

The synthesis of olefin, carbonyl and thiolate complexes of platinum(IV) in the $[(\eta^5 - C_5Me_5)Pt(IV)]$ system. Crystal and molecular structure of $(\eta^5 - C_5Me_5)PtMe_2[S(p-CH_3(C_6H_4)]^{\dagger})$

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(Received 9 June 1997; accepted 1 July 1997)

Abstract—A number of Cp*PtMe₂X and Cp*PtMe₂(L)⁺(OTf)⁻ complexes have been prepared [Cp* = η^{5} -C₅Me₅; OTf = OSO₂CF₃; X = OTf, I, N₃, S(*p*-tol); L = CO, C₂H₄, CH₂—CHMe, NH₃, NH₂Buⁱ]. The complexes Cp*PtMe₂(CO)⁺(OTf)⁻, Cp*PtMe₂(C₂H₄)⁺(OTf)⁻, and Cp*PtMe₂(CH₂—CHMe)⁺(OTf)⁻ represent a rare type of compound in which a π acid ligand is coordinated to a high valent metal center predominantly through σ -donation and π -backbonding plays only a limited role in the metal–ligand interaction. The aryl-thiolate complex, Cp*PtMe₂[S(*p*-tol)], has been structurally characterized by X-ray diffraction. ① 1998 Elsevier Science Ltd. All rights reserved

Keywords: platinum; Pt(IV); pentamethylcyclopentadienyl; alkene; azide; carbonyl; thiolate; azide; triflate complexes.

Although alkoxide complexes of platinum(II) have been well-studied [1], such derivatives of platinum(IV) are much rarer [2], and so the chemistry and the physical properties of these compounds have not been thoroughly examined. Bradley has done extensive work on the use of metal alkoxides as precursors for the deposition of metal oxides [3], and we have recently described the use of volatile cis-bis(η^2 , η^1 -pent-4-en-1-yl)platinum in the deposition of pure thin platinum films [4]. We sought to synthesize various alkoxide derivatives of platinum(IV) in order to study their fundamental chemistry and to examine their potential as precursors in chemical vapor deposition.

The pentamethylcyclopentadienyl ligand (*abbv*. Cp^*) has been used to stabilize a variety of alkoxo and amido derivatives of the late transition metals such as $Cp^*Ir(PPh_3)(OEt)(H)$ [5] and $Cp^*Ni(P-Me_3)(NH(p-tol))$ [6], but this ligand has not been used extensively in platinum chemistry. In fact, only seven [Cp^*Pt] compounds had been reported in the literature before 1990 [7]. Since platinum(IV) complexes are invariably six-coordinate, the three-coordinate

monovalent Cp* ligand seems ideally suited as an ancillary ligand for stabilizing alkoxide derivatives of Pt(IV). Useful synthetic routes into [Cp*Pt(IV)] compounds were provided independently by the research groups of Sharp [8] and Roesky [9] in 1990. These researchers described a number of [Cp*Pt(IV)] derivatives with halide and methyl ligands, but [Cp*Pt(IV)] complexes with oxygen-, nitrogen-, or sulfur-based ligands were not reported.

The goals of this work are to synthesize new derivatives of [Cp*Pt(IV)] having bonds between Pt and electronegative atoms such as O, S and N and to study the physical and chemical properties of these compounds. Although we have not been able to isolate and fully characterize simple Cp*-substituted platinum alkoxides or aryloxides, we have found the Cp* ligand to be useful for stabilizing several unusual [Pt(IV)-ligand] moieties, including some with Pt—O and Pt—S bonds. Platinum(IV) complexes with triflate, olefin, carbonyl, and arylthiolate functional groups have been isolated and are described herein.

