellow precipitate forms in quantitative yield; the ^{1}H NMR spectrum indicates that this precipitate is a 3:2 mixture of the isomers **2** and **3**, when X is either chloride or tetrafluoroborate. The formation of the complexes **2** and **3** and the subsequent reductive elimination to give the methylplatinum(II) product **4** are shown in Scheme 2. The complexes **2** and **3** react with triethylamine to undergo loss of HX with formation of $[Et_3NH]Cl$ and $[PtMe_2(BPMA)]$, **1**. These are the only products observed, whether starting from pure **2** or the mixture of isomers **2** and **3**.

The complexes [PtMe(BPMA)][X] (X = BF_4, Cl), 4. Complex **4**, $[PtMe(BPMA)]^+$, results from the reductive elimination of methane from $[PtHMe_2(BPMA)]^+$. The complexes [PtMe(BPMA)]X (**4a**, X = Cl; **4b**, X = BF_4) are virtually insoluble in chlorinated solvents, such as dichloromethane, and precipitate as they are formed in this solvent. They are more soluble in acetone and acetonitrile. The complexes are air stable in the solid state, but they decompose in solution when exposed to air for extended time periods. The ^{1}H NMR spectrum of **4** shows one set of four pyridyl resonances, and the ^3J(PtH) coupling to the *ortho* proton of 49 Hz is

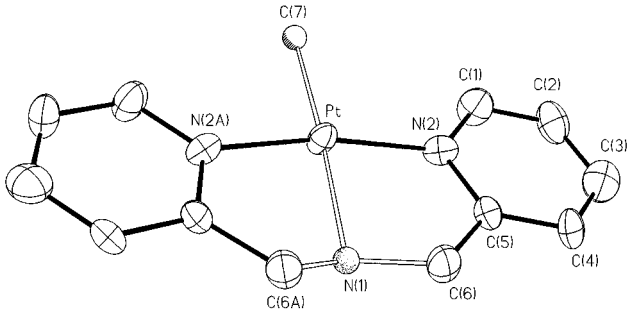


Figure 2. A view of the structure of the cation $[PtMe(BPMA)]^+$, with *mer*-tridentate BPMA. The chloride ion, which is not bonded, is not shown.

significantly larger than in the platinum(IV) complexes **2** and **3**. The CH_2 protons give rise to an AB pattern at $\delta = 4.96$ and 4.77, and both couple to the NH proton. The NH resonance for **4b** appears at $\delta = 6.28$, which is downfield from complex **1** (δ(NH) = 4.75), but similar to the cationic complexes in the series where no N−H···X hydrogen bonding is observed. Finally, the methyl resonance occurs at $\delta = 0.79$, with ^2J(PtH) = 78 Hz.

The structure of **4a** was determined crystallographically, and a view of the cation is shown in Figure 2. Selected bond distances and angles are listed in Table 2. The cation has a crystallographic 2-fold symmetry, the 2-fold axis containing the platinum atom and bisecting the two pyridylmethyl groups. There is disorder of the atoms C(7) and N(1), which lie slightly off the 2-fold axis, with 50% occupation on either side; only one form is shown in Figure 2 for simplicity. The platinum atom has distorted square planar coordination and is bonded to the methyl group and all three nitrogen atoms of the BPMA ligand. The Pt(BPMA) unit contains two five-membered chelate rings, and it is likely that the distortion from planarity is due to angle strain. For example, the angles C(5)−C(6)−N(1) and C(6)−N(1)−C(6A) of 114(1)° and 122(2)° are larger than the ideal tetrahedral angle of 109°. The angles N(1)−Pt−N(2) and N(1)−Pt−N(2A) are less than 90°, while C(7)−Pt−N(2) and C(7)−Pt−N(2A) are larger than 90°, due to the constraints of the chelate ligand. The distances Pt−N(2) and Pt−N(2A) are shorter than Pt−N(1) due to the high *trans*-influence of the methyl group.[16,20] The Cl^- ion has no short contacts with the cation and is not hydrogen bonded to the NH group.

