

**Water and Protic Acids as Oxidants for Platinum(II):
Diorgano(hydrido)platinum(IV) and
Diorgano(hydroxo)platinum(IV) Chemistry, Including
Structural Studies of Poly(pyrazol-1-yl)borate Complexes
Pt(OH)R₂{(pz)₃BH} (R = Methyl, *p*-Tolyl) and
Pt(OH)Me₂{(pz)₄B}·H₂O**

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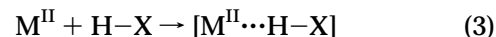
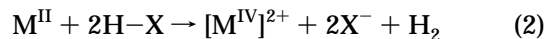
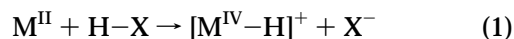
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The tris(pyrazol-1-yl)borate complexes K[PtR₂{(pz)₃BH}] (R = Me (**1**), *p*-tolyl (**2**)) may be isolated on addition of K[(pz)₃BH] to solutions of [PtR₂(SEt₂)₂]. Complexes **1**, **2**, and [PtMe₂{(pz)₄B}]⁻ react with acetic acid to form PtHR₂{(pz)₃BH} (R = Me (**3**), *p*-tolyl (**5**)) and PtHMe₂{(pz)₄B} (**4**). The hydridoplatinum(IV) complexes decompose at ~140 (**3**) and ~85 (**4**) °C in toluene-*d*₈ and ~90 °C (**5**) in nitrobenzene-*d*₅ to form methane (**3**, **4**) and toluene (**5**), where isolation of **5** has provided the first opportunity to study the decomposition of aryl(hydrido)platinum(IV) complexes. The hydridoplatinum(IV) complexes are deprotonated on addition of aqueous sodium hydroxide in acetone-*d*₆ to form **1**, **2**, and [PtMe₂{(pz)₄B}]⁻. The hydroxoplatinum(IV) complexes Pt(OH)R₂{(pz)₃BH} (R = Me (**6**), *p*-tolyl (**8**)) or Pt(OH)Me₂{(pz)₄B}·H₂O (**7**) may be readily isolated in 45–82% yield upon oxidation of the platinum(II) anions **1**, **2**, or [PtMe₂{(pz)₄B}]⁻ by water. The hydridoplatinum(IV) complexes **3–5** also react slowly with water in acetone-*d*₆ to form hydrogen and complexes **6–8**. The anions [PtR₂{(pz)₃BH}]⁻ undergo oxidative-addition reactions with iodomethane to form PtMeR₂{(pz)₃BH} (R = Me, *p*-tolyl). The octahedral hydroxoplatinum(IV) complexes **6–8** are the first examples of platinum(IV) complexes formed on oxidation by water to be characterized by X-ray crystallography. The complexes display Pt–O distances of 1.974(**8**)–1.996(**6**) Å, and the Pt–N bond distances reflect the relative trans influences of the hydroxo and methyl groups. The aqua group in Pt(OH)Me₂{(pz)₄B}·H₂O (**7**) is hydrogen-bonded to the hydroxoplatinum(IV) group to form a centrosymmetric dimer, such that it is not possible to ascertain whether the coordination environment of platinum is [Pt(OH)···H₂O]₂ or [Pt(OH₂)⁺···OH⁻]₂, although the former is believed to be more likely.

Introduction

Protic acids H–X are classical examples of oxidizing agents for metal complexes^{1–3} and often react according to eqs 1 and 2, where the oxidation state of +II for the reagent has been chosen for its relevance to the new work reported herein. Reactions in which the acid forms adducts where the metal center is not oxidized have also been described (eq 3).^{3–5} In addition, the anion X⁻ may assume the role of a ligand in the complex formed in reactions 1 and 2, and for reaction 3, adduct formation

may occur via protonation of an intramolecularly coordinated donor group to form $M^{II} \cdots \overline{H-N \sim C}$.⁵



For arylplatinum(II) reagents, protonation by acids has been demonstrated for Pt(4-MeOC₆H₄)₂(2,9-dimethyl-1,10-phenanthroline)⁶ and for intramolecular coordination systems, e.g., $\overline{Pt^{II}(C \sim N)_2}$ reacts with CF₃CO₂H in CDCl₃ to form $\overline{Pt^{IV}(C \sim N)_2H(O_2CCF_3)}$ (C~N = 8-(dimethylamino)naphthyl).⁷ However, for alkylplatinum(II) systems, protonation to form alkyl(hydrido)-

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platinum(IV) complexes has been achieved only since 1995,^{6,8–11} with examples shown in eqs 4 and 5.¹²

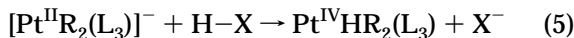


R = Me, L₂ =

2,9-dimethyl-1,10-phenanthroline, X = Cl;⁶ R =

Me, L₂ = 2,2'-bipyridyl (bpy), X = Cl;⁸ R =

Me, L₂ = *N,N,N',N'*-tetramethylethylenediamine (tmeda), X = Cl⁹



R = Me,

L₃ = tris(pyrazol-1-yl)borate [(pz)₃BH], HX =

PhOH or HBF₄ (**3**);¹⁰ R = Me or Ph, L₃ =

tris(3,5-dimethylpyrazol-1-yl)borate

[(Me₂pz)₃BH], X = Cl¹¹

Water, as a weak acid H–OH, is known to undergo reactions analogous to that of eqs 1 and 2 with electron rich metal–carbon σ -bonded organometallic complexes.¹³ For organoplatinum(II) species as reactants, reports to date appear to be limited to the reaction mode of eq 2,^{3,13–15} exemplified by Pt^{II}Me₂(bpy)¹³ and Pt^{II}R₂{(py)₃COH} ((py)₃COH = tris(pyridin-2-yl)methanol),¹⁵ which form [Pt^{IV}(OH)Me₂(bpy)(OH₂)]⁺ and [Pt^{IV}(OH)R₂{(py)₃COH}]⁺ (R = Me, Ph), respectively. It is considered that these reactions may proceed via transient undetected organo(hydrido)platinum(IV) intermediates,^{3,13,15} i.e., via eq 1 followed by hydrolysis of the hydrido complex. The hydrido species formed in reaction 5 are stable to high temperatures,^{10,11} whereas the products of reaction 4 decompose at or below ambient temperature.^{6,8,9} Water is known to oxidize organopalladium(II) complexes containing [(pz)₃BH][–] as a ligand,^{15a,16,17} and thus, poly(pyrazol-1-yl)borate ligands appear to be ideal supporting ligands for an exploration of the relationships between oxidation of organoplatinum(II) species by strong acids and by water.

We report here the first structural studies of organoplatinum(IV) complexes formed using water as an

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oxidant and the reductive elimination of arene on decomposition of a diaryl(hydrido)platinum(IV) complex and demonstrate that protonation of [PtMe₂{(pz)₃BH}][–] and related species is reversible. A preliminary communication of part of this work has appeared.¹⁶

Experimental Section

The reagents K[(pz)₃BH], K[(pz)₄B],¹⁸ [PtR₂(SEt₂)₂ (R = Me, *p*-tolyl (*p*-tol)),¹⁹ PtMe₂(cod) (cod = 1,5-cyclooctadiene), Pt(*p*-tol)₂(nbd) (nbd = norbornadiene),²⁰ and PtHMe₂{(pz)₃BH} (**3**),¹⁰ were prepared as described; **3** was also prepared by a new method. Solvents were dried and distilled; acetic acid was distilled from acetic anhydride and KMnO₄ and stored under nitrogen; and all syntheses were carried out under nitrogen. Microanalyses were by the Central Science Laboratory, University of Tasmania; and NMR spectra were recorded with a Bruker AM 300 spectrometer, with chemical shifts given in ppm relative to Me₄Si.

