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Solid-State Structure of Tp′PtMe$_2$H, a Dimethylhydrido Platinum(IV) Complex

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Abstract: The solid-state X-ray structure of Tp′PtMe$_2$H has been determined. This platinum(IV) hydride derivative is stable at room temperature and crystallizes in an orthorhombic cell (space group P_{cmn}, $Z = 4$, $a = 8.1292(8)$ Å, $b = 13.3862(9)$ Å, and $c = 17.9670(16)$ Å). The hydride ligand was not located. The complex was synthesized as one of a series of organometallic platinum(IV) derivatives with Tp′ (Tp′ = hydridotris(3,5-dimethylpyrazolyl)borate) in the coordination sphere. These octahedral platinum(IV) Tp′PtMe$_2$X and Tp′PtPh$_2$X complexes were prepared by formal oxidation of platinum(II) intermediates ([K][Tp′PtMe$_2$] and [K][Tp′PtPh$_2$]) with electrophiles (HX, MeI, I$_2$). Thermogravimetric analysis (TGA) was employed to determine the solid-state decomposition temperatures for these platinum(IV) organometallic complexes.

Introduction

Three separate research groups published papers reporting platinum(IV) alkylhydrido complexes during 1995.[1−3] All three laboratories utilized NMR spectra to characterize the hydride complexes prior to reductive elimination, which occurred at or below room temperature in each case. Protonation of platinum(II) alkyl precursors was the synthetic route in each instance. The formation of platinum(IV) and palladium(IV) species as a result of electrophilic attack on d^8 monomers has recently been summarized in an article by Canty and van Koten.[4]

Also reported in 1995, by Canty and co-workers, was the use of the tris(pyrazolyl)borate (Tp) ligand to stabilize a series of organo palladium(IV) complexes.[5] The solid-state X-ray structure of an octahedral hydroxodimethyl platinum(IV) complex containing the Tp ligand has also been reported.[6]

With this flurry of activity as a backdrop, we report here the synthesis and solid-state X-ray structure of Tp′PtMe$_2$H. This complex is one of a series of platinum(IV) alkyl and aryl complexes that we have synthesized in an effort to develop a general route to polypyrazolylborate complexes of platinum(IV).

Experimental Section

Materials and Methods. All reactions were performed under purified nitrogen using standard Schlenk techniques. Tetrahydrofuran (THF) and hexanes were distilled from sodium benzophenone ketyl; methylene chloride was distilled from phosphorus pentoxide; acetonitrile was distilled from calcium hydride; and toluene was distilled from sodium. NMR solvents were degassed and stored over 4 Å molecular sieves prior to use. KTp′ (KTp′ = potassium hydridotris(3,5-dimethylpyrazolyl)borate),[7] PtCl$_2$(SMe$_2$)$_2$,[8] [Pt(CH$_3$)$_2$(SMe$_2$)]$_2$[9] (**1**), and Pt(C$_6$H$_5$)$_2$(SMe$_2$)$_2$[10] (**2**) were prepared by literature methods. All other reagents were purchased and used without purification.

^{1}H and ^{13}C NMR spectra were recorded on a Varian XL 400 (400 MHz) or a Bruker WM 250 (250 MHz) spectrometer. Thermogravimetric analyses (TGA) were performed on a Seiko RTG 220. All elemental analyses were performed by Atlantic Microlab of Norcross, GA.

[K][Tp′PtPh$_2$]. An NMR tube was charged with 0.019 g (0.040 mmol) of PtPh$_2$(SMe$_2$)$_2$ and 0.021 g (0.062 mmol) of KTp′. Acetone-d_6 was added and the reaction was monitored by ^{1}H NMR. After 1 h the PtPh$_2$(SMe$_2$)$_2$ signals were gone, and signals compatible with [K][Tp′PtPh$_2$] and KTp′ were the only Tp′ containing species observed. After 15 h, 25 μL (0.92 mmol) of methyl iodide was added and an ^{1}H NMR was quickly taken. The intermediate, presumably [K][Tp′PtPh$_2$], had disappeared; Tp′PtPh$_2$Me and KTp′ were the only identifiable species present. [K][Tp′PtPh$_2$]: ^{1}H NMR (acetone-d_6, δ) 7.46 (m, 4H, $^3J_{\mathrm{Pt-H}} = 68.0$ Hz, H$_o$) , 6.54 (m, 4H, H$_m$), 6.39 (m, 2H, H$_p$), 5.73 (s, 1H, Tp′C*H*), 5.61 (s, 2H, Tp′C*H*), 2.33, 2.16, 1.72, 1.67 (s, 6H, 3H, 3H, 6H, Tp′CC*H*$_3$).

Tp′PtPh$_2$Me. To a THF (5 mL) slurry of 0.129 g (0.329 mmol) of cis and trans PtCl$_2$(SMe$_2$)$_2$ at 0 °C was added 0.55 mL of 1.8 M (0.99 mmol, 3.0 equiv) phenyllithium in cyclohexane−ether. The reaction mixture was warmed to room temperature and stirred for 5 h. A drop of water was added to quench excess phenyllithium, and then the solvent was removed under vacuum. To the solid PtPh$_2$(SMe$_2$)$_2$, were added 0.112 g (0.333 mmol) of KTp′ and 5 mL of THF. The reaction mixture was stirred at room temperature for 15 h to give a brown heterogeneous reaction mixture. To this heterogeneous THF solution was added 0.10 mL (1.6 mmol, 7.9 equiv) of methyl iodide, and the mixture was stirred at room temperature for 15 min to give a brown solution with a dark precipitate. The solvent was removed *in vacuo* to give a brown solid. The solid was extracted three times with 10 mL of toluene to extract the product. The toluene extracts were combined, and the solvent was removed via rotary evaporation to give a gray-brown solid. The solid was triturated with acetonitrile to give 0.128 g (59% yield) of tan Tp′PtPh$_2$Me. ^{1}H NMR (CDCl$_3$, −28 °C, δ): 7.75 (d, 2H, $^3J_{\mathrm{Pt-H}} = 43.2$ Hz, $^3J_{\mathrm{H-H}} = 8.0$ Hz , H$_o$), 7.17 (m, 2H, $^4J_{\mathrm{Pt-H}} = 12.0$ Hz, H$_m$), 6.91 (m, 2H, H$_p$), 6.64 (m, 2H, H$_m$′), 6.56 (d, 2H, $^3J_{\mathrm{Pt-H}} = 44.8$ Hz, $^3J_{\mathrm{H-H}} = 8.4$ Hz, H$_o$′), 5.79 (s, 1H, $^4J_{\mathrm{Pt-H}} = 5.6$ Hz, Tp′C*H*), 5.70 (s, 2H,$^4J_{\mathrm{Pt-H}} = 4.8$ Hz, Tp′C*H*), 2.48 2.42, 1.37, 1.02 (s, 3H, 6H, 6H, 3H, Tp′C*H*$_3$), 1.75 (s, 3H, $^2J_{\mathrm{Pt-H}} = 70.4$ Hz, PtC*H*$_3$). ^{13}C NMR (CDCl$_3$, 20 ° C, δ): 150.1 (s, 2C, $^2J_{\mathrm{Pt-C}} = 20$ Hz, Tp′*C*CH$_3$), 149.3 (s, 1C,