RESULTS AND DISCUSSION

As shown in Scheme 1, $Cp*PtMe_2(OTf)$ (OTf = OSO₂CF₃) may be isolated as an air-stable,

[†] Dedicated to Professor Donald C. Bradley, whose research has greatly influenced much of the work that has gone on in our group during the past several years.



bright orange crystalline solid in greater than 90% yield by reaction of Cp*PtMe₃ [9] with slightly less than one equivalent of trifluoromethanesulfonic acid (i.e., triflic acid) at -78°C. Using more triflic acid only results in a lower yield of Cp*PtMe₂(OTf). The presence of the triflate ligand in Cp*PtMe₂(OTf) is confirmed by a singlet in the ¹⁹F NMR spectrum (CD₂Cl₂) at -15.8 ppm and by very strong absorptions at 1294 cm⁻¹, 1250 cm⁻¹, 1176 cm⁻¹, and 1032 cm⁻¹ in the infrared spectrum [10]. Also shown in

Scheme 1 is the synthesis of $Cp*PtMe_2I$, which may be isolated in 59% yield as an air-stable, reddish orange solid from the reaction of $[Me_2PtI_2]_x$ with Cp*Li at room temperature, similar to Sharp's synthesis of $Cp*PtMe_2Br$ [8].

The results of investigating the reactivity of $Cp*PtMe_2(OTf)$ are illustrated in Scheme 2. The triflate ligand is easily displaced from the platinum center in $Cp*PtMe_2(OTf)$ by various dative ligands (L) such as C_2H_4 , CH_2 =CHMe, Co, NH₃, and



 $NH_{2}Bu^{t}$ to afford the salts $Cp^{*}PtMe_{2}(L)^{+}(OTf)^{-}$, all of which may be isolated in ca. 85-95% yields. The bound ethylene ligand in $Cp*PtMe_2(C_2H_4)^+(OTf)^$ has resonances in the 'H NMR spectrum at 3.71 ppm (s, ${}^{2}J_{Pt-H} = 52 \text{ Hz}$) and in the ${}^{13}C{}^{1}H{}$ NMR spectrum at 72.3 ppm (s, ${}^{1}J_{Pt C} = 101$ Hz). The carbonyl ligand of Cp*PtMe₂(CO)⁺(OTf)⁻ is characterized by a v_{CO} stretching frequency of 2114 cm⁻¹ in the infrared spectrum and by a singlet at 155.9 ppm in the ${}^{13}C{}^{11}_{1}H{}^{1}_{1}$ NMR spectrum (CD₂Cl₂). Ethylene coordination and carbon monoxide coordination to Cp*PtMe₂(OTf) are reversible, so that Cp*PtMe₂(OTf) may be regenerated simply by evaporating a solution of $Cp^*PtMe_2(L)^+(OTf)^-$ (L = C₂H₄, CO) to dryness. Both Cp*PtMe₂(NH₃)⁺(OTf)⁻ and Cp*PtMe₂(NH₂ Bu^{t})⁺(OTf)⁻ are stable under reduced pressure, however.

The π acidic carbonyl and olefin ligands in $Cp*PtMe_2(L)^+(OTf)^- (L = CO, C_2H_4, CH_2)$ are coordinated to cationic platinum (IV) centers. To our knowledge, only a handful of platinum(IV) carbonyl complexes [11-13] and only one other platinum(IV) olefin derivative [14] have been reported previously. In $Cp^*PtMe_2(L)^+(OTf)^-$ (L = CO, C₂H₄, CH₂=CHMe), the carbonyl and olefin ligands are bound to the platinum centers primarily through σ donation, and very little, if any, π backbonding is expected [15]. Indeed, the v_{CO} stretching frequency in $Cp*PtMe_2(CO)^+(OTf)^-$ is much higher than those for some Pt(II)carbonyl derivatives (1968-2044 cm^{-1}) and intermediate between those of other platinum(IV) carbonyl compounds (2060–2191 cm⁻¹) (see Table 1). Nevertheless, the v_{CO} value for $Cp*PtMe_2(CO)^+(OTf)^-$ is lower than 2143 cm⁻¹, the stretching frequency for free CO [16], which indicates that some degree of π backbonding does stabilize the [Pt-CO] bond.