Synthesis of Anionic Platinum(II) Complexes. K[PtMe₂{(pz)₃BH}] (1**).** A solution of [PtMe₂(SEt₂)₂] (0.030 g, 0.048 mmol) and K[(pz)₃BH] (0.024 g, 0.095 mmol) in tetrahydrofuran (THF) (3 mL) was stirred for 75 min, followed by evaporation to dryness in a vacuum. The residue was extracted with tetrahydrofuran/diethyl ether (1:6) and filtered through Celite under nitrogen, and the solution was evaporated to give an oily residue from which a white precipitate formed on addition of pentane (0.042 g, 92%). ¹H NMR (acetone-*d*₆): δ 8.55 (d, ³*J* = 2.0 Hz, 1, H3 or 5 (uncoordinated)), 7.68 (d, ³*J* = 2.0 Hz, ³*J*_{PtH} = 10 Hz, 2, H3), 7.57 (d, ³*J* = 2.0 Hz, 2H, H5), 7.39 (d, ³*J* = 2.0 Hz, 1, H3 or 5 (uncoordinated)), 6.13 (t, 2, H4), 6.02 (t, 1, H4 (uncoordinated)), 0.54 (s, ²*J*_{PtH} = 86 Hz, 6, PtCH₃); tetrahydrofuran resonances at 3.63 and 1.79 ppm. ¹³C{¹H} NMR (acetone-*d*₆): δ 139.8, 139.2, 136.0, 135.2, 105.0, 104.1, –19.7 (¹*J*_{PtC} = 835 Hz, PtCH₃). MS (LSIMS for negative ion): 439, as calculated for [PtMe₂{(pz)₃BH}][–] with calculated isotope distribution. IR (KBr disk): 2500 cm^{–1} ($\nu_{\text{B-H}}$). Anal. Calcd for C₁₁H₁₆BN₆KPt·0.5THF: C, 30.4; H, 3.9; N, 16.3. Found: C, 30.0; H, 4.3; N, 15.9.

K[Pt(*p*-tol)₂{(pz)₃BH}] (2**).** A solution of [Pt(*p*-tol)₂(SEt₂)₂] (0.03 g, 0.032 mmol) and K[(pz)₃BH] (0.016 g, 0.062 mmol) in tetrahydrofuran (3 mL) was stirred for 1.5 h, followed by evaporation to dryness in a vacuum. The residue was extracted with tetrahydrofuran/diethyl ether (1:2) and filtered through Celite under nitrogen, and the solution was evaporated to give an oily residue from which a white precipitate formed on addition of pentane (0.035 g, 89%). ¹H NMR (acetone-*d*₆): δ 8.92 (dd, ³*J* = 3.0 Hz, 1, H3 or 5 (uncoordinated)), 7.60 (dd, ³*J* = 3.0 Hz, 2, H3 or 5), 7.41 (dd, ³*J* = 2.5 Hz, 1, H3 or 5 (uncoordinated)), 7.35 (d, ³*J* = 8.0 Hz, ³*J*_{PtH} = 69 Hz, 4, H2,6), 6.54 (d, ³*J* = 8.0 Hz, 4, H3,5), 6.15 (m, 1, H4 (uncoordinated)), 6.0 (m, 2, H4), 2.07 (s, 6, CH₃). ¹³C{¹H} NMR (acetone-*d*₆): δ 141.1, 139.8, 133.8, 128.1, 127.0, 136.0, 106.8, 104.6, 21.0 (CH₃). MS (LSIMS for negative ion): 590, as calculated for [Pt(*p*-tol)₂{(pz)₃BH}][–] with calculated isotope distribution. IR (KBr disk): 2450 cm^{–1} ($\nu_{\text{B-H}}$). Anal. Calcd for C₂₃H₂₄BN₆KPt: C, 43.9; H, 3.8; N, 13.3. Found: C, 44.2; H, 4.3; N, 12.7.

Synthesis of Diorgano(hydrido)platinum(IV) Complexes. PtHMe₂{(pz)₄B} (4**).** A solution of [PtMe₂(SEt₂)₂] (0.020 g, 0.032 mmol), K[(pz)₄B] (0.020 g, 0.060 mmol) in acetone (15 mL), and acetic acid (15 μ L, 0.25 mmol) was stirred for 2 h. The solvent was evaporated in a vacuum; the residue was extracted with diethyl ether, and the solvent was evaporated. The residue obtained was extracted with diethyl ether/pentane (1:8) to give a white solid (0.02 g, 62%). ¹H NMR

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(CDCl₃): δ 8.03 (d, $^3J = 2.0$ Hz, 1, H3 or 5 (uncoordinated)), 7.96 (br, 1, H3 or 5 (uncoordinated)), 7.73 (d, $^3J = 2.0$ Hz, 2), 7.71 (m, 2, H3 or 5), 7.64 (d, $^3J = 2.0$ Hz, 1, H5 trans to H), 7.53 (m, $^3J_{\text{PtH}} \approx 8$ Hz, 1, H3 trans to H), 6.62 (br, 1, H4 (uncoordinated)), 6.26 (br, 1, H4 trans to H), 6.22 (t, 2, H4), 1.15 (s, $^2J_{\text{PtH}} = 68$ Hz, CH₃), -20.1 (s, $^1J_{\text{PtH}} = 1360$ Hz, 1, PtH). ¹³C{¹H} NMR (CDCl₃): δ 142.5, 141.8, 138.1, 136.7, 135.4, 131.7, 129.5, 107.7, 106.9, -19.62 ($^1J_{\text{PtC}} = 613$ Hz, PtCH₃). IR (KBr disk): 2260 cm⁻¹ ($\nu_{\text{Pt-H}}$). Anal. Calcd for C₁₄H₁₉BN₈Pt: C, 33.3; H, 3.8; N, 22.2. Found: C, 33.5; H, 3.9; N, 22.1.

PtH(*p*-tol)₂{(pz)₃BH} (5). A solution of [Pt(*p*-tol)₂(SEt₂)₂] (0.024 g, 0.050 mmol) and K[(pz)₃BH] (0.023 g, 0.091 mmol) in tetrahydrofuran (8 mL) was stirred before adding acetic acid (3.5 μ L, 0.061 mmol). The solution stirred for 1.5 h, the solvent was evaporated in a vacuum, and the residue was dissolved in a minimum amount of benzene; impurities precipitated by the addition of pentane. The solution was separated from the solids and reduced to very low volume; pentane (2 mL) was added to further precipitate impurities. The solution was separated from the solids and taken to dryness under a vacuum (0.020 g, 67%). ¹H NMR (CDCl₃): δ 7.74 (d, $^3J = 2.3$ Hz, 1, H3 or 5 trans to H), 7.63 (d, $^3J = 2.3$ Hz, 2, H3 or 5), 7.61 (d, $^3J = 2.3$ Hz, 1, H3 or 5 trans to H), 7.19 (d, $^3J = 2.0$ Hz, 2, H3 or 5), 7.10 (d, $^3J = 8.1$ Hz, $^3J_{\text{PtH}} = 54$ Hz, H2,6), 6.68 (d, $^3J = 8.1$ Hz, 4, H3,5), 6.27 (t, 1, H4 trans to H), 6.05 (t, 2, H4), 2.15 (s, 6, CH₃), -19.53 (t, $^1J_{\text{PtH}} = 1400$ Hz, PtH). ¹³C{¹H} NMR (CDCl₃): δ 140.7 ($^2J_{\text{PtC}} = 29.7$ Hz, C3), 139.5 ($^3J_{\text{PtC}} = 13.1$ Hz, C3), 136.8 ($^2J_{\text{PtC}} = 29.8$ Hz, C3), 133.9 (C3,5 (tol)), 131.8 ($^3J_{\text{PtC}} = 9.9$ Hz, C5), 127.3 ($^2J_{\text{PtC}} = 56.2$ Hz, C2,6), 123.5 ($^4J_{\text{PtC}} = 9.7$ Hz, C4 (tol)), 119.7 ($^1J_{\text{PtC}} = 863.4$ Hz, C1), 105.0 and 104.7 (C4), 19.7 (CH₃). IR (KBr disk): 2470 ($\nu_{\text{B-H}}$), 2280 cm⁻¹ ($\nu_{\text{Pt-H}}$). Anal. Calcd for C₂₃H₂₅BN₆Pt: C, 46.7; H, 4.8; N, 14.2. Found: C, 47.3; H, 4.5; N, 14.9.