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$^{2}J_{\mathrm{Pt-C}} = 10$ Hz, Tp′*C*CH$_3$), 143.3 (s, 2C, Tp′*C*CH$_3$), 143.1 (s, 1C, $^{3}J_{\mathrm{Pt-C}} = 10$ Hz, Tp′*C*CH$_3$), 138.0 (broad, 2C, C$_m$), 132.7 (broad, 2C, $^{2}J_{\mathrm{Pt-C}} = 40$ Hz, C$_o$), 126.7 (s, 2C, $^{2}J_{\mathrm{Pt-C}} = 20$ Hz, C$_o$′), 126.4 (s, 2C, C$_p$), 125.8 (s, 2C, $^{1}J_{\mathrm{Pt-C}} = 890$ Hz, C$_{ipso}$), 123.4 (s, 2C, $^{3}J_{\mathrm{Pt-C}} = 10$ Hz, C$_m$′), 107.8 (s, 2C, $^{3}J_{\mathrm{Pt-C}} = 10$ Hz, Tp′*C*H), 107.3 (s, 1C, $^{3}J_{\mathrm{Pt-C}} = 10$ Hz, Tp′ *C*H), 14.5 (s, 1C, $^{3}J_{\mathrm{Pt-C}} = 6$ Hz, Tp′*C*H$_3$), 12.9 (s, 4C, Tp′*C*H$_3$), 12.5 (s, 1C, Tp′*C*H$_3$), −2.9 (s, 1C, $^{1}J_{\mathrm{Pt-C}} = 660$ Hz, $^{1}\mathrm{J}_{\mathrm{C-H}} = 133$ Hz, Pt*C*H$_3$). Anal. Calcd for $C_{28}H_{35}BN_6Pt$: C, 50.84; H, 5.33; N, 12.70. Found: C, 50.94; H, 5.38; N, 12.61.

Tp′PtPh$_2$I. To a THF (5 mL) slurry of 0.222 g (0.569 mmol) of cis and trans PtCl$_2$(SMe$_2$)$_2$ at 0 °C was added 1.3 mL of 1.8 M (2.3 mmol, 4.1 equiv) phenyllithium in cyclohexane−ether. The reaction mixture was warmed to room temperature and stirred for 4 h. A drop of water was added to quench excess phenyllithium, and then the solvent was removed under vacuum. To the solid PtPh$_2$(SMe$_2$)$_2$ were added 0.191 g (0.569 mmol) of KTp′ and 5 mL of THF. The reaction mixture was stirred at room temperature for 15 h to give a brown heterogeneous reaction mixture. Under positive nitrogen pressure 0.148 g (0.584 mmol) of elemental iodine was added. The reaction mixture immediately turned orange-brown. It was then stirred at room temperature for 1 h. The solvent was removed under vacuum, and the resulting solid was extracted three times with 5 mL of toluene. The extracts were combined. The solvent volume was reduced to 5 mL, and 15 mL of acetonitrile was added. After storing the solution at −30 °C for 1 week, 0.190 g (51% yield) of yellow crystals of Tp′PtPh$_2$I had formed. ^{1}H NMR (CDCl$_3$, δ): 8.49 (d, 2H, $^{3}J_{\mathrm{Pt-H}} = 39.6$ Hz, $^{3}J_{\mathrm{H-H}} = 7.6$ Hz, H$_o$), 7.07 (m, 2H, $^{4}J_{\mathrm{Pt-H}} = 8.0$ Hz, H$_m$), 6.91 (m, 2H, H$_p$), 6.60 (m, 2H, H$_m$′), 6.10 (d, 2H, $^{3}J_{\mathrm{Pt-H}} = 36.8$ Hz, $^{3}J_{\mathrm{H-H}} = 8.4$ Hz, H$_o$′), 5.76 (s, 2H, Tp′C*H*), 5.74 (s, 1H, $^{4}J_{\mathrm{Pt-H}} = 15.2$ Hz, Tp′C*H*), 2.48, 2.45, 1.70, 0.82 (s, 3H, 6H, 6H, 3H, Tp′C*H*$_3$). ^{13}C NMR (CDCl$_3$, δ): 152.7 (s, 2C, $^{2}J_{\mathrm{Pt-C}} = 20$ Hz, Tp′*C*CH$_3$), 149.1 (s, 1C, $^{2}J_{\mathrm{Pt-C}} = 40$ Hz, Tp′*C*CH$_3$), 143.8 (s, 2C, Tp′*C*CH$_3$), 143.5 (s, 1C, $^{3}J_{\mathrm{Pt-C}} = 20$ Hz, Tp′*C*CH$_3$), 139.0 (s, 2C, $^{2}J_{\mathrm{Pt-C}} = 30$ Hz, C$_o$), 137.2 (s, 2C, $^{3}J_{\mathrm{Pt-C}} = 10$ Hz, C$_m$), 126.8 (s, 2C, $^{2}J_{\mathrm{Pt-C}} = 40$ Hz, C$_o$′), 126.6 (s, 2C, $^{3}J_{\mathrm{Pt-C}} = 30$ Hz, C$_m$′), 124.6 (s, 2C, $^{4}J_{\mathrm{Pt-C}} = 10$ Hz, C$_p$), 120.5 (s, 2C, $^{1}J_{\mathrm{Pt-C}} = 740$ Hz, C$_{ipso}$),108.6 (s, 1C, $^{3}J_{\mathrm{Pt-C}} = 20$ Hz, Tp′*C*H), 108.4 (s, 2C, $^{3}J_{\mathrm{Pt-C}} = 30$ Hz, Tp′*C*H), 15.8 (s, 2C, Tp′*C*H$_3$), 14.4 (s, 1C, $^{3}J_{\mathrm{Pt-C}} = 11$ Hz, Tp′*C*H$_3$), 13.2 (s, 1C, Tp′*C*H$_3$), 12.8 (s, 2C, Tp′*C*H$_3$). Anal. Calcd for $C_{27}H_{32}BIN_6Pt\cdot CH_3CN$: C, 42.76; H, 4.33; N, 12.03. Found: C, 42.93; H, 4.30; N, 11.74.

