Tp′PtH$_3$: A Stable Platinum(IV) Trihydride

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*Summary: Tp′PtMe$_2$H (**1**) reacts with Et$_3$Si−H to form Tp′Pt(SiEt$_3$)(H)$_2$ (**2**), which serves as a precursor to Tp′PtH$_3$ (**3**). Cleavage of the Pt−SiEt$_3$ bond of **2** with methanol provides a clean route to Tp′PtH$_3$ (**3**), a rare N-supported monomeric platinum(IV) trihydride complex.*

Introduction

Transition metal hydride complexes display fascinating structural and spectroscopic features,[1−3] and they are important in homogeneous hydrogenations.[4] While high oxidation state transition metal polyhydrides of the general formula $L_mM(H)_n$ ($n \geq 3$) are known for group V to group IX metals, platinum(IV) hydride monomers have been restricted to monohydride and dihydride derivatives,[5] with the exception of [(triphos)PtH$_3$]$^+$.[6]

Trispyrazolylborate ligands[7] anchor the octahedral coordination sphere of stable palladium(IV)[8] and platinum(IV)[8a,9] complexes. The chemistry of TpPt(R)(R′)H [Tp = hydridotris(pyrazolyl)borate;[5a,9a,b] Tp′ = hydridotris(3,5-dimethylpyrazolyl)borate;[9c−e] R, R′ = combinations of alkyl, hydride, and aryl groups] has been particularly extensively studied, but surprisingly the parent trihydride, Tp′PtH$_3$, is unknown.[10] During our exploration of platinum(II)/platinum(IV) interconversions in bond activation processes, the thermolysis of Tp′PtMe$_2$H (**1**)[9c] in benzene was investigated. Reductive elimination of methane from **1** with subsequent C−H activation of the solvent was observed, ultimately leading to Tp′PtPh$_2$H.[11] Other recent results showed that iron silyl complexes[12] react with methanol to form the corresponding hydride species.[13] We report in this note the sequential application of these reaction strategies to first form Tp′Pt(SiEt$_3$)(H)$_2$ (**2**) via a Si−H bond activation route and then subsequent reaction of **2** with methanol to yield Tp′PtH$_3$ (**3**).

Results and Discussion

Thermolysis of the dimethylhydride **1** in refluxing Et$_3$SiH for 7 h, removal of volatiles, and chromatography of the resulting brown residue on alumina results in the formation of the silyldihydride **2** as an off-white, air-stable powder in 24% yield (Scheme 1).

The solid-state IR spectrum of Tp′Pt(SiEt$_3$)(H)$_2$ (**2**) (KBr) shows an absorption at 2524 cm^{-1} for the B−H stretch of the Tp′ ligand, indicative of a κ^3 coordination mode.[14] A broad absorption at 2262 cm^{-1} is seen for the Pt−H stretches.[15] The ^{1}H NMR spectrum of **2** displays a 2:1 pattern for the resonances of the Tp′ ligand, indicative of mirror symmetry, and the hydrides resonate at −20.15 ppm (^1J(Pt,H) = 1178 Hz). The spectral features of **2** are reminiscent of the data reported recently for TpPtH$_2$Me.[5a]

To support the spectroscopic evidence, single crystals of the silyldihydride **2**, obtained by slow evaporation of a methylene chloride solution, were subjected to X-ray structural analysis; an ORTEP diagram is shown in Figure 1. The hydride ligands on platinum could not be located in the difference Fourier map and were placed in calculated positions. Reflecting the strong trans

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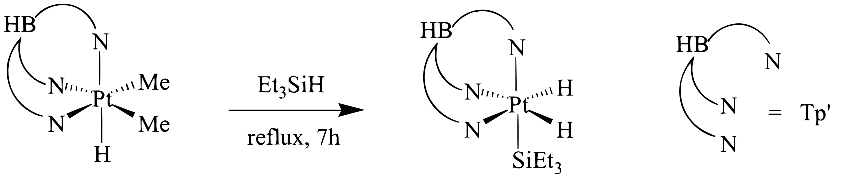
Scheme 1. Synthesis of Tp′Pt(SiEt$_3$)(H)$_2$, 2