Complex **3** was prepared similarly, except that the residue was dissolved in a minimum volume of acetone and extracted with diethyl ether (2 \times 2 mL). The diethyl ether solution was reduced almost to dryness and extracted with pentane (2 \times 3 mL), and the pentane was removed to give a white solid (55%). ¹H NMR: as reported previously.¹⁰ ¹³C{¹H} NMR (CDCl₃): δ 140 ($^2J_{\text{PtC}} = 25$ Hz), 136.3, 134.7, 133.1, 105.5, 104.9, -20.4 ($^1J_{\text{PtC}} = 621$ Hz, PtCH₃).

Synthesis of Diorgano(hydroxo)platinum(IV) Complexes. Pt(OH)Me₂{(pz)₃BH} (6). A suspension of [PtMe₂(SEt₂)₂] (0.100 g, 0.159 mmol) and K[(pz)₃BH] (0.080 g, 0.317 mmol) in undried acetone (15 mL) was stirred for 3 h. The solvent was evaporated in a vacuum, and the residue was extracted with diethyl ether. The solvent was evaporated in a vacuum to give an oil. The product crystallized from chloroform/hexane (0.065 g, 45%). ¹H NMR (CDCl₃): δ 7.74 (d, $^3J = 2.0$ Hz, 2, H3 or 5), 7.70 (d, $^3J = 2.0$ Hz, 3, H5 trans to OH and H3 or 5), 7.45 (d, $^3J_{\text{PtH}} = 14.2$ Hz, $^3J = 2.0$ Hz, 1, H3 trans to OH), 6.30 (t, 2, H4), 6.27 (t, 1, H4 trans to OH), 1.55 (s, $^2J_{\text{PtH}} = 69.4$ Hz, 6, CH₃). ¹³C{¹H} NMR (CDCl₃): δ 138.7, 138.3, 136.8, 135.6, 107.3, 106.7, -3.69 ($^1J_{\text{PtC}} = 553$ Hz, PtCH₃). IR (KBr disk): 2500 ($\nu_{\text{B-H}}$), 3300–3500 (s br) cm⁻¹ ($\nu_{\text{O-H}}$). Anal. Calcd for C₉H₁₀BN₆OPT: C, 29.0; H, 3.8; N, 18.5. Found: C, 29.3; H, 3.9; N, 18.2.

Pt(OH)Me₂{(pz)₄B}·H₂O (7). Water (0.2 mL) was added to a solution of [PtMe₂{(pz)₄B}]⁻ prepared from [PtMe₂(SEt₂)₂] (0.050 g, 0.080 mmol) and K[(pz)₄B] (0.050 g, 0.16 mmol) in freshly dried tetrahydrofuran (4 mL). The solution was stirred for 12 h, the solvent was evaporated in a vacuum, and the residue was extracted with diethyl ether. The diethyl ether solution was evaporated in a vacuum, and the residue crystallized from CH₂Cl₂/diethyl ether to give a white crystalline solid (0.067 g, 82%). ¹H NMR (CDCl₃): δ 8.15 (d, $^3J = 2.0$ Hz, 2, H3 or 5), 8.00 (d, $^3J = 2.0$ Hz, 1, H3 or 5 (uncoordinated)), 7.97 (d, $^3J = 2.0$ Hz, 1, H3 or 5 (uncoordinated)), 7.83 (d, $^3J = 2.0$ Hz, H3 or 5), 7.51 (d, $^3J_{\text{PtH}} = 10$ Hz, $^3J = 2.0$ Hz, H3 trans to OH), 6.80 (d, $^3J = 2.0$ Hz, 1, H5 trans to OH), 6.63 (t, 1, H4 (uncoordinated)), 6.35 (t, 2, H4), 6.20 (t, 1, $^4J_{\text{PtH}} = 8.0$ Hz, H4 trans to OH), 1.60 (s, $^2J_{\text{PtH}} = 68$ Hz, 6, PtCH₃). ¹³C{¹H} NMR

(CDCl₃): δ 143.1, 139.4, 136.4, 135.8, 129.7, 119.0, 116.3, 108.1, 107.1, -3.38 ($^1J_{\text{PtC}} = 622$ Hz, PtCH₃). IR (KBr disk): 3300–3500 (s br) cm⁻¹ ($\nu_{\text{O-H}}$). Anal. Calcd for C₁₄H₁₉BN₈OPT·H₂O: C, 31.2; H, 3.9; N, 20.8. Found: C, 31.4; H, 3.7; N, 20.6.

Pt(OH)(*p*-tol)₂{(pz)₃BH} (8). A suspension of [Pt(*p*-tol)₂(SEt₂)₂] (0.210 g, 0.240 mmol), K[(pz)₃BH] (0.133 g, 0.528 mmol), and water (0.25 mL) in acetone (25 mL) was stirred for 12 h, by which time the solid had dissolved. The solvent was removed under vacuum to give an oily solid, which was dissolved in a minimum amount of diethyl ether and crystallized by addition of pentane. The product was washed with diethyl ether (3 \times 4 mL) and then extracted with chloroform. The chloroform was removed under vacuum, and the product recrystallized from CH₂Cl₂/pentane (0.154 g, 53%). ¹H NMR (CDCl₃): δ 8.15 (d, $^3J = 2.6$ Hz, 1, H5 trans to OH), 7.98 (d, $^3J = 2.1$ Hz, 2, H3 or 5), 7.45 (d, $^3J = 2.4$ Hz, $^3J_{\text{PtH}} = 10.9$ Hz, 1, H3 trans to OH), 7.35 (d, $^3J = 2.1$ Hz, 2, H3 or 5), 7.05 (d, $^3J = 8.2$ Hz, $^3J_{\text{PtH}} = 36.6$ Hz, H2,6), 6.76 (d, $^3J = 8.5$ Hz, H3,5), 6.48 (t, 1, H4 trans to OH), 6.30 (t, 2, H4), 2.23 (s, 6, CH₃). ¹³C{¹H} NMR (CDCl₃): δ 142.3 ($^2J_{\text{PtC}} = 39.3$ Hz, C3 trans to OH), 140.3 (C3), 136.3, 135.1, 134.4, 132.8, 128.0 ($^2J_{\text{PtC}} = 39.8$ Hz, C2,6), 122.5 ($^1J_{\text{PtC}} = 808.4$ Hz, C1), 107.0 (C4), 106.4 (C4), 20.5 (CH₃). IR (KBr disk): 2502 ($\nu_{\text{B-H}}$), 3500 (s br) cm⁻¹ ($\nu_{\text{O-H}}$). Anal. Calcd for C₂₃H₂₅BN₆OPT: C, 45.5; H, 4.1; N, 13.8. Found: C, 45.3; H, 4.1; N, 13.6.

