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Five-Coordinate Trispyrazolylborate Dihydridosilyl Platinum(IV) Complexes

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Reductive elimination of C−H and C−C bonds from octahedral platinum(IV) complexes has been shown to occur from a five-coordinate intermediate generated by ligand dissociation.[1] Given the importance of such intermediates in bond activation at platinum, we wish to communicate isolation of well-defined five-coordinate platinum(IV) silyldihydride complexes.[2]

The chemistry of TpPt(R)(R′)H [Tp = hydridotris(pyrazolyl)-borate; Tp′ = hydridotris(3,5-dimethylpyrazolyl)borate; *R,R′* = combinations of alkyl, aryl, silyl and hydride ligands] has blossomed since 1995.[3] The stability of these complexes stems from canonical tridentate coordination of the tris(pyrazolyl)borate ligand.[4] Other stable platinum(IV) alkyl hydride complexes also contain chelating ligands in the platinum coordination sphere.[5] Protonation under mild conditions induces reductive elimination of methane from Tp′PtMe$_2$H and Tp′PtMe(H)$_2$ via five-coordinate intermediates, leading to isolable cationic platinum(II) complexes after addition of a trapping ligand.[3g,6]

Given the ability of silyl and hydride ligands to stabilize high-oxidation state metals,[3f,7] and noting the elongated Pt−N bond (2.30 Å) trans to the triethylsilyl ligand in Tp′Pt(SiEt$_3$)(H)$_2$ (**1**),[3f] it seemed plausible that we could access a stable five-coordinate platinum(IV) complex **2** simply by protonation of **1** (eq 1).

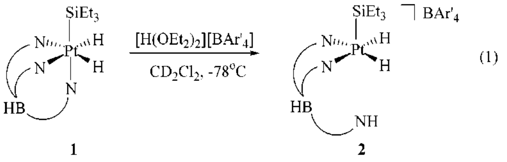


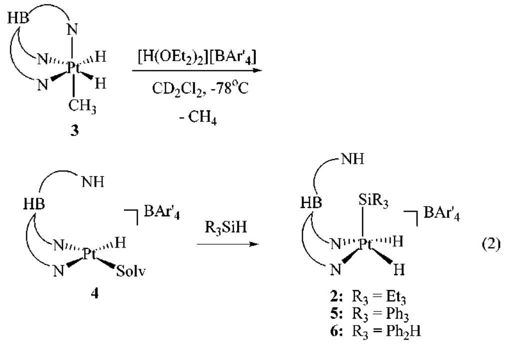
Table 1. Spectroscopic Data for Complexes **2**, **5**, **6**[a]

complex	SiR$_3$	δ (Pt−H) ppm	$^1J_{Pt-H}$ Hz	ν (Pt−H) cm^{-1}	δ (Si−H) ppm	ν (Si−H) cm^{-1}
2	SiEt$_3$	−16.69	1049	2258		
5	SiPh$_3$	−15.05	986	2254		
6	SiPh$_2$H	−15.35	983	2247	4.88	2100

[a] IR data obtained in CH$_2$Cl$_2$ solution at room temperature.

Protonation of complex **1** with one equivalent of the acid [H(OEt$_2$)$_2$][BAr′$_4$][8] in CD$_2$Cl$_2$ at −78 °C yields a single new compound with mirror symmetry according to both ^{1}H and ^{13}C NMR spectra (Table 1).[9] A resonance at 10.1 ppm is assigned to a protonated pyrazole ring,[3g,6,10] and the lone hydride resonance at −16.69 ppm ($^1J_{Pt-H}$ = 1049 Hz) integrates for two hydrogens. A solution IR spectrum (CH$_2$Cl$_2$) displays a single absorption at 2258 cm^{-1} for the Pt−H stretching vibrations, as previously observed for related Tp′PtR(H)$_2$ complexes.[3f,6] These data are most compatible with the five-coordinate dihydridosilyl Pt(IV) complex, [κ^2-((Hpz*)BHpz*$_2$)Pt(H)$_2$(SiEt$_3$)][BAr′$_4$] (**2**). Complex **2** slowly decomposes in CH$_2$Cl$_2$ solution to form Tp′PtH$_3$,[3f] presumably through heterolytic Pt−Si cleavage, a common decomposition pathway.[11]

Complex **2** can also be obtained by protonation of the methyldihydride complex **3** and subsequent trapping with triethylsilane. Protonation of **3** leads exclusively to reductive elimination of methane and formation of the platinum(II) solvent (presumably diethyl ether) adduct, [κ^2-((Hpz*)BHpz*$_2$)Pt(H)(Solv)][BAr′$_4$] (**4**) (eq 2).[6] *Chiral* intermediate **4** is trapped with one equivalent of triethylsilane, and complex **2** with *mirror symmetry* is the sole product.