The roughly planar *mer* configuration of the ligand BPMA (**c**, Chart 1) has not been observed previously, but there is a resemblance to the conformation of PNN (*N*-(2-(diphenylphosphino)benzilidene)(2-(2-pyridyl)ethyl)-amine) in the complex $[PdMe(PNN)]^+$.[21] The ligand PNN gives rise to two six-membered chelate rings in $[PdMe(PNN)]^+$, and the complex appears less strained and has more regular square planar stereochemistry compared to **4a**.

Deuterium Labeling Experiments. It was of interest to determine if treatment of **1** with DCl might lead to reversible H/D exchange within the resulting $Pt(CH_3)_2D$ groups prior to reductive elimination of methane, as found recently in related reactions.[6] In

(20) Levy, C. J.; Vittal, J. J.; Puddephatt, R. J. *Organometallics* **1996**, *15*, 35.
(21) Rülke, R. E.; Kaasjager, V. E.; Wehman, P.; Elsevier, C. J.; van Leeuwen, P. W. N. M.; Vrieze, K.; Fraanje, J.; Goubitz, K.; Spek, A. L. *Organometallics* **1996**, *15*, 3022.

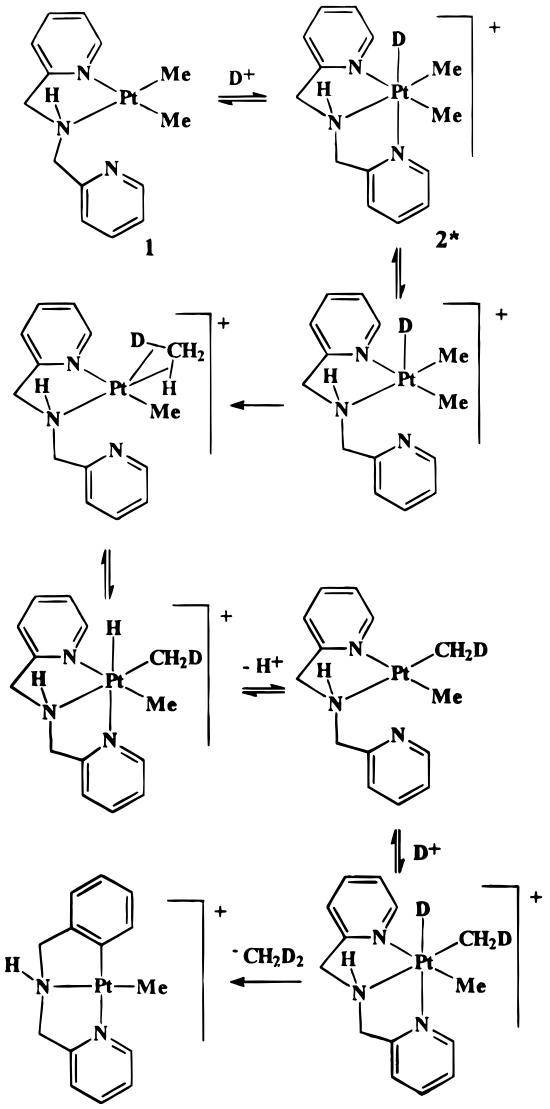
these experiments, DCl was generated in two different ways giving differing results.

In the first method, DCl was generated stoichiometrically in CD_2Cl_2 solution by reaction of Me_3SiCl with D_2O. The reaction of **1** with DCl was then monitored by ^1H NMR over the course of 10 h. Under these conditions, there was no evidence for formation of $PtCH_2D$ groups but only $[PtHMe_2(BPMA)]^+$ and $[PtDMe_2(BPMA)]^+$ were present. The hydride was present in significant quantity and considerably more than could be accounted for by the presence of adventitious water, almost certainly due to H/D exchange between D_2O and/or DCl with the NH proton of BPMA. The organic product of the subsequent reductive elimination was a mixture of CH_4 and CH_3D, with no CH_2D_2 detected.