In the absence of a dative trapping ligand, Cp*PtMe₂(OTf) slowly decomposes at room temperature to a mixture of compounds, one component of which is Cp*PtMe₃. Presumably Cp*PtMe₃ is formed when Cp*PtMe₂(OTf) abstracts a methyl group from another molecule of Cp*PtMe₂(OTf). Qualitatively, the rate of thermal decomposition is solvent

Table 1. v_{CO} Stretching frequencies for carbonyl complexes of platinum(IV) and [Cp*Pt(II)]

Compound	$v_{\rm CO}$ (cm ⁻¹)	Reference
[PtCl ₅ (CO)] ⁻	2191	12
$Cp*PtMe_2(CO)^+(OTf)$	2114	this work
$fac-[Pt(I)(Me)_3(SMe_2)(CO)]$	2090	13
[Pt(Me)(I)(Cl)(py)(CO)	2060	11
$\{CH(py)CH_2CH_3\}]^+(Cl)^-$		
Cp*Pt(CO)(Cl)	2044	7c
Cp*Pt(CO)Pt(CO)Cp	2005, 1984	7c
[Cp*Pt(CO)] ₂	1989, 1968	7c

dependent; $Cp*PtMe_2(OTf)$ decomposes faster in THF than in benzene.

The formation of Cp*PtMe₃ in the thermal degradation of Cp*PtMe₂(OTf) suggests that the electrophilic Cp*PtMe₂(OTf) has an affinity for methyl groups. Indeed, Cp*PtMe₂(OTf) can also abstract a methyl group from either Cp₂ZrMe₂ (Cp = η^{5} -C₅H₅) or SnMe₄ immediately to yield Cp*PtMe₃ [17], but there is no reaction with SiMe₄.

Cp*PtMe₂(OTf) also demonstrates an affinity for halides and pseudohalides. Thus, treatment of a benzene solution of Cp*PtMe₂(OTf) with MeI slowly yields Cp*PtMe₂I and MeOTf [18] within three hours at room temperature : no reaction was observed, however, between Cp*PtMe₂(OTf) and PhBr [19]. Cp*PtMe₂(OTf) readily reacts with excess NaN₃ in THF to yield Cp*PtMe₂N₃, which exhibits a very strong $v(N_3)$ absorption in the infrared spectrum at 2008 cm⁻¹ [20].

Sharp has indicated that the reaction of $Cp*PtMe_2Br$ with LiNHBu' only gives back the starting materials in low yields with no tractable products [8]. We reasoned that $Cp*PtMe_2(OTf)$ may serve as a more useful precursor for amide and alkoxide derivatives of [Cp*Pt(IV)] since the triflate ligand is a better leaving group than the bromide ligand. A red solid, tentatively characterized as $Cp*PtMe_2(OPh)$ [21], may be isolated by treating Cp*PtMe(OTf) with LiOPh in Et₂O at -78°C, but the yield is low and some other [Cp*Pt] by-products, one of which is $Cp*PtMe_3$, are also formed.

Both Cp*PtMe₂(OTf) and Cp*PtMe₂I react cleanly, however, with the sulfur-based nucleophile KS(p-tol) to afford Cp*PtMe₂[S(p-tol)], which has been characterized by X-ray diffraction. An ORTEP diagram is shown in Fig. 1 while relevant crystallographic and metrical data are given in Tables 2 and 3. The X-ray study revealed the [Pt-S] bond length of 2.344(1) Å to be similar to the sum of the covalent radii (2.35 Å) of six-coordinate platinum(IV) (1.31 Å) and sulfur (1.04 Å) [22], and the [Pt-S-C] bond angle to be $108.4(2)^{\circ}$. With a maximum difference of 0.043(6) Å, there is little variation among the five aromatic [C—C] bond lengths in the Cp* ligand, contrasting with the structure of Cp*PtMe Cl in which the Cp* ligand shows a small deviation toward "diene-like" geometry [9].