Is complex **2** a dihydridosilyl Pt(IV) complex (**A** in Scheme 1) or a Pt(II) silane adduct, [κ^2-((Hpz*)BHpz*$_2$)Pt(H)(H-SiEt$_3$)]-

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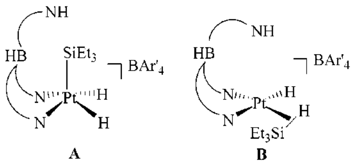
Scheme 1



[BAr′$_4$] (**B** in Scheme 1)? Rapid exchange between M−H and Si−H, a well-known phenomena,[7a,12] could cause their equivalency on the NMR time scale.

Several NMR observations are inconsistent with the platinum(II) silane description. (1) Addition of excess acetonitrile to a CD_2Cl_2 sample of **2** does *not* lead to silane displacement. (2) The Pt−H signal exhibits *no* coupling to ^{29}Si. (3) Protonation of Tp′PtMe(H)$_2$ (**1**) and subsequent reaction with Et_3SiD (>95% D) leads to formation of [κ^2-((Hpz*)BHpz*$_2$)Pt(H)(D)(SiEt$_3$)][BAr′$_4$] (**2-*d*$_1$**). The ^{1}H NMR spectrum of **2-*d*$_1$** displays only a small isotopic downfield shift (0.06 ppm) for the hydride resonance relative to the resonance for **2**. Zero-point energy differences between Pt−H and Si−H−Pt would be expected to produce a large chemical shift difference upon partial deuteration if a silane ligand were averaging with a hydride in the ground-state structure.[13]

Single crystals of complex **2** were subjected to X-ray analysis; an ORTEP diagram is shown in Figure 1. Although the hydride ligands on platinum were not located in the difference Fourier map, this structure provides key information. (1) There is no solvent in the platinum coordination sphere. (2) Both N11−Pt1−Si1 and N21−Pt1−Si1 angles are essentially identical, compatible with a square-pyramidal structure. (3) All angles involving the silicon atom are near the tetrahedral angle; side-bound σ-silane should show substantial deviations[14,15] (see Table 2).

Protonation of the methyldihydride complex **3** and subsequent trapping of intermediate **4** with Ph_3Si-H at low temperature leads to formation of [κ^2-((Hpz*)BHpz*$_2$)Pt(H)$_2$(SiPh$_3$)][BAr′$_4$], (**5**). The spectroscopic features of **5** are congruent with those of **2** (Table 1).[16] At 233 K, mirror symmetry is evident in the NMR spectra. A resonance for the protonated pyrazole N−H at 9.26 ppm, a signal for the platinum bound hydrides at −15.05 ppm ($^1J_{\mathrm{Pt-H}} = 986$ Hz), and an absorption at 2254 cm^{-1} for vibrations of the Pt(H)$_2$ moiety all indicate a platinum(IV) silyldihydride formulation.

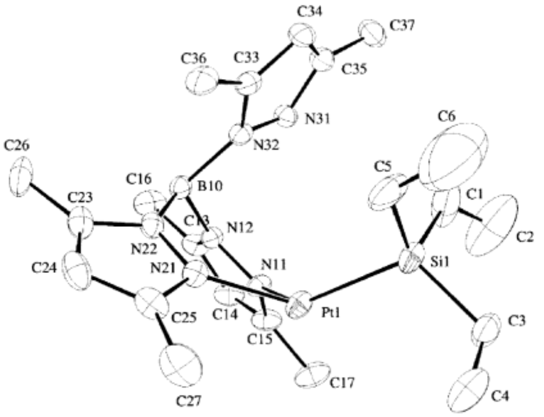


Figure 1. ORTEP diagram of [κ^2-((Hpz*)BHpz*$_2$)Pt(H)$_2$(SiEt$_3$)][BAr′$_4$] (**2**); ellipsoids are drawn at the 50% probability level, and the BAr′$_4$ counterion is omitted for clarity.