Tp′PtPh$_2$H. To a THF (5 mL) slurry of 0.167 g (0.428 mmol) of cis and trans PtCl$_2$(SMe$_2$)$_2$ at 0 °C was added 0.95 mL of 1.8 M (1.7 mmol, 4.0 equiv) phenyllithium in cyclohexane−ether. The reaction mixture was warmed to room temperature and stirred for 12 h. A drop of water was added to quench excess phenyllithium, and solvent was removed under vacuum to give a brown solid. To the solid PtPh$_2$(SMe$_2$)$_2$ were added 0.145 g (0.432 mmol) of KTp′ and 5 mL of THF. The reaction mixture was stirred at room temperature for 36 h to give a brown heterogeneous reaction mixture. To the reaction mixture was added 0.43 mL of 1.0 M (0.43 mmol) of anhydrous HCl in diethyl ether. The reaction was stirred for 1 h, and then the solvent was removed *in vacuo* to give a brown solid. To isolate the product the solid was extracted three times with 5 mL of toluene. The extracts were combined and the solvent was removed via rotary evaporation. The residual solid was briefly triturated with acetonitrile to give 0.073 g (26% yield) of white Tp′PtPh$_2$H. ^{1}H NMR (CDCl$_3$, −47 °C, δ): 8.09 (d, 2H, $^{3}J_{\mathrm{Pt-H}} = 58.8$ Hz, $^{3}J_{\mathrm{H-H}} = 8.0$ Hz, H$_o$), 7.09 (m, 2H, $^{4}J_{\mathrm{Pt-H}} = 10.4$ Hz, H$_m$), 6.93 (m, 2H, H$_p$), 6.71 (m, 4H, H$_m$′, H$_o$′), 5.90 (s, 1H, Tp′C*H*), 5.69 (s, 2H, $^{4}J_{\mathrm{Pt-H}} = 6.4$ Hz Tp′C*H*), 2.51, 2.39, 1.43, 1.39 (s, 3H, 6H, 3H, 6H, Tp′C*H*$_3$), −18.94 (s, 1H, $^{1}J_{\mathrm{Pt-H}} = 1360$ Hz, Pt-*H*). ^{13}C NMR (CDCl$_3$, −47 °C, δ): 149.7 (s, 2C, $^{2}J_{\mathrm{Pt-C}} = 30$ Hz, Tp′*C*CH$_3$), 149.3 (s, 1C, $^{2}J_{\mathrm{Pt-C}} = 20$ Hz, Tp′*C*CH$_3$), 143.5 (s, 2C, Tp′*C*CH$_3$), 143.3 (s, 1C, Tp′*C*CH$_3$), 139.2 (s, 2C, $^{2}J_{\mathrm{Pt-C}} = 70$ Hz, C$_o$), 136.8 (s 2C, $^{3}J_{\mathrm{Pt-C}} = 20$ Hz, C$_m$), 126.7 (s, 2C, $^{2}J_{\mathrm{Pt-C}} = 60$ Hz, C$_o$′), 126.5 (s, 2C, $^{3}J_{\mathrm{Pt-C}} = 40$ Hz, C$_m$′), 123.9 (s, 2C, $^{1}J_{\mathrm{Pt-C}} = 840$ Hz, C$_{ipso}$), 123.0 (s, 2C, $^{4}J_{\mathrm{Pt-C}} = 10$ Hz, C$_p$), 106.9 (s, 1C, $^{3}J_{\mathrm{Pt-C}} = 10$ Hz, Tp′*C*H), 106.1 (s, 2C, $^{3}J_{\mathrm{Pt-C}} = 20$ Hz, Tp′ *C*H), 14.9 (s, 1C, Tp′*C*H$_3$), 14.0 (s, 2C, $^{3}J_{\mathrm{Pt-C}} = 17$ Hz, Tp′*C*H$_3$), 12.9 (s, 3C, Tp′*C*H$_3$). Anal. Calcd for $C_{27}H_{33}BN_6Pt$: C, 50.08; H, 5.14; N, 12.98. Found: C, 50.11; H, 5.15; N, 13.05.