1 2

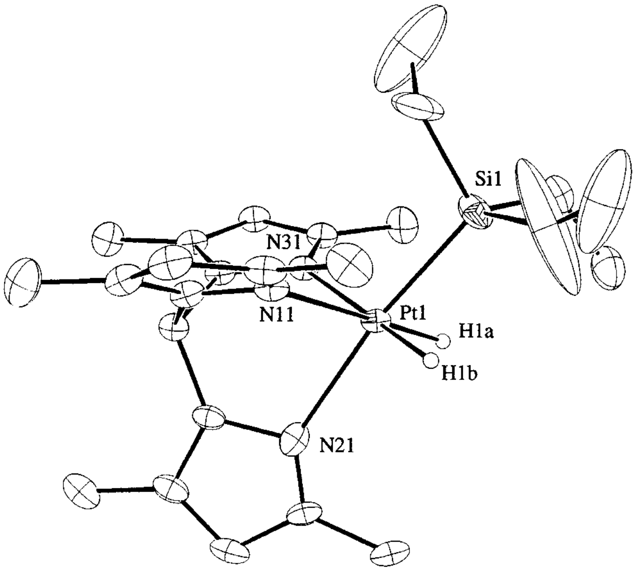


Figure 1. ORTEP diagram of Tp′Pt(SiEt$_3$)(H)$_2$, **2**; ellipsoids are drawn with 50% probability. Selected bond distances (Å) and angles (deg): Pt1−Si1 2.325(3), Pt1−N11 2.169(3), Pt1−N21 2.299(10), Pt1−N31 2.161(3); Si1−Pt1−N11 100.54(11), Si1−Pt1−N21 171.15(18), Si1−Pt1−N31 103.16(11), N11−Pt1−N21 81.82(25), N11−Pt1−N31 89.77(11), N21−Pt1−N31 85.32(18).

influence of the silyl group, the Pt−N distance trans to the silyl ligand of 2.299(10) Å is significantly longer (0.13 Å) than the Pt−N distances of 2.169(3) and 2.161(3) Å trans to the hydride ligands. The Pt−Si bond length of 2.325(3) Å is similar to those in other late transition metal silyl complexes.[16] The fact that both Si−Pt−N$_{cis}$ angles are larger than 100° reflects the steric bulk of both the Tp′ and the triethylsilyl ligand.

Scheme 2 outlines a possible route for the formation of the silyldihydride **2** from the dimethylhydride **1**. In analogy with the thermolysis of Tp′PtMe$_2$H (**1**) in benzene, we propose that reductive elimination of methane from **1** followed by Si−H activation of the triethylsilane solvent leads to the formation of Tp′PtMe(SiEt$_3$)H (**4**). We believe that the silyldihydride **2** is produced by irreversible reductive elimination of MeSiEt$_3$[17] from the unsymmetrical intermediate **4** and subsequent activation of Et$_3$Si−H. By analogy with results in benzene, where conversion to Tp′PtPh$_2$H is observed, methane elimination from the methylsilylhydride **4** and activation of Et$_3$Si−H would be expected to produce Tp′Pt(SiEt$_3$)$_2$H (**5**), but we see no evidence for the formation of **5** during thermolysis. In a related study, Aizenberg and Milstein observed both C−H and C−Si reductive elimination from *fac*-(PMe$_3$)$_3$Ir(Me)(SiR$_3$)H, a d^6 monomer analogous to the proposed intermediate **4** in Scheme 2. For R = Et, the ratio of Me−H to Me−SiEt$_3$ elimination reactions was 80:20 in the Ir system.[18]

Attempts to prepare [Tp′PtH$_2$]$^-$, a precursor to Tp′PtH$_3$, via reaction of hydride reagents with platinum(II) halide complexes were unsuccessful. Access to Tp′Pt(SiEt$_3$)(H)$_2$ (**2**) provided a possible alternative route to the desired trihydride product (Scheme 3).

Heating **2** in a mixture of methanol and CH$_2$Cl$_2$ (ca. 10:1) produced Tp′PtH$_3$ (**3**) as a white, air-stable powder after removal of all volatiles, washing with pentane, and chromatography of the resulting brown residue. The solid-state IR spectrum of the trihydride complex **3** (KBr) shows an absorption at 2524 cm^{-1} for the B−H stretch and an absorption at 2247 cm^{-1} for the Pt−H stretches. As in the case of the silyldihydride **2**, the three hydride ligands in **3** do not show strong vibrational coupling. The simple ^{1}H NMR spectrum of **3** consists of only four resonances and reflects C_{3v} symmetry: a total of three singlets are seen for the Tp′ ligand and the hydride ligands resonate at −20.03 ppm (^1J(Pt,H) = 1169 Hz).