Although we are unaware of any other structurally characterized arylthiolate complexes of platinum(IV) with two-coordinate sulfur atoms, the cubic complex [PtMe₃(μ -SPh)]₄, which contains four-coordinate sulfur atoms, has been structurally characterized [23]. The average [Pt—S] bond length [2.506(5) Å] and the average [Pt—S—C] bond angle [118.1(7)°] in [PtMe₃(μ -SPh)]₄ are longer and greater, respectively, than those in Cp*PtMe₂[S(p-tol)], which may be attributed to differences in the coordination numbers of the sulfur atoms. Some arylthiolate complexes of platinum(II) with two-coordinate sulfur atoms have been structurally characterized [24,25], and the





Table 2. Crystal and intensity collection data for Cp*PtMe₂[S(*p*-tol)]

Formula Formula weight Lattice Cell constants	$C_{19}H_{28}SPt$ 483.6 Primitive a = 8.41400(10) Å b = 12.72130(10) Å c = 16.9927(3) Å $\alpha = 90.0^{\circ}$ $\beta = 97.578(1)^{\circ}$ $\gamma = 90.0^{\circ}$
Z radiation (λ , Å) Space group ρ (calcd), g cm ⁻³ μ (Mo K α), cm ⁻¹ Goodness of fit R R_w	$V = 1802.96(4) \text{ Å}^{3}$ 4 Mo K\$\alpha\$ (0.71069) P2_1/c (No. 14) 1.781 78.60 1.06 0.021 0.027

Table 3. Selected bond lengths Å and angles (deg.) for $Cp*PtMe_2[S(p-tol)]$

Pt—S	2.344(1)	S—C(13)	1.790(4)	
Pt—C(11)	2.075(5)	C(1)—C(2)	1.446(7)	
Pt—C(12)	2.067(5)	C(2)—C(3)	1.453(6)	
PtC(1)	2.265(5)	C(3)C(4)	1.410(6)	
Pt—C(2)	2.196(4)	C(4) - C(5)	1.437(6)	
Pt—C(3)	2.300(4)	C(5) - C(1)	1.421(6)	
Pt—C(4)	2.324(4)			
PtC(5)	2.306(4)			
Pt—S—C(13)	108.4(2)	SPtC(11)	86.1(1) ³	
S—Pt—C(12)	92.2(1) ^c	C(11)—PtC(12)	82.5(2)	

geometry of the [Pt—S—C] moieties in these compounds is similar to that of Cp*PtMe₂[S(*p*-tol)]. For example, the [Pt—S] bond length in [Cp(CO)Mn{ μ -C(PMe₃) C₆H₄Me}Pt(*p*-tol)(PMe₃)] is 2.365(3) Å and the [Pt—S—C] bond angle is 109.3(3)[°] [26].

EXPERIMENTAL DETAILS

General considerations

Unless otherwise noted, all reactions and manipulations were carried out under nitrogen using standard Schlenk and vacuum techniques or in a Braun inert atmosphere box (N_2) . Infrared spectra were taken on a Mattson Galaxy 3000-Fourier Transform Infrared spectrometer (FTIR). All ¹H, ¹³C {¹H}, and ¹⁹F NMR spectra were obtained at room temperature on a Bruker AMX-400 spectrometer at the frequencies 400 MHz, 100.6 MHz, and 376.5 MHz, respectively. ¹⁹F NMR spectra were referenced externally to trichlorofluoromethane. Elemental analyses were performed by the University of California-Berkeley Microanalytical facility on a Perkin Elmer 2400 series II CHNO/S Analyzer. The single crystal X-ray analysis of Cp*PtMe₂[S(p-tol)] was carried out by Dr Frederick J. Hollander at the University of California, Berkeley X-ray facility.

Unless otherwise noted, reagents were purchased from commercial suppliers and used without further purification. Hexanes, pentane, diethyl ether, tetrahydrofuran, benzene, and toluene were distilled from sodium/benzophenone ketyl under N₂ prior to use. Methylene chloride was distilled from CaH₂ under N₂. (Me₂PtI₂)_x [27], Cp*PtMe₃ [9], Cp*Li [28], and Cp₂ZrMe₂ [29] were synthesized according to published procedures. KS(*p*-tol) was synthesized by treating a hexane solution of KH with a hexane solution of $HSC_6H_4CH_3$ and was recrystallized from hexane at $-35^{\circ}C$.