Tp′PtMe$_3$. To a THF (5 mL) slurry of 0.079 g (0.203 mmol) of cis and trans PtCl$_2$(SMe$_2$)$_2$ at 0 °C was added 0.33 mL of 1.4 M (0.46 mmol, 2.3 equiv) methyllithium in diethyl ether. The reaction mixture was stirred at 0 °C for 2 h. While still at 0 °C, a drop of water was added to quench excess methyllithium. The reaction mixture was warmed to room temperature, and solvent was removed *in vacuo*. The solid was dried under vacuum for 6 h. To the solid [PtMe$_2$(SMe$_2$)]$_2$ were added 0.068 g (0.203 mmol) of KTp′ and 5 mL of THF. The reaction mixture was stirred at room temperature for 15 h to give a brown reaction mixture. To this heterogeneous THF solution was added 0.10 mL (1.6 mmol, 7.9 equiv) of methyl iodide, and the mixture was stirred at room temperature for 1 h at which time a gray precipitate in a lightly colored solution had formed. The solvent was removed under vacuum to give a brown solid. The solid was extracted three times with 5 mL of toluene. The extracts were combined, and the solvent was removed via rotary evaporation. The resulting tan solid was triturated with 10 mL of acetonitrile to give 0.0310 g (28% yield) of white Tp′PtMe$_3$. NMR, IR, and analytical data for Tp′PtMe$_3$ have previously been reported.[11]

Tp′PtMe$_2$H. To a THF (5 mL) slurry of 0.181 g (0.463 mmol) of cis and trans PtCl$_2$(SMe$_2$)$_2$ at 0 °C was added 0.75 mL of 1.4 M (1.1 mmol, 2.3 equiv) methyllithium in diethyl ether. The reaction mixture was stirred at 0 °C for 1.5 h. While still at 0 °C, a drop of water was added to quench excess methyllithium. The reaction mixture was warmed to room temperature and solvent was removed *in vacuo*. To the solid [PtMe$_2$(SMe$_2$)]$_2$ were added 0.155 g (0.462 mmol) of KTp′ and 5 mL of THF. The reaction mixture was stirred at room temperature for 36 h to give a brown heterogeneous reaction mixture. To the reaction mixture was added 0.50 mL of 1.0 M (0.50 mmol) anhydrous HCl in diethyl ether. The reaction was stirred at room temperature for 1 h to give a lightly colored solution with a brown precipitate. The solvent was removed *in vacuo*, and the resulting brown residue was extracted two times with 5 mL of toluene. The extracts were combined and the solvent was removed via rotary evaporation. The gray solid was triturated with 5 mL of acetonitrile at 0 °C. The resulting light gray solid was dissolved in methylene chloride and filtered through a Celite column. Removal of the solvent gave 0.107 g (44% yield) of white Tp′PtMe$_2$H. Recrystallization from methylene chloride and hexanes at room temperature provided crystals for X-ray analysis. ^{1}H NMR (CDCl$_3$, δ): 5.72 (s, 1H, Tp′C*H*), 5.71 (s, 2H, $^{4}J_{\mathrm{Pt-H}} = 8.0$ Hz, Tp′C*H*), 2.34, 2.29, 2.27, 2.18 (s, 3H, 6H, 3H, 6H, Tp′C*H*$_3$), 1.19 (s, 6H, $^{2}J_{\mathrm{Pt-H}} = 67.5$ Hz, Pt(C*H*$_3$)$_2$), −20.95 (s, 1H, $^{1}J_{\mathrm{Pt-H}} = 1358$ Hz, Pt−H). ^{13}C NMR (CDCl$_3$, δ): 149.7 (s, 1C, $^{2}J_{\mathrm{Pt-C}} = 20$ Hz, Tp′*C*CH$_3$), 149.0 (s, 2C, $^{2}J_{\mathrm{Pt-C}} = 20$ Hz, Tp′*C*CH$_3$), 143.5 (s, 2C, Tp′*C*CH$_3$), 143.3 (s, 1C, Tp′*C*CH$_3$), 107.3 (s, 1C, $^{3}J_{\mathrm{Pt-C}} = 10$ Hz, Tp*C*H), 106.0 (s, 2C, $^{3}J_{\mathrm{Pt-C}} = 10$ Hz, Tp*C*H), 14.4 (s, 1C, $^{3}J_{\mathrm{Pt-C}} = 10$ Hz, Tp′*C*H$_3$), 12.8 (s, 1C, Tp′*C*H$_3$), 12.7 (s, 4C, Tp′*C*H$_3$), −21.6 (s, 2C, $^{1}J_{\mathrm{Pt-C}} = 624$ Hz, $^{1}\mathrm{J}_{\mathrm{C-H}} = 130$ Hz, $^{2}\mathrm{J}_{\mathrm{H-C}} = 4$ Hz, Pt(*C*H$_3$)$_2$). Anal. Calcd for $C_{17}H_{29}BN_6Pt$: C, 39.01; H, 5.59; N, 16.06. Found: C, 38.92; H, 5.61; N, 15.78.

X-ray Structure of Tp′**PtMe$_2$H (4b).** Crystals of Tp′PtMe$_2$H were grown from methylene chloride/hexanes. The crystal was orthorhombic (P_{cmn} space group). The cell dimensions were $a = 8.1292(8)$ Å, $b = 13.3862(9)$ Å, and $c = 17.9670(16)$ Å. The cell volume was 1955.2(3) Å^3 , $Z = 4$ molecules per unit cell, $D_{\mathrm{calc}} = 1.778$ g/cm^3, λ (Mo Kα) = 0.71073 Å, $\mu = 7.26$ mm^{-1}, and $F(000) = 1016.68$. The X-ray data were collected on a Rigaku diffractometer using the ω scan mode. Experimental details are given in Table 1. Of the 5399 unique reflections, 1549 reflections possessed $I > 2.5\sigma(I)$, and these were used in the structure determination. Final agreement indices were $R = 2.7\%$ and $R_w = 3.3\%$, with hydrogen placed in computed positions 0.96 Å from the bonded atom and included in the refinement using a riding model. All other atoms were refined anisotropically. An ORTEP diagram is shown in Figure 2.