In the second method, DCl was generated instead by the reaction of excess CD_3OD with a stoichiometric amount of MeCOCl in CD_2Cl_2 and then a solution of **1** was added. The solution, therefore, contained 1 equiv of DCl but excess CD_3OD which, of course, can also take part in H/D exchange. The reaction was monitored by ^1H NMR over a period of 4 h. In this case, there was evidence for slow formation of $PtCH_2D$ groups within the platinum(IV) complex **2** but only for the MePt group *trans* to the amine. The first-formed organic products again contained only CH_4 and CH_3D, but as time passed, resonances due to CH_2D_2 also grew in.[6,22] Thus, in the presence of excess CD_3OD, there is evidence for H/D exchange within the $PtD(CH_3)$ groups of **2** and it appears to be selective for the methylplatinum groups *trans* to amine; evidently scrambling of the CH_2D and CH_3 groups does not occur easily under these conditions. A probable sequence of reactions giving rise to formation of CH_2D_2 is shown in Scheme 3, based on the mechanism proposed for related H/D exchange.[6] It is proposed that all steps involving reductive elimination involve preliminary dissociation of a pyridyl group to give a five-coordinate intermediate, though some such steps are omitted in Scheme 3 for simplicity.

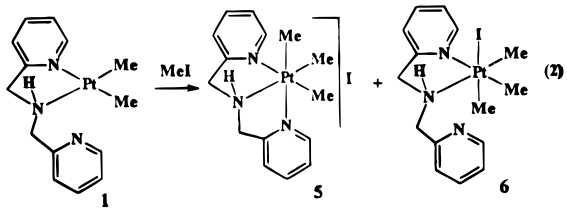
Scheme 3 presents the exchange as occurring through an η^2-methane complex.[6] This is, of course, speculative since it cannot be directly observed. On the basis of the arguments presented elsewhere for reactions involving reductive elimination of C−C bonds from platinum(IV),[6,23] it can be expected that dissociation of pyridine from **2*** is followed by the formation of an agostic PtH interaction from a methylplatinum group, thus facilitating C···D bond formation (Scheme 4). In the extreme, this intermediate could be considered as $[PtHD(CH_2)Me(\eta^2\text{-BPMA})]^+$, a carbene derivative or platinum-stabilized carbonium ion. It is proposed that a Pt−C bonding interaction is maintained through this sequence to rationalize why the methane is not very rapidly lost from the "methane complex". Of course, once the methane complex is formed, reversal of the reaction sequence can lead to H−D exchange. A possible complicating feature is shown in Scheme 4. If the elimination of hydride occurs on the platinum face where the free pyridyl group is located, then the pyridine may aid the deprotonation which equilibrates

Scheme 3



the hydridoplatinum(IV) cation with the platinum(II) precursor. Further protonation can then occur on the other face.

Oxidative Addition of MeI with Formation of $[PtMe_3(BPMA)][I]$. Oxidative addition reactions of CH_3I and CD_3I with **1** were carried out in order to study the stereochemistry of oxidative addition in a system where the platinum(IV) products should be thermally stable. As monitored by ^1H NMR, complex **1** reacts immediately with CH_3I to yield $[PtMe_3(BPMA)]I$, **5**, and a second complex which is proposed to be the neutral $[PtMe_3(I)(BPMA)]$, **6**, having bidentate BPMA, as shown in eq 2. Complexes **5** and **6** were initially formed in a



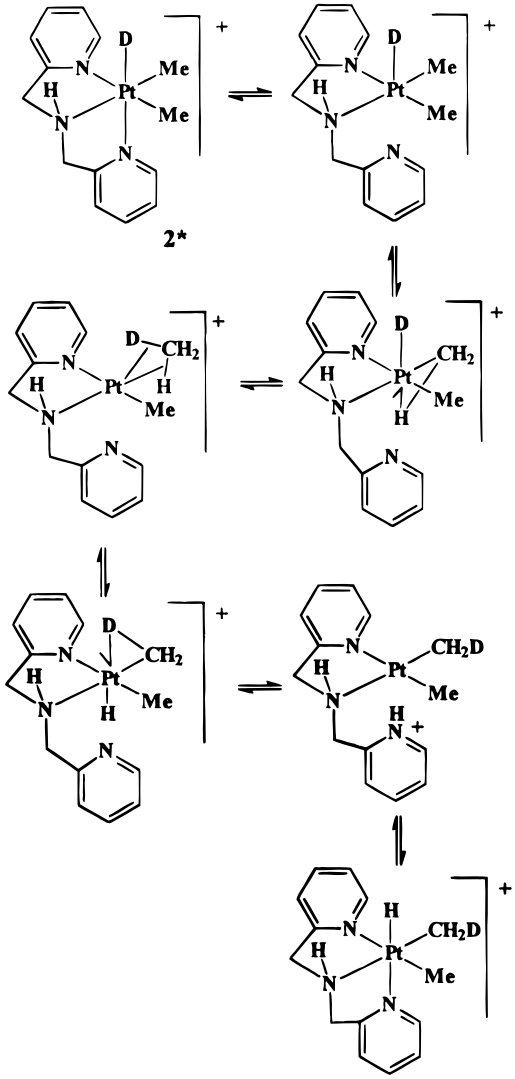
3:1 ratio. Complex **6** is short-lived, undergoing isomerization to **5** over a period of 2 h.