Cp*PtMe₂(OTf)

Under N₂, a -78° C solution of HOTf (260 μ l, 2.94 mmol) in Et₂O (10 ml) was added slowly by cannula to a stirred solution of Cp*PtMe₃ (1.22 g, 3.25 mmol) in Et₂O (20 ml) which was immersed in a -78 ⁵C bath. The mixture, which turned orange immediately, was allowed to warm to room temperature and stirred for 15 min. The volatile components were removed in vacuo, leaving a dark orange residue. The remainder of this procedure was carried out in the air. The product was extracted into C_6H_6 (10 ml), and the black extract was passed through a fritted column containing silanized silica (60 Å). The column was washed with C₆H₆ until the washes were colorless, and all washes were combined with the original filtrate. The volatile components of the bright orange filtrate were removed in vacuo leaving an orange crystalline solid which was washed with pentane $(2 \times 10 \text{ ml portions})$ and vacuum-dried. Yield: 1.41 g (94% based on HOTf). Anal. Calc. for $C_{13}H_{21}F_{3}O_{3}SPt$: C, 30.65%; H, 4.15%. Found: C, 30.45%; H, 4.42%. IR (KBr pellet, cm⁻¹): 2960 (m), 2897 (m), 2854 (w), 2802 (w), 1628 (w), 1527 (m), 1483 (w), 1452 (s), 1383 (s), 1350 (m), 1294 (vs), 1250 (vs), 1176 (vs), 1076 (w), 1032 (vs), 957 (w), 835 (m), 798 (w), 768 (m), 644 (vs), 615 (w) 582 (m), 548 (w), 521 (m). ¹H NMR (CD₂Cl₂): δ 1.79 ppm [s, 15 H, { η^{5} -C₅(CH₃)₅}, ${}^{3}J_{Pt-H} = 21$ Hz]; δ 1.40 ppm [s, 6 H, 2{CH₃}, ²J_{Pt H} = 70 Hz]. ^{19}F NMR (CD₂Cl₂): -15.8 ppm [s]. $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2) : 7.3 ppm [s, 2 C, 2 $\{CH_3\}$, ${}^{1}J_{Pt-C} = 724$ Hz]; 8.8 ppm [s, 5 C, { η^{5} -C₅(CH₃)₅}]; 109.3 ppm [s, 5 C, { η^{5} -C₅(CH₃)₅}, ¹J_{Pt C} = 40 Hz]; 119.0 ppm $[q, 1 C, {OSO_2CF_3}, {}^1J_{C-F} = 312 Hz].$

Cp*PtMe₂I

A mixture of Cp*Li (0.17 g, 1.22 mmol) and (Me₂ PtI_2 , (0.50 g, 1.05 mmol) in THF (5 ml) was stirred at room temperature overnight (ca 12 h). The volatile components were removed in vacuo leaving a dark brown-black residue. The remainder of this procedure was carried out in the air. The product was extracted from the dark residue with C₆H₆ (10 ml) and the extract was passed through a fritted column containing silica gel (60 Å particles). The silica column was washed with C_6H_6 until the washes were colorless, and these washes were combined with the initial C₆H₆ extract. The volatile components of the filtrate were removed in vacuo leaving a reddish orange crystalline solid which was washed with pentane (10 ml) at -78° C and vacuum-dried. Yield : 0.30 g (59%). Anal. Calc. for C₁₂H₂₁IPt: C, 29.58%; H, 4.34%. Found: C, 29.47%; H, 4.42%. IR (KBr pellet, cm⁻¹): 2976 (s), 2958 (s), 2893 (vs), 2852 (m), 2721 (w), 1522 (s), 1493 (m), 1443 (vs), 1427 (s), 1377 (vs), 1350 (s), 1225 (vs), 1200 (m), 1153 (s), 1074 (w), 1022 (vs), 953 (w), 833 (w), 793 (w), 609 (w), 544 (m). ¹H NMR (CD₂Cl₂): δ 1.87 ppm [s, 15 H, { η^{5} -C₅(CH₃)₅}, ³J_{Pt-H} = 14 Hz]; δ 1.19 ppm [s, 6 H, 2 {CH₃}, ²J_{Pt-H} = 81 Hz]. ¹³C{¹H} NMR (CD₂Cl₂): -6.1 ppm [s, 2 C, 2 {CH₃}, ¹J_{Pt-C} = 678 Hz]; 8.6 ppm [s, 5 C, { η^{5} -C₅(CH₃)₅}; 107.0 ppm [s, 5 C, { η^{5} -C₅(CH₃)₅}, ¹J_{Pt-C} = 20 Hz].