Thermogravimetric Analysis (TGA) Studies. Thermogravimetric studies were conducted using a Seiko RTG 220. In a representative experiment Tp′PtPh$_2$H (**3c**) was placed in an aluminum TGA pan. The sample was heated at a rate of 5 °C per min from 30 to 350 °C under a nitrogen gas flow of 200.0 mL per min. A diagram of the weight loss as a function of temperature is shown in Figure 3. The same

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Table 1. Crystallographic data collection parameters for Tp′PtMe$_2$H (**4b**)

molecular formula	PtC$_{17}$H$_{29}$BN$_6$
formula wt, g/mol	523.35
crystal dimenss, mm	0.25 × 0.25 × 0.15
space group	P$_{cmn}$
cell parameters	
a, Å	8.1292 (8)
b, Å	13.3862 (9)
c, Å	17.9670 (16)
volume, Å^3	1955.2 (3)
Z	4
density calcd, g cm^{-3}	1.778
Collection and Refinement Parameters	
radiation (wavelength, Å)	Mo Kα (0.71073)
monochromator	graphite
scan type	*ω* scan mode
background	0.1 of scan time
2Θ limits, deg	30−40
h; k; l ranges	0, 9; 0, 15; 0, 21
total no. of reflcns	5399
data with $I \geq 2.5\sigma(I)$	1549
R significant [all others],%	2.7, [3.6]
R_w significant, [all others],%	3.3, [3.6]
GOF[a]	1.23
no. of parameters	127
largest parameter shift	0.001

[a] Goodness of fit.

instrumental conditions were employed for Tp′PtPh$_2$Me (**3a**), Tp′PtPh$_2$I (**3b**), and Tp′PtMe$_2$H (**4b**). Decomposition temperatures are given in Table 5.

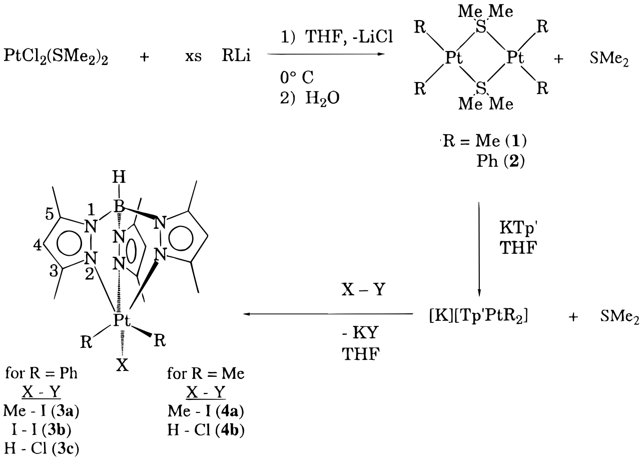
Results and Discussion

Both the d^6 configuration and the high oxidation state of platinum(IV) promote octahedral coordination, the paradigm of inorganic chemistry. Given the proclivity of Tp′ to favor octahedral geometries and the greater electron donating ability of Tp′ compared to Tp, it seemed worthwhile to pursue a general synthetic route to Tp′PtX$_3$ complexes. The synthesis of Tp′PtMe$_3$ from [Pt(Me)$_3$I]$_4$ and KTp′[11] proved difficult to generalize. Canty's work accessed palladium(IV) Tp complexes through oxidation of palladium(II) Tp intermediates,[12] and electrophilic addition to anionic platinum(II) intermediates offered a potentially attractive route to a variety of Tp′PtR$_2$X complexes.

Note that we unsuccessfully attempted several simple preparations with both platinum(IV) and platinum(II) reagents. Direct reaction of platinum(IV) halides and the potassium salt of Tp′ (Tp′ = hydridotris(3,5-dimethylpyrazolyl)borate) in our hands ruptured the Tp′ ligand backbone and produced platinum pyrazole complexes or a bis(3,5-dimethylpyrazolyl)borane dimer[13] as the only isolable products. Difficulties arose in the selection of a suitable platinum(II) source. Ligand exchange reactions with either Pt(Me)$_2$(COD) (COD = 1,5-cyclooctadiene) or Pt(Me)$_2$(COE)$_2$ (COE = cyclooctene) followed by oxidation were unsuccessful. Clean oxidation of the Tp′ analog of the previously reported platinum(II) [TpPtMe]$_x$ oligomer[14] proved elusive.

[K][Tp′PtPh$_2$]. A number of groups have successfully used platinum(II) sulfide complexes for exchange reactions with nitrogen donor ligands; the sulfide ligands are extremely labile.[6,8,10,15] The monomeric platinum(II) complex, Pt(Ph)$_2$(SMe$_2$)$_2$, was combined with a slight excess of KTp′ in acetone-d_6 in an NMR tube and the reaction was monitored by ^{1}H NMR. After 1 h all of the metal reagent, Pt(Ph)$_2$(SMe$_2$)$_2$, had been consumed, and only one platinum-containing species was observed based on clues provided by platinum coupling to aryl protons (^{195}Pt, I = $^1/_2$, 33.8% abundant). The resulting spectrum has been assigned to [K][Tp′PtPh$_2$], a platinum(II) intermediate analogous to the palladium(II) Tp intermediate generated and utilized, but not observed, by Canty.[5]

Scheme 1. Reaction Scheme for the Synthesis of Tp′ Platinum(IV) Complexes[a]



[a] The numbering scheme for the pyrazole rings is also given.

The ortho protons of [K][Tp′PtPh$_2$] are observed at 7.46 ppm with 68.0-Hz platinum coupling. The meta protons are seen at 6.54 ppm and the para at 6.39 ppm. A 2-to-1 pattern was observed for the pyrazole protons and the methyl groups of the Tp′ ligand, indicating that a molecular mirror plane contains one Tp′ ring with the other two rings equivalent. The three pyrazole rings are not undergoing rapid exchange on the NMR time scale. Other work has indicated that Tp and B(pyrazole)$_4$-platinum(II) complexes are fluxional as the pyrazole rings are exchanged by interchange between four- and five-coordinate geometries in solution.[16] While the ^{1}H NMR of [K][Tp′PtPh$_2$] here has provided clear evidence that the three pyrazole rings do not exchange, it is not known whether the predominate platinum(II) species in solution at room temperature is four- or five-coordinate.

Tp′PtPh$_2$Me. Addition of excess MeI to the NMR solution of the reactive platinum(II) [K][Tp′PtPh$_2$] species resulted in the formation of a platinum(IV) monomer, Tp′PtPh$_2$Me (**3a**). This complex can be synthesized on a preparative scale as shown in Scheme 1.