Synthesis of Triorgano platinum(IV) Complexes. Pt-Me₃{(pz)₃BH} (9). Iodomethane (1 mL) was added to a solution of K[PtMe₂{(pz)₃BH}] prepared from [PtMe₂(SEt₂)₂] (0.04 g, 0.06 mmol) and K[(pz)₃BH] (0.03 g, 0.12 mmol) in tetrahydrofuran (2 mL). A yellow solid (KI) precipitated within 5 min, but stirring was continued for 1 h. After the mixture was centrifuged, the pale yellow solution was separated from the solid and evaporated to dryness. The residue was extracted with diethyl ether to give a white crystalline solid, on removal of solvent (0.05 g, 100%). The complex has a ¹H NMR spectrum the same as reported.²¹

PtMe(*p*-tol)₂{(pz)₃BH} (10). A solution of [Pt(*p*-tol)₂(SEt₂)₂] (0.040 g, 0.046 mmol) and K[(pz)₃BH] (0.026 g, 0.101 mmol) in tetrahydrofuran (2 mL) was stirred before adding iodomethane (15 μ L, 0.24 mmol). The solution was stirred for 2 h, the solvent was evaporated in a vacuum, and the residue was extracted with benzene (1 mL); impurities precipitated by the addition of pentane (3 mL). The solution was separated from the solids and reduced to very low volume, and pentane (3 mL) was added to further precipitate impurities. The solution was separated from the solids and taken to dryness under a vacuum (0.046 g, 82%). ¹H NMR (CDCl₃): δ 7.71 (d, $^3J = 2.4$ Hz, 1, H3 or 5 trans to Me), 7.65 (d, $^3J = 2.2$ Hz, 2, H3 or 5), 7.41 (d, $^3J = 1.8$ Hz, 1, H3 or 5 trans to Me), 7.30 (d, $^3J = 2.4$ Hz, 2, H3 or 5), 6.86 (d, $^3J_{\text{PtH}} = 44.6$ Hz, $^3J = 8.1$ Hz, H2,6), 6.68 (m, 4, H3,5), 6.16 (t, 1, H4 trans to Me), 6.12 (t, 2, H4), 2.16 (s, 6, C₆H₄CH₃), 1.75 (s, $^2J_{\text{PtH}} = 70.3$ Hz, 3, PtCH₃). ¹³C{¹H} NMR (CDCl₃): δ 139.3 ($^2J_{\text{PtC}} = 12.9$ Hz, C3 trans to Me), 138.1 ($^2J_{\text{PtC}} = 19.4$ Hz, C3), 134.4 ($^3J_{\text{PtC}} = 8.9$ Hz, C4), 134.1, 131.8 ($^3J_{\text{PtC}} = 9.1$ Hz, C4 trans to Me), 126.7 ($^2J_{\text{PtC}} = 51.6$ Hz, C2,6), 122.9 ($^1J_{\text{PtC}} = 902.6$ Hz, C1), 104.7, 19.6 (C₆H₄CH₃), 0.13 ($^1J_{\text{PtC}} = 672.3$ Hz, PtCH₃). IR (KBr disk): 2483 cm⁻¹ ($\nu_{\text{B-H}}$). Anal. Calcd for C₂₄H₂₇BN₆Pt: C, 47.7; H, 4.5; N, 13.9. Found: C, 48.1; H, 4.1; N, 13.4.

Detection of Hydrogen as a Product of Reactions. Hydrogen was detected as a product in the reactions of [PtMe₂{(pz)₄B}]⁻, [PtR₂{(pz)₃BH}]⁻ (R = Me, *p*-tol), PtHMe₂{(pz)₄B}, and PtHR₂{(pz)₃BH} (R = Me, *p*-tol) with water in acetone or tetrahydrofuran. In a typical experiment, a solution of [PtMe₂{(pz)₃BH}]⁻ prepared from [PtMe₂(SEt₂)₂] (0.025 g, 0.04 mmol) and K[(pz)₃BH] (0.02 g, 0.08 mmol) in tetrahydrofuran (0.7 mL) was added to a small vial (2 mL) containing 50 μ L of water. The vial was then fitted with a septum secured with a Teflon tap. After the vial was allowed to stand for 12 h, the gas phase was sampled using a microsyringe and

Table 1. Specific Crystallographic Details

	Pt(OH)Me ₂ {(pz) ₃ BH} (6) ^a	Pt(OH)Me ₂ {(pz) ₄ B}·H ₂ O (7) ^b	Pt(OH)(<i>p</i> -tol) ₂ {(pz) ₃ BH} (8) ^c
formula	C ₁₁ H ₁₇ BN ₆ O ₂ Pt	C ₁₄ H ₁₉ BN ₈ O ₂ Pt·H ₂ O	C ₂₃ H ₂₅ BN ₆ O ₂ Pt
cryst syst	orthorhombic	monoclinic	monoclinic
space group	<i>Pnma</i> (<i>D</i> _{2h} ¹⁶ No. 62)	<i>P2₁/c</i> (<i>C</i> _{2h} ⁵ No. 14)	<i>C2/c</i> (<i>C</i> _{2h} ⁶ No. 15)
<i>a</i> (Å)	15.06(1)	12.251(3)	18.384(7)
<i>b</i> (Å)	11.259(5)	10.330(4)	13.107(4)
<i>c</i> (Å)	8.730(3)	14.846(3)	20.051(6)
β (deg)		99.89(2)	104.81(3)
<i>V</i> (Å ³)	1480	1851	4671
<i>Z</i>	4	4	8
mw	455.2	539.3	607.4
<i>D</i> _{calcd} (g cm ⁻³)	2.04	1.94	1.73
cryst size (mm)	0.52 × 0.44 × 0.09	0.18 × 0.30 × 0.42	0.55 × 0.42 × 0.04
μ (cm ⁻¹)	95	76	60
<i>F</i> (000)	864	1040	2368
2θ _{max} (deg)	70	60	60
<i>A</i> * _{min,max} (analytical)	4.44, 15.87	2.99, 6.4	1.27, 6.9
<i>N</i> , <i>N</i> ₀	3371, 2600	5399, 3750	5357, 2947
<i>R</i> , <i>R</i> _w	0.035, 0.039	0.042, 0.044	0.041, 0.044
<i>n</i> _v	104	236	289

^a The hydroxyl hydrogen atom was located in the mirror plane in a difference map but was not refineable; for compatibility with **7** and **8**, C(a) is set as its mirror image, c.f. the preliminary publication.¹⁶ ^b Hydroxylic hydrogen atoms were not located. ^c Hydroxylic hydrogen atom not located; the cell has a weak superlattice in *c*.

analyzed by GC-MS using a HP1 column (25 m × 0.32 mm) on a Kratos ISQ mass spectrometer (10 eV ET with helium carrier gas), which showed the presence of hydrogen.

Studies of the Decomposition of Diorgano(hydrido)platinum(IV) Complexes. In a typical experiment, Pt(*p*-tol)₂{(pz)₃BH} in nitrobenzene-*d*₅ was heated for 10 min at 10 °C intervals until a decrease in the hydridoplatinum(IV) resonance was apparent. The temperature was kept constant until decomposition was complete (30 min), and the resulting solution was examined by mass spectrometry (LSIMS) and GC-MS. LSIMS: from **3**, PtMe{(pz)₃BH}, calcd 423, found 423; from **4**, PtMe{(pz)₄B}, calcd 489, found 489; from **5**, Pt₂(*p*-tol)₂{(pz)₃BH}₃, calcd 1211.4, found 1211.4 and 1212.4.

X-ray Structure Determinations. Crystals of **7** were obtained from acetone and of **8** from an acetone/water solution. For each complex, a unique data set was measured at 295 K, using an Enraf-Nonius CAD-4 diffractometer operating in conventional 2θ-θ scan mode with monochromatic Mo Kα radiation (λ = 0.710 73 Å), yielding *N* independent reflections, *N*₀ with *I* > 3σ(*I*) being considered observed and used in the full-matrix least-squares refinement after analytical absorption correction and solution of the structures by vector methods. Residuals *R* and *R*_w are quoted on |*F*| at convergence; statistical weights derived from σ²(*I*) = σ²(*I*_{diff}) + 0.0004σ⁴(*I*_{diff}) were employed. Neutral atom complex scattering factors were used;²² computation used the XTAL 3.0 program system implemented by Hall.²³ For the ligands, (*x*, *y*, *z*, *U*_{iso})_H were included at estimated values; the treatment of the hydroxylic hydrogen atoms is given in Table 1.