Cp*PtMe₂(C₂H₄)(OTf)

C₂H₄ (1 atm) was admitted to a Schlenk tube containing an orange, homogeneous solution of Cp*PtMe₂(OTf) (0.30 g, 0.59 mmol) in C₆H₆ (5 ml). The mixture, which immediately became cloudy and off-white, was stirred 5 min. at room temperature. The reaction mixture was then allowed to settle and the supernatant was decanted off the off-white product. The product was washed with benzene $(2 \times 5 \text{ ml})$ and pentane $(1 \times 10 \text{ ml})$ and dried by exposure to a gentle stream of air. Yield: 0.29 g (91%). Anal. Calc. for C₁₅H₂₅F₃O₃SPt: C, 33.52%; H, 4.69%. Found: C, 33.39%; H, 4.72%. IR (KBr pellet, cm⁻¹): 2983 (s), 2916 (s), 2899 (s), 2860 (w), 2825 (w), 1616 (w), 1525 (w), 1506 (m), 1460 (s), 1429 (s), 1383 (s), 1350 (w), 1261 (vs), 1221 (vs), 1198 (m), 1157 (vs), 1076 (w), 1036 (vs), 957 (w), 837 (w), 802 (w), 764 (w), 752 (w), 729 (w), 654 (s), 638 (s), 617 (w), 573 (m), 552 (w), 517 (m), 461 (w). ¹H NMR (CD₂Cl₂): δ 1.96 ppm [s, 15 H, { η^{5} -C₅(CH₃)₅}, ${}^{3}J_{Pt-H} = 11$ Hz]; δ 1.02 ppm [s, 6 H, 2 { CH_3 }, ${}^2J_{Pt H} = 70$ Hz]; δ 3.71 ppm [s, 4 H, $\{C_2H_4\}, {}^2J_{Pt-H} = 52 \text{ Hz}]. {}^{19}\text{F NMR} (CD_2Cl_2): -16.2$ ppm [s]. ${}^{13}C{}^{1}H{}$ NMR (CD₂Cl₂): 2.6 ppm [s, 2 C, $2\{CH_3\}, \ ^1J_{Pt-C} = 563 \ Hz]; \ 8.2 \ ppm \ [s, 5 \ C, \ \{\eta^5 C_5(CH_3)_5$; 112.0 ppm [s, 5 C, { η^5 - $C_5(CH_3)_5$ }, ${}^{1}J_{Pt-C} = 20 \text{ Hz}$; 72.3 ppm [s, 2 C, { $C_{2}H_{4}$ }, ${}^{1}J_{Pt-C} = 101$ Hz]; 121.6 ppm [q, 1 C, $\{OSO_2CF_3\}$, ${}^1J_{C-F} = 330$ Hz).