Complex **5** has symmetry, and its ^1H NMR spectrum is relatively simple. There is one set of four pyridyl

(22) Monaghan, P. K.; Puddephatt, R. J. *Organometallics* **1984**, *3*, 444.

(23) (a) Byers, P. K.; Canty, A. J.; Crespo, M.; Puddephatt, R. J.; Scott, J. D. *Organometallics* **1988**, *7*, 1363. (b) Roy, S.; Puddephatt, R. J.; Scott, J. D. *J. Chem. Soc., Dalton Trans.* **1989**, 2121. (c) Goldberg, K. I.; Yan, J. Y.; Breitung, E. M. *J. Am. Chem. Soc.* **1995**, *117*, 6889.

Scheme 4

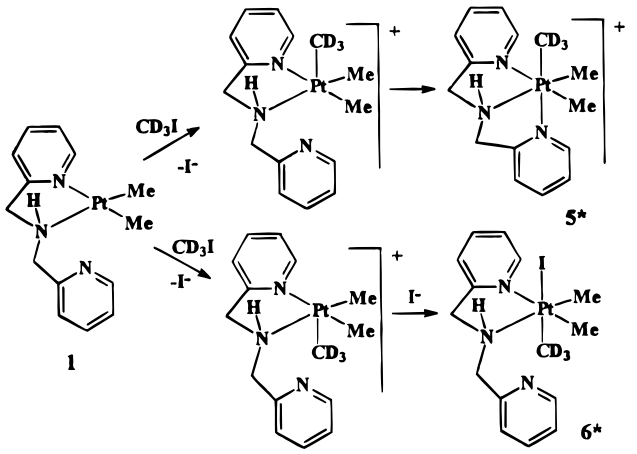


resonances at $\delta = 8.47-7.35$, one AB pattern for the CH_2 protons, and two MePt resonances in a 2:1 ratio at $\delta = 1.05$ and 0.89, with $^2J(PtH) = 68$ and 72 Hz for the methyl groups *trans* to amine and pyridyl, respectively. The assignment of these peaks is straightforward based on the relative intensities and strongly supports the assignment proposed above for complexes **2**. The resonance of the NH proton is shifted downfield to $\delta = 7.47$, indicating the presence of NH···I hydrogen bonding. The COSY spectrum of **5** indicates that the *syn*-CH_2 proton at $\delta = 5.05$ is coupled to NH. The ^{13}C NMR spectrum of **5** is also straightforward and contains methylplatinum resonances at $\delta = -2.27$ (*trans* to NH, $^1J(PtC) = 686$ Hz) and -11.36 (*trans* to py, $^1J(PtC) = 658$ Hz).

The ^1H NMR resonances for complex **6** are partly obscured by the more intense resonances of **5**, but most of the expected resonances are clearly identified. There are two sets of pyridyl resonances, and it is clear that only one pyridyl group is bound to platinum and the other is not, based on the absence of $^3J(PtH)$ coupling to the *ortho* proton. Three methylplatinum resonances are observed at $\delta = 1.39$, 1.24, and 0.94, with $^2J(PtH) = 71$, 71, and 73 Hz, respectively, again indicating the absence of a mirror plane in the molecule. The N−H resonance could not be located.