The aromatic signals of Tp′PtPh$_2$Me in the ^{1}H NMR are broad at room temperature. Though the two phenyl rings are related by a molecular mirror plane, in each phenyl ring the individual ortho and meta protons are inequivalent due to restricted rotation of the phenyl rings. A 14.8-kcal/mol barrier to phenyl rotation around the platinum−carbon bond was calculated following variable-temperature NMR studies.

The spectrum of Tp′PtPh$_2$Me at low temperature revealed two distinct signals for ortho protons: one downfield at 7.75 ppm with 43.2-Hz two-bond platinum coupling, the other upfield at 6.56 ppm with 44.8-Hz platinum coupling. Because of the symmetry equivalency of the two phenyl rings, each aromatic

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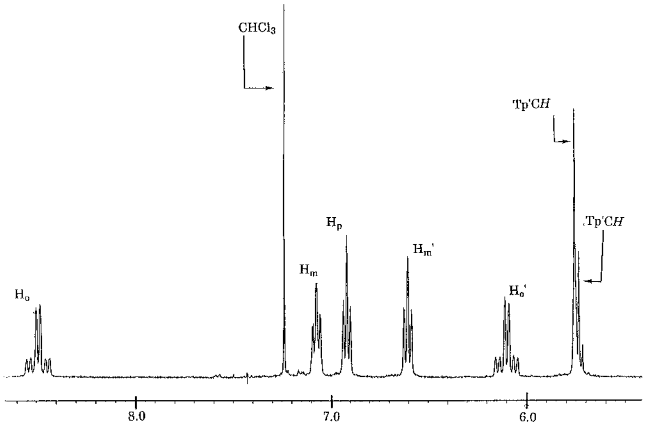

Figure 1. ^{1}H NMR of the aromatic region of $Tp'PtPh_2I$ (**3b**) in $CDCl_3$.

signal integrated for two protons, one from each phenyl ring. The differences in chemical shifts may be due to shielding effects of the five aromatic rings, three pyrazoles and two phenyls, that surround the crowded metal center. The protons of the Tp′ ligand are observed in a 2-to-1 ratio with the unique ring trans to the methyl group. Four-bond platinum coupling is observed to the 4 position of all of the pyrazole rings. The protons of the platinum-bound methyl group are observed at 1.81 ppm with 70.8-Hz platinum coupling.

In the ^{13}C NMR, two distinct environments for both ortho and meta carbons are observed, with a large difference in chemical shifts and substantial platinum coupling. The ipso carbon is observed at 125.8 ppm with 890-Hz platinum coupling. Platinum coupling is seen not only throughout the backbone of the Tp′ ligand but also to the carbon of the methyl group in the 3 position of the unique pyrazole ring. The carbon of the methyl group bound to the platinum(IV) metal center is observed at −2.9 ppm with 660-Hz one-bond platinum coupling.

$Tp'PtPh_2I$. Oxidation of [K][$Tp'PtPh_2$] with elemental iodine yields $Tp'PtPh_2I$ (**3b**). In the room temperature ^{1}H NMR, no rotation of the phenyl rings is evident. High-temperature ^{1}H NMR studies allowed calculation of a barrier to rotation of 18.1 kcal/mol. The downfield region of the spectrum is shown in Figure 1. The ortho protons are even farther separated in $Tp'PtPh_2I$ (**3b**) than in $Tp'PtPh_2Me$ (**3a**) as they occur at 8.49 ($^3J_{Pt-H} = 39.6$ Hz) and 6.10 ppm ($^3J_{Pt-H} = 36.8$ Hz), a chemical shift difference of 2.39 ppm. Large four-bond platinum coupling is observed to the 4-position of the Tp′ pyrazole ring trans to the iodide ligand ($^4J_{Pt-H} = 15.2$ Hz). One of the methyl groups on the Tp′ ligand is observed at 0.82 ppm, unusually far upfield.

In the ^{13}C NMR spectrum platinum coupling is observed to all of the carbons of the phenyl rings ($^4J_{Pt-C_{para}} = 10$ Hz). The signals for the Tp′ carbons resemble those observed for $Tp'PtPh_2Me$. Coupling of 11 Hz is observed between platinum and the methyl group at the 3-position of the unique pyrazole ring.

$Tp'PtPh_2H$. The [K][$Tp'PtPh_2$] intermediate can be protonated with HCl to give $Tp'PtPh_2H$ (**3c**). This platinum(IV) aryl hydride species is stable in the solid-state and in solution. The phenyl rings are rotating on the NMR time scale at room temperature, and the proton signals in the aromatic region are quite broad. The coalescence temperature for exchange of the ortho protons was found to be 55 °C, and variable-temperature NMR studies allowed us to calculate a rotation barrier of 13.6 kcal/mol. Of the three platinum(IV) aryl complexes synthesized, the hydride exhibited the smallest barrier to phenyl ring rotation, probably a consequence of steric factors. Again, the pattern of one downfield doublet and one upfield doublet is observed for the ortho protons of the phenyl rings, with large platinum(IV) coupling to the downfield ortho proton ($^3J_{Pt-H} = 58.8$ Hz). The Tp′ resonances are similar to those seen for the methyl and iodide derivatives with platinum coupling to the proton at the 4-position of the two equivalent rings; no platinum coupling to the 4-position of the unique ring trans to the hydride was observed.

Table 2. ^{1}H NMR Data for **3c** and **4b** and Other Selected Platinum(IV) Hydride Complexes

complex	Pt−H, ppm	$^1J_{Pt-H}$, Hz	trans ligand	ref
$Tp'PtPh_2H$ (**3c**)	−18.94	1360	N	this work
$Tp'PtMe_2H$ (**4b**)	−20.95	1358	N	this work
$[(tmeda)Pt(CH_2Ph)(H)(Cl)]^a$	−24	1230	Cl	1
$[PtCl(H)Me_2(^tBu_2bpy)]^b$	−21.80	1590	Cl	2
$[Pt(H)XMe_2(dmphen)]^c$	−22	1400	N	3
trans $[PtHI_3(PEt_3)_2]^d$	−16.41	784	I	17

[a] tmeda = *N*,*N*,*N*′,*N*′-tetramethylenediamine, CD_2Cl_2, −78 °C. [b] CD_2Cl_2, −78 °C. [c] X = Cl or Br, dmphen = 2,9-dimethyl-1,10-phenanthroline, acetone-d_6. [d] CD_2Cl_2, −40 °C.