Crystal data and selected geometries of the complexes are given in Tables 1–3, and views of the complexes are shown in Figures 1–3.

Results and Discussion

Reaction of Diorganoplatinum(II) Reagents with Poly(pyrazol-1-yl)borate Ligands. The reactions of diorganoplatinum(II) reagents with poly(pyrazol-1-yl)borates were studied initially by ¹H NMR spectroscopy in acetone-*d*₆, a solvent suitable for K[(pz)₃BH] and K[(pz)₄B]. Diethylsulfide was found to be readily displaced from [PtMe₂(SET₂)₂], but [Pt(*p*-tol)₂(SET₂)₂] is

insufficiently soluble for NMR studies. 1,5-Cyclooctadiene is not displaced from PtMe₂(cod) by [(pz)₃BH]⁻, but noting that norbornadiene is more easily displaced than cod from its complexes,²⁴ Pt(*p*-tol)₂(nbd) was explored as a reagent for NMR studies and found to be both soluble in acetone-*d*₆ and ideal for displacement reactions. Thus, solutions of the anions [PtMe₂{(pz)₄B}]⁻ and [PtR₂{(pz)₃BH}]⁻ (R = Me, *p*-tol) formed readily at ambient temperature, and the anions containing tris(pyrazol-1-yl)borate were subsequently isolated in preparative procedures using [PtR₂(SET₂)₂] reagents.

The isolated complexes are very sensitive to moisture and give NMR spectra that confirm the presence of the anions when generated in solution from diorganoplatinum(II) reagents and K[(pz)₃BH] (see above), which can be readily assigned, e.g., K[PtMe₂{(pz)₃BH}] (**1**) exhibits ²J_{PtH} = 86 Hz and ¹J_{PtC} = 835 Hz for the PtCH₃ group, and K[Pt(*p*-tol)₂{(pz)₃BH}] (**2**) exhibits ³J_{PtH} = 69 Hz for the aryl group. The anion [PtMe₂{(pz)₄B}]⁻, for which isolation was not attempted, exhibits δ (PtMe) 0.47 (²J_{PtH} = 84 Hz).

In studies of reactions of the anions with acids and water, described in the following sections, solutions of the anions generated *in situ* were used, followed by confirmation that identical results are obtained for representative reactions of the isolated salts K[PtR₂{(pz)₃BH}] (R = Me, *p*-tol).

Reaction of Diorganoplatinum(II) Anionic Reagents with Acids. The complex PtHMe₂{(pz)₃BH} (**3**) has been isolated on reaction of the weak acid phenol (p*K*_a 9.95)²⁵ with [PtMe₂{(pz)₃BH}]⁻,¹⁰ and although phenol was found to protonate [PtMe₂{(pz)₄B}]⁻, reaction does not occur with [Pt(*p*-tol)₂{(pz)₃BH}]⁻. Thus, a range of stronger acids were examined in the NMR studies in acetone-*d*₆ (eq 6), and although the dimethylplatinum(II) anions were readily protonated by all of the acids studied, including pentafluorophenol (p*K*_a 5.49),²⁵ [Pt(*p*-tol)₂{(pz)₃BH}]⁻ required the stronger acids CH₃CO₂H (p*K*_a 4.75), CF₃CO₂H (p*K*_a 0.20), or

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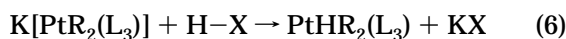
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Table 2. Selected Bond Distances (Å) and Angles (deg) for Pt(OH)Me₂{(pz)₃BH} (6), Pt(OH)Me₂{(pz)₄B}·H₂O (7), and Pt(OH)(*p*-tol)₂{(pz)₃BH} (8)

	6	7	8
Bond Distances			
Pt–O	1.984(5)	1.996(6)	1.974(8)
Pt–N(a2)	2.151(3)	2.147(6)	2.128(9)
Pt–N(b2)	[2.151(3)]	2.144(6)	2.123(8)
Pt–N(c2)	2.022(5)	2.014(7)	2.052(8)
Pt–C(a)	2.048(5)	2.030(9)	2.02(1)
Pt–C(b)	[2.048(5)]	2.049(9)	2.01(1)
B–N(a1)	1.524(6)	1.56(1)	1.55(2)
B–N(b1)	[1.524(6)]	1.530(9)	1.51(2)
B–N(c1)	1.569(9)	1.55(1)	1.53(1)
O···O(1,1')		2.811(9), 2.937(8)	
O···O'		3.450(9)	
"Bite Distances" for the Tris(pyrazol-1-yl)borate Ligands			
N(a2)···N(b2)	2.888(5)	2.864(9)	2.90(1)
N(a2)···N(c2)	2.899(6)	2.864(10)	2.88(1)
N(b2)···N(c2)	[2.888(5)]	2.873(9)	2.86(1)
Bond Angles			
O–Pt–N(a2)	90.4(1)	91.7(2)	90.1(4)
O–Pt–N(b2)	[90.4(1)]	89.9(2)	86.9(3)
O–Pt–N(c2)	177.8(2)	177.1(2)	172.8(3)
O–Pt–C(a)	89.9(2)	88.8(4)	89.9(4)
O–Pt–C(b)	[89.9(2)]	90.3(3)	90.4(4)
N(a2)–Pt–N(b2)	84.4(1)	83.8(2)	86.1(3)
N(a2)–Pt–N(c2)	88.0(1)	86.9(3)	86.9(3)
N(a2)–Pt–C(a)	177.6(2)	177.4(4)	177.3(3)
N(a2)–Pt–C(b)	93.3(2)	93.2(3)	91.6(4)
N(b2)–Pt–N(c2)	[88.0(1)]	87.4(2)	86.3(3)
N(b2)–Pt–C(a)	91.7(2)	93.7(3)	91.2(3)
N(b2)–Pt–C(b)	[177.6(2)]	176.9(3)	176.5(4)
N(c2)–Pt–C(a)	91.7(2)	92.4(4)	92.7(4)
N(c2)–Pt–C(b)	[91.7(2)]	92.4(3)	96.3(4)
C(a)–Pt–C(b)	89.1(2)	89.4(4)	91.1(4)
Pt–N(a2)–N(a1)	117.2(3)	119.8(5)	118.1(6)
Pt–N(a2)–C(a3)	135.4(3)	132.5(6)	134.2(2)
Pt–N(b2)–N(b1)	[117.2(3)]	119.6(4)	119.3(6)
Pt–N(b2)–C(b3)	[135.4(3)]	131.8(5)	132.5(1)
Pt–N(c2)–N(c1)	119.6(4)	118.0(5)	117.6(6)
Pt–N(c2)–C(c3)	133.6(4)	133.8(6)	135.3(8)
Pt–C(a)–C(a12)			120.5(8)
Pt–C(a)–C(a16)			123.2(8)
Pt–C(b)–C(b12)			123.7(8)
Pt–C(b)–C(b16)			121.2(9)
N(a1)–B–N(b1)	109.8(5)	107.2(6)	109.3(9)
N(a1)–B–N(c1)	108.6(3)	108.3(5)	109.3(8)
N(a1)–B–N(d1)		111.2(6)	
N(b1)–B–N(c1)	[108.6(3)]	109.1(6)	109(1)
N(b1)–B–N(d1)		113.2(5)	
N(c1)–B–N(d1)		107.7(6)	

HBF₄ (aq). These results are consistent with the



R = Me, L₃ = (pz)₃BH, H–X =

HBF₄ (aq), CF₃CO₂H, MeCO₂H, C₆F₅OH,

PhOH (**3**); R = Me, L₃ = (pz)₄B, H–X = HBF₄

(aq), CF₃CO₂H, MeCO₂H, C₆F₅OH, PhOH (**4**); R =

p-tolyl, L₃ = (pz)₃BH, H–X = HBF₄ (aq),

CF₃CO₂H, MeCO₂H (**5**)

expected greater nucleophilic character of [PtMe₂{(pz)₃BH}][–] compared to [Pt(*p*-tol)₂{(pz)₃BH}][–], as suggested by kinetic studies showing that the 1,10-phenanthroline complex PtMe₂(phen) has a second order rate constant ~130 times larger than the diarylplatinum-