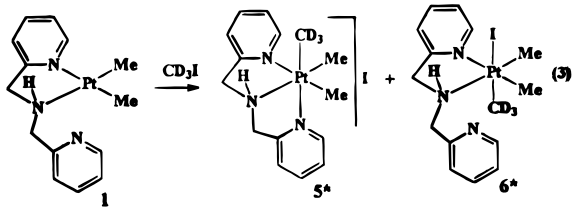
The oxidative addition of methyl iodide and primary alkyl halides to $[PtMe_2(bipy)]$ and related compounds

Scheme 5



has been shown to proceed via the S_N2 mechanism,[24] and in some cases, the cationic intermediates $[PtMe_3(solvent)(bipy)]^+I^-$ have been identified by low-temperature NMR before further reaction occurs to give $[PtIMe_3(bipy)]$.[25] It was, therefore, initially surprising that, in the present case, the neutral complex **6** rearranges to the ionic isomer **5**. A more detailed study using CD_3I was carried out in order to gain a better understanding.

Reaction of CD_3I with **1** gave a mixture of $[PtMe_2(CD_3)(BPMA)][I]$, **5***, and its neutral isomer $[PtIMe_2(CD_3)(BPMA)]$ in a 3:1 ratio immediately after mixing. For each complex, the ^1H NMR spectrum contained two methylplatinum resonances in a 1:1 ratio for **5*** and a 1:1 ratio for **6***, as is expected if each is formed by selective *trans* oxidative addition (eq 3). Over the course

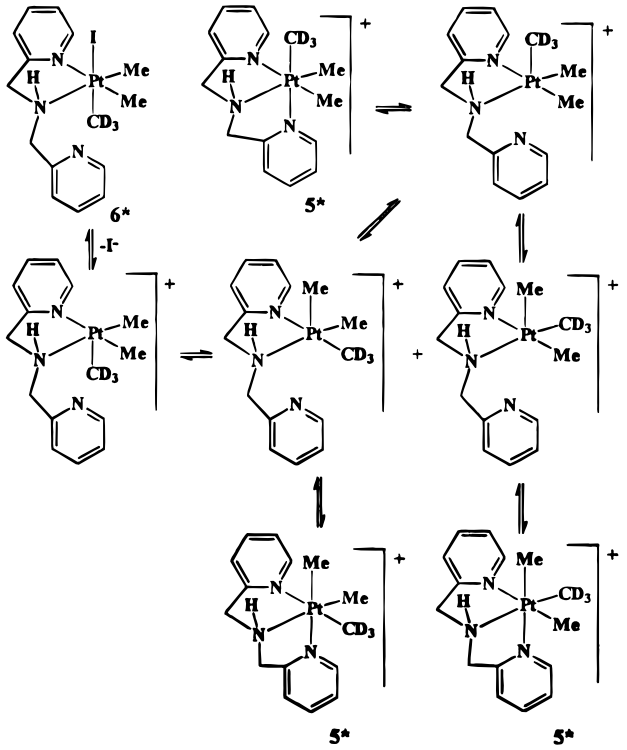


of 2 h, the resonances due to **6*** disappear and those due to **5*** grow in, as expected from the earlier study with CH_3I. During and after this reaction, the relative intensities of the two methylplatinum resonances of **5*** change steadily from 1:1 to a final value which is closer to the statistical value of 2:1 (as found in **5**).

It is almost certain, based on earlier precedents,[3,6,25] that the scrambling of CH_3 and CD_3 groups within **5*** and the isomerization of **6*** to **5*** must involve a coordinatively unsaturated intermediate. In order to explain all of the above observations, the mechanisms of Schemes 5 and 6 are proposed. Consider first the oxidative-addition reaction to give **5*** and **6***. It is important to recognize that attack of CD_3I can occur at either face of $[PtMe_2(BPMA)]$ and that the two faces are not equivalent. If attack occurs at the face which is *syn* to the NH group, the free pyridyl group is ideally placed to coordinate and, therefore, gives **5*** (Scheme 5). However, if attack occurs at the other face, the free

(24) Atwood, J. D. *Inorganic and Organometallic Reaction Mechanisms*; Brooks/Cole: Belmont, CA, 1985; p 172.
(25) Crespo, M.; Puddephatt, R. J. *Organometallics* **1987**, *6*, 2548.