Cp*PtMe₂(CH₂=CHMe)(OTf)

CH₂=CHMe (1 atm) was admitted to a Schlenk tube containing an orange, homogeneous solution of $Cp*PtMe_2(OTf)$ (0.30 g, 0.59 mmol) in C_6H_6 (5 ml). The mixture, which immediately became cloudy and pale yellow, was stirred 5 min. at room temperature. The very thick reaction mixture was centrifuged, washed with benzene $(2 \times 5 \text{ ml})$ and pentane $(2 \times 10 \text{ ml})$ ml), and dried by exposure to a gentle stream of air. Yield : 0.30 g (92%). Anal. Calc. for $C_{16}H_{27}F_3O_3SPt$: C, 34.84%; H, 4.93%. Found: C, 34.24%; H, 4.88%. IR (KBr pellet, cm^{-1}): 2981 (s), 2958 (s), 2897 (vs), 2850 (m), 2804 (w), 1632 (w), 1527 (m), 1498 (w), 1452 (s), 1383 (s), 1350 (m), 1294 (s), 1250 (s), 1165 (s), 1074 (w), 1030 (s), 835 (w), 800 (w), 766 (w), 752 (w), 638 (s), 615 (w), 579 (m), 550 (w), 521 (m), 494 (w), 436 (w), 415 (w). ¹H NMR (CD₂Cl₂) : δ 1.92 ppm [s, 15 H, { η^5 -C₅(CH₃)₅}]; δ 0.65 ppm [s, 3 H, {CH₃}, ${}^{2}J_{Pt H} = 71 \text{ Hz}$; $\delta 1.21 \text{ ppm} [s, 3 \text{ H}, {CH_{3}}, {}^{2}J_{Pt-H} = 70$ Hz]; δ 1.71 ppm [d, 3H, {CH₂==CH(CH₃)}, ⁴J_{H-H} = 6 Hz, ³J_{Pt-H} = 37 Hz]; δ 3.64 ppm [m, 2 H, {CH₂==CH(CH₃), CH₂ proton *cis* to CH₃}; δ 4.38 ppm [m, 1 H, {CH₂==CH(CH₃), CH₂ proton *trans* to CH₃}]. ¹⁹F NMR (CD₂CL₂): -16.1 ppm [s]. ¹³C{¹H} NMR (CD₂Cl₂): 3.2 ppm [s, 1 C, {CH₃}, ¹J_{Pt-C} = 578 Hz]; 5.7 ppm [s, 1 C, {CH₃}, ¹J_{Pt-C} = 606 Hz]; 8.4 ppm [s, 5 C, { $\eta_5C_5(CH_3)_5$]; 111.9 ppm [s, 5 C { $\eta^5-C_5(CH_3)_5$]; 18.4 ppm [s, 1 C, {CH₂==CH(CH₃)}]; 71.1 ppm [s, 1 C, {CH₂==CH(CH₃)], ¹J_{Pt-C} = 108 Hz]; 93.4 ppm [s, 1 C, {CH₂==CH(CH₃)], ¹J_{Pt-C} = 83 Hz]; 121.5 ppm [q, 1 C, {OSO₂CF₃}, ¹J_{C-F} = 312 Hz].

Cp*PtMe₂(CO)(OTf)

CO (1 atm) was admitted to a Schlenk tube containing an orange, homogeneous solution of $Cp*PtMe_2(OTf)$ (0.21 g, 0.42 mmol) in C_6H_6 (5 ml). The mixture, which immediately became cloudy and off-white, was stirred 30 min. at room temperature. The off-white solid was then allowed to settle, isolated by filtration, and dried by exposure to a gentle stream of air. Yield: 0.19 g (86%). Anal. Calc. for $C_{14}H_{21}F_{3}O_{4}SPt$: C, 31.29%; H, 3.94%. Found: C, 31.27%; H, 3.99%. IR (KBr pellet): 2983 (m), 2926 (s), 2897 (m), 2852 (w), 2114 (vs), 1612 (s), 1502 (m), 1462 (s), 1425 (s), 1385 (m), 1269 (vs), 1240 (vs), 1221 (s), 1153 (vs), 1078 (w), 1030 (vs), 874 (w), 837 (w), 752 (w), 696 (w), 638 (vs), 571 (m), 517 (m), 472 (m), 442 (w), 417 (m). ¹H NMR (CD₂Cl₂): δ 2.12 ppm [s, 15 H, { η^{5} -C₅(CH₃)₅}, ${}^{3}J_{Pt-H} = 10$ Hz]; δ 1.20 ppm [s, 6 H, 2 { CH_3 }, ${}^2J_{Pt-H} = 69$ Hz]. ${}^{19}F$ NMR (CD_2Cl_2): -16.1 ppm [s]. ¹³C{¹H} NMR (CD₂Cl₂): -1.6 ppm [s, 2 C, 2 { CH_3 }, ${}^1J_{Pt-C} = 505$ Hz]; 8.8 ppm [s, 5 C, $\{\eta^{5}-C_{5}(CH_{3})_{5}\}$; 113.1 ppm [s, 5 C, $\{\eta^{5}-C_{5}(CH_{3})_{5}\}$, ${}^{1}J_{Pt-C} = 20$ Hz]; 121.6 ppm [q, 1 C, {OSO₂CF₃}, ${}^{1}J_{C F} = 311 \text{ Hz}$; 155.9 ppm [s, 1 C, {CO}].