Table 3. Deviations (Å) of Atoms from Mean Planes and Angles (deg) Between Mean Planes in Pt(OH)Me₂{(pz)₃BH} (6), Pt(OH)Me₂{(pz)₄B}·H₂O (7), and Pt(*p*-tol)₂{(pz)₃BH} (8)

	6	7	8
Deviations from Mean Planes ^a			
Pt[pz(a)]	0.058(7)	0.34(1)	0.09(2)
Pt[pz(b)]	[0.058(7)]	0.30(1)	0.03(2)
Pt[pz(c)]	0.00(-)	0.05(1)	0.24(2)
Pt[<i>tol</i> (a)]			0.10(2)
Pt[<i>tol</i> (b)]			0.16(2)
B[pz(a)]	0.12(1)	0.16(1)	0.01(2)
B[pz(b)]	0.12(4)	0.22(1)	0.05(2)
B[pz(c)]	0.00(-)	0.03(1)	0.15(2)
Angles between Mean Planes			
rings pz(a)/pz(b)	69.0(3)	80.0(3)	59.6(5)
rings pz(a)/pz(c)	55.6(3)	52.5(3)	51.6(5)
rings pz(b)/pz(c)	[55.6(3)]	47.5(3)	68.8(5)
rings pz(a)/ <i>tol</i> (a)			11.4(5)
rings pz(a)/ <i>tol</i> (b)			82.7(5)
rings pz(b)/ <i>tol</i> (a)			59.9(5)
rings pz(b)/ <i>tol</i> (b)			39.5(5)
rings pz(c)/ <i>tol</i> (a)			53.0(4)
rings pz(c)/ <i>tol</i> (b)			55.4(5)
rings <i>tol</i> (a)/ <i>tol</i> (b)			76.1(4)

^a χ² values for pyrazole rings a–c ("C₃N₂"), respectively: **6** 0.4, [0.4], 0.1; **7** 0.6, 2.7, 0.6; **8** 1.2, 0.2, 1.6. χ² values for tolyl rings a and b in **8** are 0.4 and 12, respectively.

(II) analogue PtPh₂(phen) in oxidative-addition reactions with iodomethane.²⁶

The new complexes PtHMe₂{(pz)₄B} (**4**) and PtH(*p*-tol)₂{(pz)₃BH} (**5**) were subsequently isolated in ~65% yield in reactions employing acetic acid as the protonating agent. They exhibit ¹H and ¹³C NMR and IR spectra similar to those previously reported for **3**, in particular for the hydridoplatinum(IV) groups: ν(Pt–H) = 2260 (**4**) and 2280 cm^{–1} (**5**), δ (¹H) –20.1 (¹J_{PtH} = 1360 Hz) (**4**) and –19.53 (¹J_{PtH} = 1400 Hz) (**5**), compared to 2250 cm^{–1}, –20.2 ppm (¹J_{PtH} = 1358 Hz), and –20.4 ppm (¹J_{PtC} = 621 Hz) (**3**); the PtCH₃ group of **4** has δ (¹H) 1.15 (²J_{PtH} = 68 Hz) and δ (¹³C) –19.62 (¹J_{PtC} = 613 Hz) compared to 1.08 ppm (²J_{PtH} = 68.4 Hz) and –20.4 ppm (¹J_{PtC} = 621 Hz) (**3**). ¹H NMR resonances for the pyrazole ring protons of PtHMe₂{(pz)₄B} are broader than those observed for PtXR₂{(pz)₃BH} (X = H, OH; R = Me, *p*-tol) and Pt(OH)Me₂{(pz)₄B}, even at –60 °C, indicating the possible presence of an exchange between coordinated and uncoordinated pyrazole groups, a process known to be facile for PtMe₃{(pz)₄B}.²¹

A structural study of PtHMe₂{(Me₂pz)₃BH} has been reported recently by Templeton and co-workers,¹¹ but the hydrido complexes reported here could not be obtained in a form suitable for structural analysis. The structural study did not reveal a Pt–H bond distance,¹¹ and apparently, the only structural study of a hydridoplatinum complex for which a Pt–H distance is recorded is the Pt(II) complex PtH(CH₂CMe₃)₂(Cy₂PCH₂CH₂PCy₂), which has Pt–H = 1.56(5) Å,²⁷ similar to that calculated theoretically for PtHMe₂{(H₂C=N–NH)₃BH} (1.53 Å) as a model for PtHMe₂{(pz)₃BH}.¹⁰ However, it is of interest to note that the structural study of PtHMe₂{(Me₂pz)₃BH} shows that Pt–N trans to the hydrido group is ~0.024 Å longer than that trans to the methyl groups,¹¹ as expected for the higher trans

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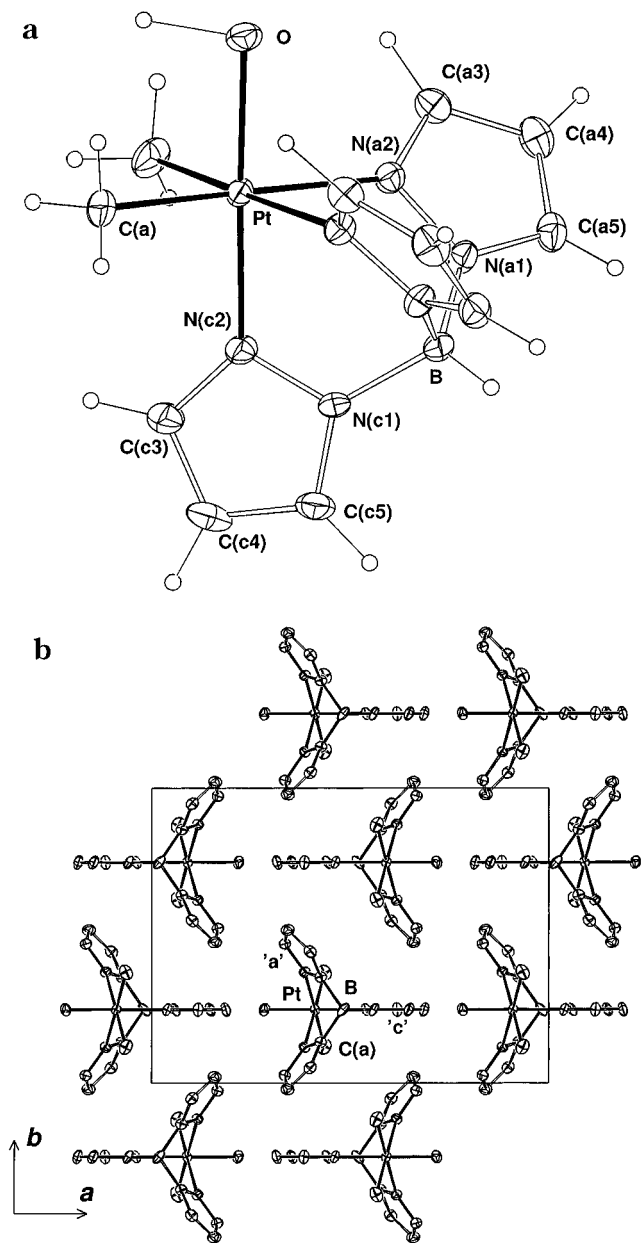


Figure 1. (a) Molecular structure and (b) unit-cell contents projected down c for $\text{Pt}(\text{OH})\text{Me}_2\{(\text{pz})_3\text{BH}\}$ (**6**), showing different views of the molecule. Thermal ellipsoids (20%) are shown for the non-hydrogen atoms, and hydrogen atoms have been given an arbitrary radius of 0.1 Å.

influence of the hydrido ligand; a similar difference (0.03 Å) has been calculated for the model using MP2 procedures.¹⁰

Reaction of Diorganoplatinum(II) Anionic Reagents with Water. The anions $[\text{PtR}_2\{(\text{pz})_3\text{BH}\}]^-$ ($\text{R} = \text{Me}, p\text{-tol}$) and $[\text{PtMe}_2\{(\text{pz})_4\text{B}\}]^-$ are stable in solution in the absence of water when studied by ^1H NMR spectroscopy, but addition of water in the presence or rigorous exclusion of oxygen results in the formation of the analogous hydroxoplatinum(IV) complexes $\text{Pt}(\text{OH})\text{R}_2(\text{L}_3)$. These complexes were found to be readily isolable in synthetic studies, and hydrogen gas was detected as a product by GC-MS; and thus, the reactions are formulated as in eq 7. The tetrakis(pyrazol-1-yl)borate complex crystallizes as a monohydrate (**7**).