Scheme 6

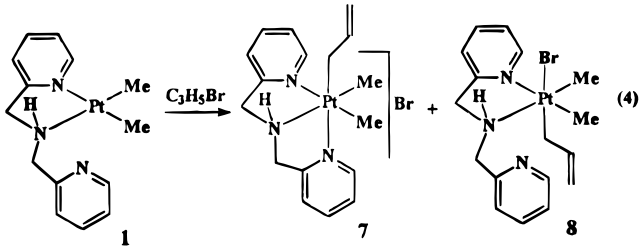


pyridyl group is unable to coordinate and, therefore, coordination of iodide occurs to give **6***.

The isomerization of **6*** to **5*** then occurs by dissociation of iodide followed by rearrangement of CH_3/CD_3 groups within the five-coordinate intermediate to the form in which the free pyridyl group can coordinate. The more general scrambling of CH_3/CD_3 groups within complex **5*** also occurs within a five-coordinate intermediate, formed by reversible dissociation of one of the pyridyl groups, as shown in Scheme 6.

When **1** reacts with CF_3SO_3Me in CD_2Cl_2, only the cationic product $[PtMe_3(BPMA)][CF_3SO_3]$ is observed by ^1H NMR, even when the spectrum is recorded immediately after mixing. The ^1H NMR spectrum is virtually identical to that of **5**, except for the NH resonance, which is shifted upfield to $\delta = 6.33$. The absence of a neutral complex analogous to **6** is due to the poor ligating ability of triflate compared to iodide, resulting in much faster formation of the thermodynamic product.

Oxidative Addition of Allyl Bromide To Give $[PtMe_2(CH_2CH{=}CH_2)(BPMA)][Br]$. $[PtMe_2(BPMA)]$ reacts rapidly with allyl bromide in CH_2Cl_2 to give colorless $[PtMe_2(CH_2CH{=}CH_2)(BPMA)][Br]$, **7**. A second, short-lived complex is also observed and is characterized as neutral $[PtBrMe_2(CH_2CH{=}CH_2)(BPMA)]$, **8**, as shown in eq 4. Complex **8** survives for only 25



(4)

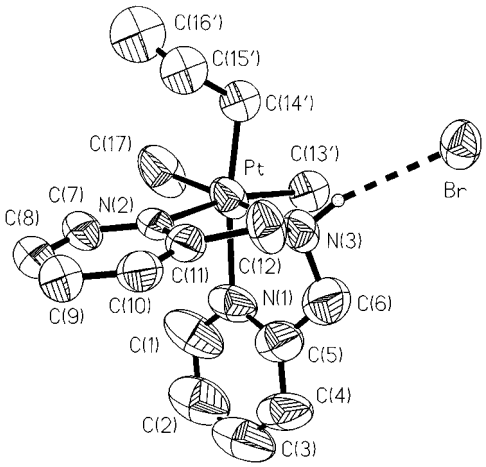


Figure 3. A view of the structure of $[PtMe_2(CH_2CH{=}CH_2)(BPMA)]Br$, with *fac*-tridentate BPMA. The NH···Br hydrogen bond is shown as a dotted line.

min at room temperature, and the short lifetime compared to **6** is attributed to the greater lability of bromide compared to iodide when bound to the soft platinum acceptor.[12] It is interesting that no such neutral intermediate was observed in the oxidative addition of HCl, described earlier. Its formation is expected but it would presumably be very short-lived due to the high *trans*-influence of hydride and the greater lability of chloride over both bromide and iodide when bound to platinum.