The hydride signal is observed upfield at −18.94 ppm with 1360-Hz coupling to platinum. Table 2 gives ^{1}H NMR data for platinum(IV) hydride complexes, including the three 1995 reports [1−3] and the 1973 report of a platinum(IV) hydride.[17] The effect of the trans ligand on the coupling constant should be noted. The chemical shift and coupling constant for $Tp'PtPh_2H$ are similar to those of other complexes with trans nitrogen donor ligands.[18,19]

In the ^{13}C NMR larger platinum coupling constants are seen throughout the phenyl ring for the hydride complex than are observed for the methyl or iodo derivatives. The ipso carbons at 123.9 ppm with 840-Hz platinum coupling do not show coupling to the cis hydride ligand. The Tp′ ligand exhibited significant platinum coupling and a 2-to-1 pattern due to the mirror plane.

In an effort to probe the solution stability of $Tp'PtPh_2H$ the complex was refluxed for 15 h in toluene. Neither incorporation of toluene nor decomposition was observed by ^{1}H NMR analysis.

$Tp'PtMe_3$. Methyl substitution for chloride in $PtCl_2(SMe_2)_2$ has previously been reported to give the highly reactive platinum dimer, $[Pt(Me)_2(SMe_2)]_2$.[9] The analogous ethyl sulfide dimer has been combined with KTp and oxidized by water/acetone to give the crystallographically characterized $TpPtMe_2(OH)$.[6] Would a similar route allow access to platinum(IV) Tp′ complexes? A [K][$Tp'PtMe_2$] intermediate was generated by ligand exchange of $[Pt(Me)_2(SMe_2)]_2$ and KTp′; characterization of this anionic intermediate was not achieved. This putative anion can be oxidized with MeI to give the previously reported $Tp'PtMe_3$[11,20] (**3a**) in reasonable yields (Scheme 1).

$Tp'PtMe_2H$. The surprising thermal stability observed for $Tp'PtPh_2H$ prompted us to explore the synthesis of an analogous dimethylhydrido platinum(IV) derivative. The anionic intermediate, [K][$Tp'PtMe_2$], can be protonated with anhydrous HCl in ether to give, in 44% yield, $Tp'PtMe_2H$ (**4b**). The hydride

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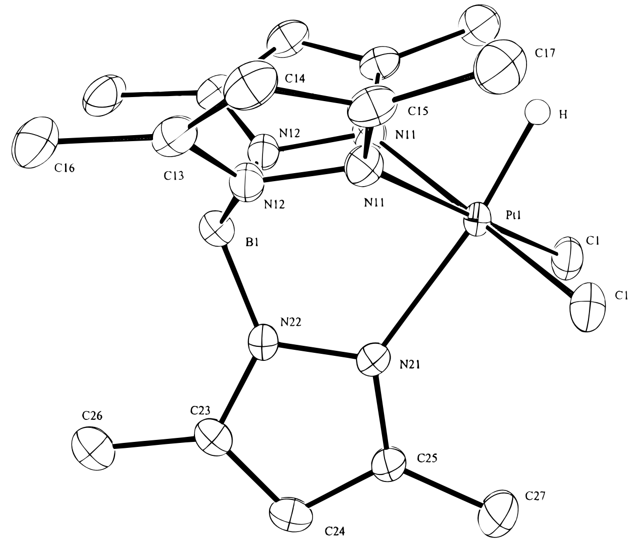

Figure 2. ORTEP diagram of Tp′PtMe$_2$H (**4b**). The hydrogen atom was not located, and is shown in a calculated position.

Table 3. Bond Lengths (Å) for Tp′PtMe$_2$H (**4b**) (Symmetry Equivalent Atoms Are Not Listed)

Pt(1)−C(1)	2.048(5)	C(14)−C(15)	1.495(8)
Pt(1)−N(11)	2.145(4)	C(15)−C(17)	1.497(8)
Pt(1)−N(21)	2.169(6)	N(21)−N(22)	1.371(8)
B(1)−N(12)	1.546(6)	N(21)−C(25)	1.344(9)
B(1)−N(22)	1.520(10)	N(22)−C(23)	1.359(10)
N(11)−N(12)	1.377(6)	C(23)−C(24)	1.379(11)
N(11)−C(15)	1.346(6)	C(23)−C(26)	1.493(11)
N(12)−C(13)	1.357(6)	C(24)−C(25)	1.387(11)
C(13)−C(14)	1.371(8)	C(25)−C(27)	1.520(12)
C(13)−C(16)	1.495(8)		

Table 4. Selected Bond Angles (deg) for Tp′PtMe$_2$H (**4b**)

C(1)−Pt(1)−C(1)a	90.07(21)	N(12)−B(1)−N(12)a	108.8(5)
C(1)−Pt(1)−N(11)	92.85(18)	N(12)−B(1)−N(22)	110.3(4)
C(1)−Pt(1)−N(11)a	177.05(18)	Pt(1)−N(11)−N(12)	117.2(3)
C(1)−Pt(1)−N(21)	92.70(19)	B(1)−N(11)−N(12)	119.6 (4)
N(11)−Pt(1)−N(11)a	84.24(14)	Pt(1)−N(21)−N(22)	117.0 (4)
N(11)−Pt(1)−N(21)	87.60(17)	B(1)−N(22)−N(21)	119.9(6)

Table 5. Solid-State Decomposition Temperatures from TGA

complex	temp, °C
Tp′PtPh$_2$Me (**3a**)	258
Tp′PtPh$_2$I (**3b**)	260
Tp′PtPh$_2$H (**3c**)	232
Tp′PtMe$_2$H (**4b**)	191