Several observations support the assertion that **3** is a classical trihydride. The T_1 of the hydride resonance in **3** at 20 °C is 1.25 s,[19] while hydrogen complexes typically show values in the millisecond range.[2a,10c,20] We were able to synthesize Tp′Pt(H)$_2$D (**3-*d*$_1$**) by thermolysis of **2** in a mixture of CH$_3$OD and CH$_2$Cl$_2$. The solid-state IR spectrum of **3-*d*$_1$** (KBr) shows an absorption at 1618 cm^{-1} for the Pt−D stretch in addition to the absorption at 2250 cm^{-1} for the Pt−H stretches. The ^{1}H NMR spectrum displays hydride resonances at −20.00 ppm for **3-*d*$_1$** (80%) and at −20.03 ppm for **3** (20%). The Tp′Pt(H)$_2$D resonance at −20.00 ppm does not show any measurable ^2J(H,D) coupling; large H−D coupling and a large chemical shift difference would be expected if a dihydrogen ligand were present in the ground-state structure.[2a,20]

Conclusion

In summary, we have successfully isolated and characterized the parent trihydride complex Tp′PtH$_3$ (**3**), along with the precursor complex Tp′Pt(SiEt$_3$)(H)$_2$ (**2**). The efficient cleavage of the metal−silyl bond of **2** by methanol to generate the trihydride **3** is a potentially

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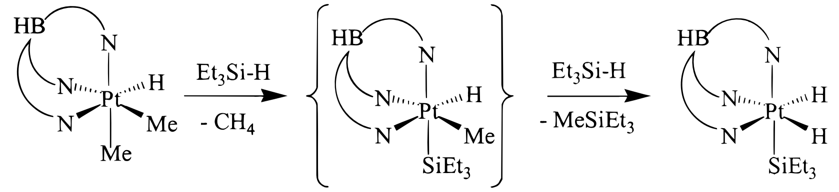
[17] MeSiEt$_3$ was detected in the reaction mixture by GC/MS: *m*/*z* = 130 [M$^+$], 115 [M$^+$ − Me], 101 [M$^+$ − Et], 73 [EtSiH$_2^+$].

[18] Aizenberg, M.; Milstein, D. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 317−319.

[19] The T_1 of the hydride resonance in Tp′PtMe$_2$H (**1**) at 20 °C is 2.00 s.

[20] The 0.03 ppm downfield shift of the hydride resonance of Tp′PtH$_2$D upon deuterium incorporation is a reasonable value, see for example: Heinekey, D. M.; Hinkle, A. S.; Close, J. D. *J. Am. Chem. Soc.* **1996**, *118*, 5353−5361.

Scheme 2. Proposed Pathway for the Formation of Tp′Pt(SiEt$_3$)(H)$_2$, 2, from Tp′PtMe$_2$H, 1

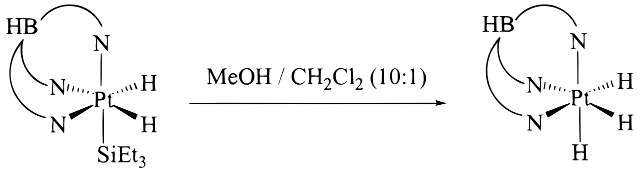


1

4

2

Scheme 3. Methanol Promoted Formation of Tp′PtH$_3$, 3, from Tp′Pt(SiEt$_3$)(H)$_2$, 2



2

3

general and useful procedure for preparing elusive late transition metal hydride complexes.

Experimental Section

All operations were carried out under a nitrogen atmosphere. All solvents used were degassed and purified following standard methods.