Complex **7** is stable in solution under N_2 and is air stable indefinitely in the solid state. The ^1H NMR spectrum of complex **7** is straightforward; both pyridyl groups are coordinated to platinum, as indicated by the observation of coupling $^3J(PtH)$ to the *ortho* protons, and the CH_2 protons exhibit a single AB pattern with additional coupling to the NH proton. The methyl resonances are found at $\delta = 0.93$ and 1.07, with $^2J(PtH) = 72$ and 68 Hz, respectively. The NH resonance is shifted downfield to $\delta = 7.66$, indicating NH···Br hydrogen bonding. Finally, all protons of the allyl group are nonequivalent and exhibit independent resonances: a multiplet at $\delta = 5.81$ for the $CH_2CH{=}CH_2$ proton, multiplets at $\delta = 4.79$ and 4.44 for the protons $CH_2CH{=}CH_2$, and two triplets at $\delta = 2.88$ and 2.32 for the $CH_2CH{=}CH_2$ protons, each showing $^2J(PtH)$ coupling of 84 Hz. Several of the resonances for the neutral complex $[PtBrMe_2(CH_2CH{=}CH_2)(BPMA)]$, **8**, are obscured by the more intense resonances of **7**, but the methylplatinum resonances were clearly defined at $\delta = 1.21$ and 1.06, with $^2J(PtH) = 70$ and 66 Hz, respectively. Once isomerization of **8** to **7** was complete, no further changes in the ^1H NMR spectra were observed, indicating that the structure **7** with allyl *trans* to one of the pyridyl groups is thermodynamically preferred over the structure with allyl *trans* to amine.

The structure of $[PtMe_2(CH_2CH{=}CH_2)(BPMA)][Br]$, **7**, was determined crystallographically, and a view is shown in Figure 3. There is disorder of the allyl and methyl groups *trans* to the pyridyl groups, and only one disorder form is shown for clarity. Bond distances and angles are listed in Table 3. The geometry around platinum is slightly distorted from octahedral, with coordination by BPMA in a *fac*-tridentate mode, two methyl groups and one allyl group. The angles N−Pt−N (N(1)−Pt−N(2), 85.9(2); N(1)−Pt−N(3), 80.0(4); N(2)−

Pt−N(3), 78.3(3)) are less than 90°, while the angles C−Pt−N (C(14)−Pt−N(1), 105.5(7); C(17)−Pt−N(1), 99.4(5); C(17)−Pt−N(2), 97.4(4)°) are greater than 90° due to the constraints of the BPMA ligand. The N(2)···Br nonbonded contact is 3.405 Å, which indicates that there is an N−H···Br hydrogen bond, as predicted from the NMR data discussed above. Note that the angle at the amine nitrogen C(6)−N(3)−C(12) = 113.8(8)° is much closer to the ideal tetrahedral angle than is the corresponding angle in **4** (C(6)−N(1)−C(6A) = 122(2)°), perhaps indicating that the *fac*-tridentate bonding mode is preferred over the *mer*-tridentate one for this ligand.

Conclusions

It has been shown that the ligand BPMA can coordinate to platinum in a bidentate and *fac*- or *mer*-tridentate manner. The complex $[PtMe_2(BPMA)]$ undergoes easy oxidative addition with alkyl halides, RX, to give $[PtMe_2R(BPMA)]X$, with *fac*-tridentate BPMA, and the short-lived $[PtXMe_2R(BPMA)]$, with bidentate BPMA. It is suggested that these complexes arise from attack of the alkyl halide on platinum on the face *syn* or *anti* to the NH proton of the amine group. The reaction with HX gives only the ionic complex $[PtHMe_2(BPMA)]X$, which can exist in two isomeric forms and which undergoes slow loss of methane to give [PtMe(BPMA)]X, containing *mer*-tridentate BPMA. We suggest that if protonation occurs *anti* to the NH proton (*syn* to the free pyridyl group), then it may rapidly deprotonate (Scheme 4) by interaction with the pyridine base and that this possible product is not detectable. The complex ion $[PtHMe_2(BPMA)]^+$ is the first example of a cationic alkyl(hydrido)platinum(IV) complex, and it has a thermal stability intermediate betweeen the less stable $[PtHXMe_2(bipy)]$ and the more stable $[PtHMe_2Tp]$. This sequence can be understood in terms of a mechanism of reductive elimination in which a ligand must dissociate from platinum before loss of methane can occur.

Acknowledgment. We thank the NSERC (Canada) for financial support.

Supporting Information Available: Tables giving crystal data, positional and thermal parameters, and bond distances and angles for **4** and **7** (11 pages). Ordering information is given on any current masthead page.

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