The hydroxoplatinum(IV) complexes exhibit spectra similar to those of the hydrido complexes, except that

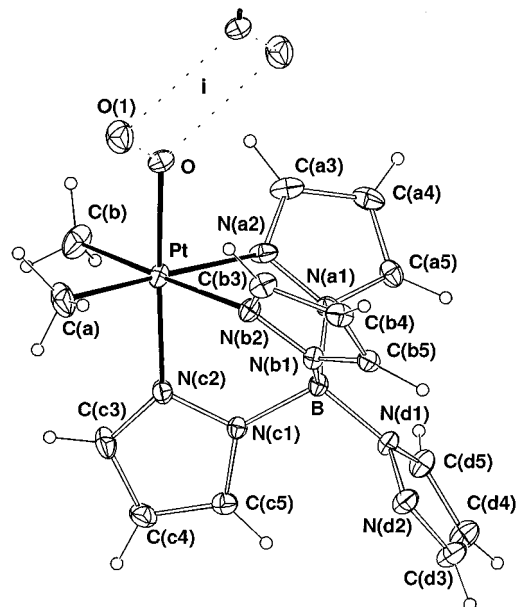


Figure 2. Molecular structure of $\text{Pt}(\text{OH})\text{Me}_2\{(\text{pz})_4\text{B}\} \cdot \text{H}_2\text{O}$ (**7**), showing the interaction between groups containing oxygen atoms O and O(1).

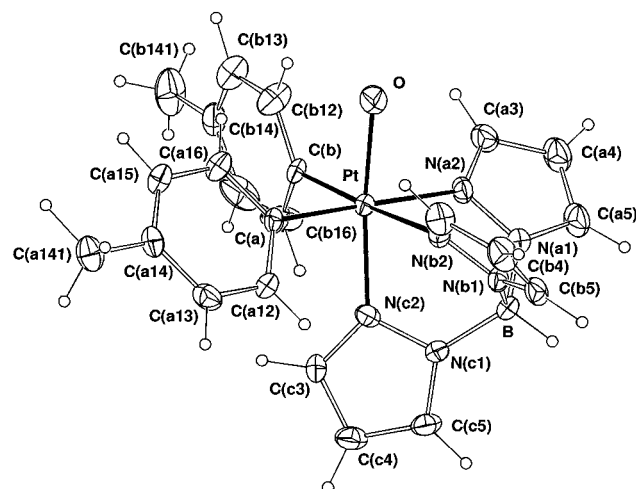
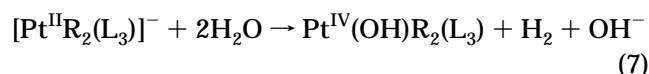


Figure 3. Molecular structure of $\text{Pt}(\text{OH})(p\text{-tol})_2\{(\text{pz})_3\text{BH}\}$ (**8**).



$\text{R} = \text{Me}, \text{L}_3 = (\text{pz})_3\text{BH}$ (**6**) or $(\text{pz})_4\text{B} \cdot \text{H}_2\text{O}$ (**7**);

$\text{R} = p\text{-tol}, \text{L}_3 = (\text{pz})_3\text{BH}$ (**8**)

IR absorptions and ^1H NMR resonances attributable to Pt–H are absent, and ^1H NMR spectra exhibit $^3J_{\text{PtH}}$ coupling for the pyrazole group trans to the hydroxo group (10–14.2 Hz) (Figure 4). The presence of the latter coupling for the hydroxo complexes but not for the hydrido complexes is consistent with the weaker trans influence of the hydroxo group compared with the hydrido and methyl groups, as noted in the previous section.

Reaction of Diorgano(hydrido)platinum(IV) Complexes with Water. The hydridoplatinum(IV) complexes are stable when generated in acidic solution (eq 6) but are unstable in neutral or basic solution. Thus, addition of NaOH (10% in D_2O) to a solution of $\text{PtHMe}_2\{(\text{pz})_3\text{BH}\}$ generated from $[\text{PtMe}_2\{(\text{pz})_3\text{BH}\}]^-$

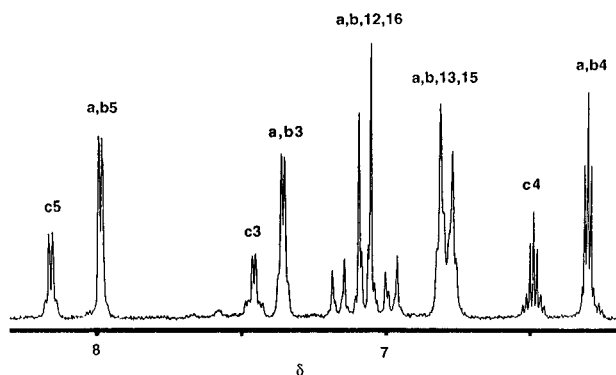
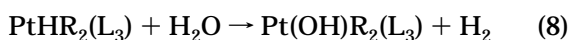


Figure 4. ^1H NMR spectrum of $\text{Pt}(\text{OH})(p\text{-tol})_2\{(\text{pz})_3\text{BH}\}$ (**8**) in CDCl_3 in the aromatic region recorded at 200 MHz, illustrating the presence of J_{PtH} for the *p*-tolyl group and the pyrazole group trans to OH. Following the atom numbering in Figure 3 and from low to high field: H(c5) ($^3J_{\text{PtH}} = 2.6$ Hz), H(c3) ($^5J_{\text{HPt}} = 2.4$ Hz), H(a,b,12,16) ($^3J_{\text{HPt}} = 36.6$ Hz); J_{PtH} for the other pyrazole rings and for H(a,b,13,15) is poorly resolved.

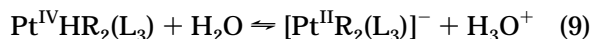
and HBF_4 (aq) in acetone- d_6 led to the partial reformation of the platinum(II) anion, together with slow formation of the hydroxoplatinum(IV) complex $\text{Pt}(\text{OH})\text{Me}_2\{(\text{pz})_3\text{BH}\}$ until the latter became the only species in solution. Similarly, the isolated hydridoplatinum(IV) complexes were found to be stable in anhydrous solvents, but ^1H NMR and GC-MS studies indicated that addition of water to acetone- d_6 solutions leads to formation of the hydroxoplatinum(IV) complexes and hydrogen (eq 8).