Tp′Pt(SiEt$_3$)(H)$_2$, 2. Tp′PtMe$_2$H, **1** (0.25 g, 4.8×10^{-4} mol), was dissolved in Et$_3$SiH (20 mL). The solution was heated at reflux for 7 h. The solvent was removed, and the remaining brown oil was triturated with pentane twice and chromatographed on alumina using pentane as eluent. After pentane removal, the off-white powder was washed with cold methanol and dried in vacuo, resulting in 70 mg (24%) of **2**. Crystals for the X-ray structure analysis were obtained by slow evaporation of CD$_2$Cl$_2$ from a concentrated NMR sample. Spectroscopic data for **2**: IR (KBr) $\tilde{\nu}$ 2524 cm^{-1} (Tp′B−H), 2262 cm^{-1} (Pt−H); ^{1}H NMR (400 MHz, CD$_2$Cl$_2$, 20 °C) δ 5.87, 5.72 (s, 2H, 1H; Tp′C−H), 2.42, 2.29, 2.25, 2.13 (s, 6H, 3H, 6H, 3H; Tp′−CH$_3$), 0.86 (s, 15H; Si−Et$_3$), −20.15 (s, ^1J(Pt,H) = 1178 Hz, 2H; Pt−H); ^{13}C{^{1}H} NMR (100 MHz, CD$_2$Cl$_2$, 20 °C) δ 150.7 (J(Pt,C) = 33.9 Hz, 2C; Tp′*C*-CH$_3$), 148.6 (J(Pt,C) = 15.5 Hz, 1C; Tp′*C*−CH$_3$), 145.5, 144.1 (2C, 1C; Tp′*C*−CH$_3$), 106.4 (^3J(Pt,C) = 12.6 Hz, 2C; Tp′*C*H), 104.7 (1C; Tp′*C*H), 16.5 (J(Pt,C) = 19.4 Hz, 2C; Tp′C-*C*H$_3$), 15.0 (J(Pt,C) = 23.3 Hz, 1C; Tp′C-*C*H$_3$), 13.2, 12.3 (2C, 1C; Tp′C-*C*H$_3$), 10.6 (^2J(Pt,C) = 60.1 Hz, 3C; Si*C*H$_2$-CH$_3$), 9.4 (^3J(Pt,C) = 30.0 Hz, 3C; SiCH$_2$*C*H$_3$). Anal. Calcd: H, 6.45; C, 41.38; N, 13.79. Found: H, 6.37; C, 41.20; N, 13.51.

Structural Data for 2: crystals from CD$_2$Cl$_2$; C$_{21}$H$_{39}$N$_6$BSiPt, M = 609.56; triclinic, space group $P1$; Z = 1; a = 8.0057(3), b = 8.0889(3), c = 11.6851(4) Å; α = 70.290(1)°, β = 77.417(1)°, γ = 62.642(1)°; U = 630.90(4) Å^3; D_c = 1.604 Mg m^{-3}; T = −100 °C; max 2θ: 65°; Mo Kα radiation (λ = 0.71073 Å); 10 077 unique reflections were obtained and 9581 of these with $I > 2.5\sigma(I)$ were used in the refinement; data were collected on a Bruker SMART diffractometer using the Ω scan method. For significant reflections merging R-value: 0.018. Residuals: R_F 0.026; R_w 0.028 (significant reflections); GoF 0.9001. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-140671. Copies of these data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax no.: +44-1223-336-033; e-mail: deposite@ccdc.cam.ac.uk).

Tp′PtH$_3$, 3. Tp′Pt(SiEt$_3$)(H)$_2$, **2** (0.13 g, 2.1×10^{-4} mol), was dissolved in a mixture of methanol/CH$_2$Cl$_2$ (ca. 10:1) and heated at reflux for 14 h. Following solvent removal, the brown residue was washed with pentane and chromatographed on alumina using CH$_2$Cl$_2$ as eluent. After CH$_2$Cl$_2$ removal, the white powder obtained was washed with cold pentane and dried in vacuo to give 58 mg (56%) of **3**. Spectroscopic data for **3**: IR (KBr) $\tilde{\nu}$ 2524 cm^{-1} (Tp′B−H), 2247 cm^{-1} (Pt−H); ^{1}H NMR (400 MHz, CD$_2$Cl$_2$, 20 °C) δ 5.85 (s, ^4J(Pt,H) = 7.8 Hz, 3H; Tp′C−H), 2.38, 2.12 (s, 9H each; Tp′-CH$_3$), −20.03 (s, ^1J(Pt,C) = 1169 Hz, 3H; Pt−H); ^{13}C{^{1}H} NMR (100 MHz, CD$_2$Cl$_2$, 20 °C) δ 149.9 (J(Pt,C) = 25.2 Hz, 3C; Tp′*C*−CH$_3$), 145.0 (3C; Tp′*C*−CH$_3$), 105.3 (^3J(Pt,C) = 9.7 Hz, 3C; Tp′*C*H), 15.8 (J(Pt,C) = 29.1 Hz, 3C; Tp′C-*C*H$_3$), 12.6 (3C; Tp′C−*C*H$_3$); MS (70 eV): m/z (%): 493 (100) [M$^+$ − H$_2$], the complex isotopic pattern matches the simulated pattern for C$_{15}$H$_{23}$N$_6$BPt. Anal. Calcd: H, 5.09; C, 36.38; N, 16.97. Found: H, 5.04; C, 36.10; N, 16.70.

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Supporting Information Available: Complete crystallographic data for **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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