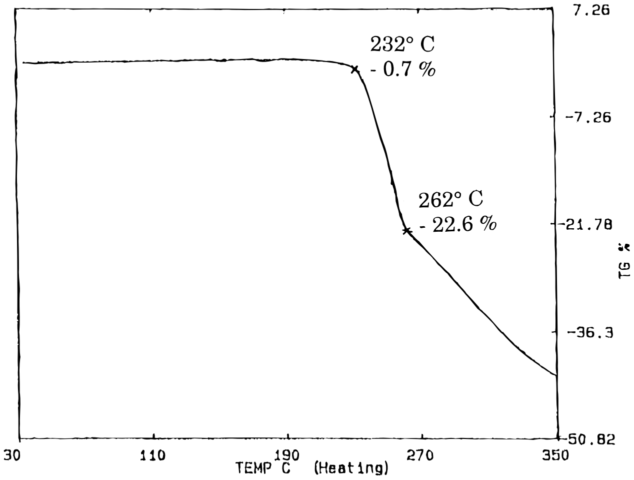

Figure 3. Thermogravimetric analysis (TGA) showing solid-state decomposition of Tp′PtPh$_2$H (**3c**).

signal is observed at −20.95 ppm with 1358-Hz platinum coupling. Both the chemical shift and the coupling constant values are comparable to other platinum(IV) hydrides (Table 1). The platinum-bound methyl groups appear at 1.19 ppm with 67.5-Hz platinum coupling. A 2-to-1 pattern is observed for the Tp′ ligand signals. Coupling of 8.0 Hz is observed to the 4-position proton of the two equivalent pyrazole rings. In the ^{13}C NMR the Tp′ ligand is similar to the diaryl derivatives with platinum coupling throughout the ligand. The platinum methyl group carbon resonance is upfield at −21.64 ppm with platinum coupling of 624 Hz, and two-bond coupling to the cis hydride of 4 Hz is evident.

Platinum(IV) methyl hydride complexes have been implicated as intermediates in protonation reactions of platinum(II) methyl complexes.[4] Electrophilic attack on d^8 square-planar complexes can yield platinum(IV) methyl hydride intermediates which reductively eliminate methane. The net reaction is the protonation of a methyl group with cleavage of the platinum(II)−carbon bond to form methane. In contrast to other platinum(IV) *cis*-methyl hydride complexes, Tp′PtMe$_2$H is reluctant to reductively eliminate methane at room temperature in solution or in the solid-state.

X-ray Structure of Tp′PtMe$_2$H. Due to the thermal stability of the complex, it was possible to obtain X-ray quality crystals of the stable platinum(IV) dimethyl hydride, **4b**, by recrystallization from methylene chloride and hexanes at room temperature. An ORTEP diagram is shown in Figure 2; bond lengths and selected bond angles are shown in Tables 3 and 4, respectively. The hydride ligand was not located.

The platinum-methyl bond length is 2.048(5) Å, coincidentally equal to the platinum−methyl bond length of 2.048(5) Å found in TpPtMe$_2$(OH).[6] The platinum−nitrogen bond lengths are 2.145(4) Å and 2.169(6) Å for the two equivalent and one unique pyrazole rings, respectively. The unique ring is trans to the hydride ligand and the two equivalent rings are trans to the methyl groups, so this provides a direct comparison of the trans influence of a methyl ligand versus a hydride in a platinum(IV) monomer. The stronger trans influence ligand, hydride, causes an increase in the trans platinum−nitrogen bond length of only 0.024 Å. The bond angle between the platinum-bound methyl groups is 90.07(21)°, consistent with the octahedral environment expected for a d^6 platinum(IV) metal center.

Solid-State Stabilities. To determine the solid-state decomposition temperatures for these compounds, thermogravimetric analyses (TGA) were performed. Previously Goldberg and coworkers employed TGA and DSC (differential scanning calorimetry) to investigate methyl iodide and ethane reductive elimination from (dppe)PtMe$_3$I (dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$). In addition to the temperature at which reductive elimination occurred, the thermodynamics of the processes and an estimation of platinum(IV)−carbon and platinum(IV)−iodide bond strengths were reported.[21]

For all three of the Tp′ platinum(IV) phenyl derivatives decomposition temperatures were found to be in excess of 230 °C (Table 5). Figure 3 shows the TGA from 30 to 350 °C for Tp′PtPh$_2$H. It can be seen that after losing about 23% of the initial mass between 230 and 260 °C, weight loss continues at higher temperatures. The initial weight loss of 23% does not correspond to simple benzene reductive elimination. Neither the organic product nor the platinum species which form at this high temperature have been identified. For Tp′PtMe$_2$H, de-

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composition occurs around 190 °C, which is extraordinary behavior for a platinum(IV) bisalkyl hydride complex. This unusual stability may be due to the tendency of the Tp′ ligand to act as an octahedral enforcer; that is, Tp′ may inhibit reductive elimination by not allowing the metal complex to easily change its geometry.[22] Furthermore, a stable square-planar geometry is not accessible for the [Tp′PtX] residue. It is now widely accepted that the initial step for reductive elimination from platinum(IV) monomers is formation of a five-coordinate intermediate in many systems.[23] The recalcitrance of the pyrazole arms of the Tp′ to dissociate from the metal center may account for the robust thermal properties of Tp′PtMe$_2$H.

Conclusions

In an effort to explore the chemistry of octahedral d^6 platinum(IV) organometallic complexes which resist facile reductive elimination, we have synthesized a series of thermally stable Tp′ hydride, alkyl, aryl, and iodide complexes. Unusually large restricted phenyl rotation barriers were observed for the aryl derivatives in these sterically demanding complexes. The room temperature solid-state X-ray structure of Tp′PtMe$_2$H offers testimony to the stability of this series of Tp′ platinum(IV) complexes. This solid-state structure beautifully illustrates an octahedral environment for an organometallic platinum(IV) hydride complex.

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Supporting Information Available: Tables of atomic positions, thermal parameters, and complete bond distances and angles (3 pages). Ordering information is given on any current masthead page.

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