$\text{R} = \text{Me}$, $\text{L}_3 = (\text{pz})_3\text{BH}$ (**6**) or $(\text{pz})_4\text{B}$ (**7**);

$\text{R} = p\text{-tol}$, $\text{L}_3 = (\text{pz})_3\text{BH}$ (**8**)

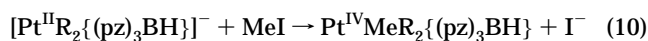
The higher stability of $\text{PtHR}_2(\text{L}_3)$ in acidic solution suggests that these hydrides are not the intermediate species in the reaction of eq 7. The deprotonation of $\text{PtHMe}_2\{(\text{pz})_3\text{BH}\}$ in basic solution indicates that the products of reaction 8 may form via the platinum(II) anionic species formed by reversible dissociation of H^+ (eq 9), followed by the reaction 7. The equilibrium of



eq 9 is analogous to the reversible protonation of platinum(0) complexes by water²⁸ and of the platinum(II) complex $\text{PtCl}(\text{CH}_2\text{Ph})(\text{tmeda})$ by HCl .⁹

The anions $[\text{PtR}_2(\text{L}_3)]^-$ were found to undergo rapid oxidative-addition reactions with iodomethane to form $\text{PtMeR}_2\{(\text{pz})_3\text{BH}\}$ (eq 10) in reactions typical of diorganoplatinum(II) species, including those containing tripodal ligands similar to $[(\text{pz})_3\text{BH}]^-$,^{11,29} in particular $[\text{PtR}_2\{(\text{Me}_2\text{pz})_3\text{BH}\}]^-$ ($\text{R} = \text{Me}$, Ph).¹¹ The complexes $\text{PtMeR}_2\{(\text{pz})_3\text{BH}\}$ ($\text{R} = \text{Me}$ (**9**), *p*-tol (**10**)) were readily isolated in high yield, and the oxidative-addition reactions were complete within seconds when studied by ^1H

NMR spectroscopy. Complexes **9** and **10** are also formed quantitatively (NMR) on addition of NaOH to a solution containing $\text{PtHR}_2\{(\text{pz})_3\text{BH}\}$ and iodomethane, via eq 9 followed by eq 10.



$\text{R} = \text{Me}$ (**9**), $\text{R} = \text{Ph}$ (**10**)

Thermal Stability and Decomposition of Diorgano(hydrido)platinum(IV) Complexes. The complex $\text{PtHMe}_2\{(\text{pz})_3\text{BH}\}$ (**3**) selectively eliminates methane when heated above ~ 140 °C in toluene- d_8 ,¹⁰ similar to the behavior of hydridoplatinum(IV) complexes of bidentate ligands documented in eq 4.^{6,8,9} However, the much higher stability of related $[(\text{Me}_2\text{pz})_3\text{BH}]^-$ complexes results in general decomposition at temperatures > 230 °C,¹¹ indicating that the latter ligand system is not ideal for studies of the decomposition of diorgano(hydrido)platinum(IV) complexes. The decomposition of complex **4** was studied in toluene- d_8 , but complex **5** could potentially give either toluene or ditolyls if a simple intramolecular reductive elimination occurs, and thus, the decomposition of this complex was monitored by ^1H NMR in nitrobenzene- d_5 .

The temperature was kept constant at the first indication of decomposition, resulting in decomposition at ~ 140 (**3**), ~ 85 (**4**), and ~ 90 °C (**5**). The resulting yellow solutions, showing no evidence of solids or platinum metal, were examined by GC-MS and mass spectrometry (LSIMS). Complexes **3** and **4** gave methane, and complex **5** gave toluene with traces of ditolyls. Platinum containing species $\text{PtMe}\{(\text{pz})_3\text{BH}\}$ (from **3**), $\text{PtMe}\{(\text{pz})_4\text{B}\}$ (from **4**), and $\text{Pt}_2(p\text{-tol})_2\{(\text{pz})_3\text{BH}\}_3$ (from **5**) were detected, consistent with loss of one mole of methane or toluene per mole of complex and an earlier report of the synthesis of polymeric $\text{PtMe}\{(\text{pz})_3\text{BH}\}$.³⁰

Complex **5** appears to be the first example of a diaryl(hydrido)platinum(IV) system amenable to studies of selectivity in decomposition and confirms that the predominant pathway involves C–H bond formation. Reductive elimination is believed to occur via anion dissociation from complexes of bidentate ligands, $\text{PtX}(\text{H})\text{Me}_2(\text{bidentate})$ ($\text{X} = \text{halogen}$),^{8,9} and the higher stability of the complexes of tripodal tridentates $[(\text{pz})_3\text{BH}]^-$ and $[(\text{Me}_2\text{pz})_3\text{BH}]^-$ compared to $\text{PtX}(\text{H})\text{Me}_2(\text{bidentate})$ complexes is consistent with this proposal. For example, occurrence of the classical “chelate effect” is expected to shorten the lifetime of five-coordinate species, and different chelate ring geometries exhibited by bidentate and tridentate $[(\text{pz})_3\text{BH}]^-$ ²⁹ may mitigate against donor group dissociation from platinum.

X-ray Structural Studies of Diorgano(hydroxo)platinum(IV) Complexes. The complexes $\text{Pt}(\text{OH})\text{Me}_2\{(\text{pz})_3\text{BH}\}$ (**6**), $\text{PtOH}(\text{Me}_2\{(\text{pz})_4\text{B}\})\cdot\text{H}_2\text{O}$ (**7**), and $\text{Pt}(\text{OH})(p\text{-tol})_2\{(\text{pz})_3\text{BH}\}$ (**8**) have distorted octahedral geometries (Figures 1–3, Table 2). It has not been possible to ascertain from a comparison of the geometries of the three complexes whether **7**, containing $\text{O}\cdots\text{O}(1)$ distances of 2.811(9) and 2.937(8) Å, is a monohydrate with hydrogen-bonding $\text{Pt}(\text{OH})\cdots\text{H}_2\text{O}$ or an aqua/hydroxide complex $\text{Pt}(\text{OH})_2^+\cdots\text{OH}^-$. However, the former seems more likely in view of the crystallization of the very

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similar complexes **6** and **8** as hydroxo complexes and from geometrical considerations (see below).

The complexes exhibit Pt–O distances of 1.974(8)–1.996(6) Å similar to but (apparently) shorter than those observed for [PtPh₂{(py)₃COH}(OH)₂]⁺ (2.04(1) Å).^{15b} The Pt–N(c2) distances trans to the oxygen atom are ~0.13 Å shorter than the Pt–N distances trans to the methyl groups, ~0.07₃ Å shorter than the Pt–N distances trans to *p*-tolyl groups, and ~0.14 Å shorter than the Pt–N distance trans to the hydrido group in PtHMe₂{(Me₂pz)₃BH},¹¹ confirming the much weaker trans influence of the hydroxo group noted above in the discussions of NMR spectra. The platinum atom lies within 0.34 Å of the mean planes of the pyrazole rings in all three complexes.

Concluding Remarks

The results reported here illustrate the close relationship between the oxidation of platinum(II) by acids and water to form hydridoplatinum(IV) (eq 1) and hydroxoplatinum(IV) species (eq 2, X[−] = OH[−] (coordinated)), respectively. Hydridoplatinum(IV) species (eq 1) are assumed to be intermediates in the reaction of eq 2, but

the demonstration that protonation of [PtR₂{(pz)₃BH}][−] (R = Me, *p*-tol) is reversible and that PtHR₂{(pz)₃BH} is stable in acidic solution indicates that PtHR₂{(pz)₃BH} is unlikely to be the key hydridoplatinum(IV) intermediate in the oxidation of [PtR₂{(pz)₃BH}][−] by water to form hydrogen and Pt(OH)R₂{(pz)₃BH}, even though PtHR₂{(pz)₃BH} reacts with water to form these products.

The cleavage of Pt^{II}–R bonds by acids, via hydridoplatinum(IV) intermediates followed by reductive elimination of R–H, has now been demonstrated for arylplatinum(II) systems, complementing previous studies for alkylplatinum(II) reagents^{6,8–11} and showing selectivity for arene over biaryl elimination from Pt(IV).

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Supporting Information Available: Tables of atom coordinates, thermal parameters, hydrogen atom parameters, and bond distances and angles for complexes **6–8** (15 pages). Ordering information is given on any current masthead page.

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