Table 2. Selected Bond Distances (Å) and Angles (deg) for Complex **2**

Pt1−Si1	2.349(2)	Pt1−N21	2.102(4)
Pt1−N11	2.090(4)	Si1−C1	1.877(9)
Si1−Pt1−N11	126.76(11)	Pt1−Si1−C5	106.0(2)
Si1−Pt1−N21	120.25(11)	C1−Si1−C3	108.9(3)
Pt1−Si1−C1	106.4(3)	C1−Si1−C5	110.2(5)
Pt1−Si1−C3	114.8(2)	C3−Si1−C5	110.4(3)

Additional evidence germane to formulating the silicon complex correctly as dihydridosilyl platinum(IV) should result from introduction of another hydrogen into the SiR$_3$ fragment. Trapping of the solvento intermediate **4** with Ph_2SiH_2 yields [κ^2-((Hpz*)BHpz*$_2$)Pt(H)$_2$(SiHPh$_2$)][BAr′$_4$] (**6**).[17] A solution IR spectrum shows absorptions at 2247 cm^{-1} for the Pt−H stretches and at 2100 cm^{-1} for the Si−H stretch, exactly as expected for the platinum(IV) silyldihydride structure and incompatible with a silane Si−H bridging bond to platinum(II).[18] Complex **6** is, like **2** and **5**, C_s symmetric according to ^{1}H and ^{13}C NMR spectra. In addition to a protonated pyrazole resonance at 9.45 ppm and a hydride resonance at −15.35 ppm (2H, $^1J_{\mathrm{Pt-H}} = 985$ Hz), the definitive silicon-bound hydrogen resonance appears at 4.88 ppm ($^2J_{\mathrm{Pt-H}} = 25$ Hz, $^1J_{\mathrm{Si-H}} = 215$ Hz). No exchange of platinum- and silicon-bound hydrogen is observed on the NMR time scale, consistent with a dihydridosilyl Pt(IV) structure. Complex **6** decomposes in CH_2Cl_2 solution at room temperature.

In summary, we have successfully isolated and characterized three different five-coordinate platinum(IV) complexes. Hydride and silyl ligands in the platinum coordination sphere stabilize these five-coordinate d^6 monomers.

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Supporting Information Available: Complete synthetic and spectroscopic data for **2**, **5**, **6** (PDF) as well as complete crystallographic data, in CIF format, for complex **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) ^{1}H NMR data for complex **2** (CD_2Cl_2, 203K, δ): 10.49 (s, 1H, pz*N*H*), 6.12 (s, 3H, HTp′C*H*), 2.33, 2.27, 2.19, 1.44 (s, 6H, 6H, 3H, 3H, HTp′C*H*$_3$), 0.72 (t, 9H, $^3J_{\mathrm{H-H}} = 7.6$ Hz, SiCH$_2$C*H*$_3$), 0.44 (q, 6H,$^3J_{\mathrm{H-H}} = 7.6$ Hz, SiC*H*$_2$CH$_3$), −16.69 (s, 2H, $^1J_{\mathrm{Pt-H}} = 1049$ Hz, Pt-*H*).

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(14) The Pt1−N32 distance of 3.503(4) Å is too long for significant π-donation from the protonated pyrazole ring to the platinum center. For a report on substantive π-interactions between a phenyl ring and a metal center in a coordinatively unsaturated complex, see: Schwarz, M.; Kickelbick, G.; Schubert, U. *Eur. J. Inorg. Chem.* **2000**, 1811.

(15) Simply adding H$^+$ to the nitrogen *trans* to silicon in **1** would create unfavorable steric interactions between the silyl group and the proximal methyl groups of the two coordinated pyrazole rings. Facile rearrangement to the more sterically open site adjacent to the protonated ring is surely available to this five-coordinate complex with mobile SiR$_3$ and H ligands in the coordination sphere, and indeed the axial silyl group is proximal to the protonated pyrazole ring.

(16) ^{1}H NMR data for complex **5** (CD_2Cl_2, 233K, δ): 9.26 (s, 1H, pz*N*H*), 7.39−7.23 (m, 15H, Si-*Ph*), 6.20 (s, 2H, HTp′C*H*), 5.50 (s, 1H, HTp′C*H*), 2.35, 1.53, 1.08 (s, 12H, 3H, 3H, HTp′C*H*$_3$), −15.05 (s, 2H, $^1J_{\mathrm{Pt-H}} = 986$ Hz, Pt-*H*).

(17) ^{1}H NMR data for complex **6** (CD_2Cl_2, 253K, δ): 9.45 (s, 1H, pz*N*H*), 7.41−7.29 (m, 10H, Si-*Ph*), 6.22 (s, 2H, HTp′C*H*), 5.49 (s, 1H, HTp′C*H*), 4.88 (s, 1H, $^1J_{\mathrm{Si-H}} = 215$ Hz,$^2J_{\mathrm{Pt-H}} = 25$ Hz, Si-*H*), 2.46, 2.37, 2.09, 1.27 (s, 6H, 6H, 3H, 3H, HTp′C*H*$_3$), −15.35 (s, 2H, $^1J_{\mathrm{Pt-H}} = 985$ Hz, Pt-*H*).

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