Cp*PtMe₂(NH₃)(OTf)

NH₃ (1 atm) was admitted to a Schlenk tube containing an orange, homogeneous solution of $Cp*PtMe_2(OTf)$ (0.30 g, 0.59 mmol) in C_6H_6 (10 ml). The mixture, the color of which immediately became tan, was stirred 5 min. at room temperature. The volatile components were removed under reduced pressure, leaving a tan crystalline solid behind. Yield : 0.28 g (89%). Anal. Calc. for C₁₃H₂₄F₃NO₃SPt: C, 29.66%; H, 4.59%; N, 2.66%. Found: C, 29.60%; H, 4.65%; N, 2.63%. IR (KBr pellet, cm^{-1}): 3280 (s), 3244 (s), 3215 (s), 3169 (s), 2949 (s), 2904 (s), 2816 (w), 1585 (w), 1510 (m), 1452 (s), 1385 (s), 1362 (m), 1325 (vs), 1277 (vs), 1257 (vs), 1236 (vs), 1157 (vs), 1103 (w), 1074 (w), 1034 (vs), 949 (w), 852 (w), 833 (w), 800 (w), 756 (m), 640 (vs), 575 (m), 542 (w), 517 (s), 480 (w), 438 (w), 422 (w). ¹H NMR (CD₂Cl₂): δ 1.83 ppm [s, 15 H, { η^{5} -C₅(CH₃)₅}]; δ 0.92 ppm [s, 6 H, $\{CH_3\}$, ${}^{2}J_{Pt-H} = 74$ Hz]; δ 3.41 ppm [br, 3 H,

{NH₃}]. ¹⁹F NMR (CD₂Cl₂): -16.2 ppm [s]. ¹³C{¹H} NMR (CD₂Cl₂): -0.5 ppm [s, 2 C, 2 {CH₃}, ¹J_{Pt-C} = 664 Hz]; 8.2 ppm [s, 5 C, { η^{5} -C₅(CH₃)₅}]; 106.5 ppm [s, 5 C, { η^{5} -C₅(CH₃)₅}, ¹J_{Pt-C} = 30 Hz]; 124.1 ppm [q, 1 C, {OSO₂CF₃}, ¹J_{C-F} = 322 Hz].

Cp*PtMe₂(NH₂Bu^t)(OTf)

NH₂Bu^t vapor (1 atm) was admitted to a Schlenk tube containing an orange, homogeneous solution of $Cp*PtMe_2(OTf)$ (0.20 g, 0.40 mmol) in C_6H_6 (10 ml). The mixture, which immediately became cloudy and yellow, was stirred 30 min. at room temperature. The reaction mixture was then allowed to settle, yielding a pale yellow crystalline solid under a pale orange supernatant. The solid was isolated by filtration, washed with pentane $(1 \times 10 \text{ ml})$, and vacuum-dried. Yield: 0.19 g (84%). Anal. Calc. for $C_{17}H_{32}F_{3}NO_{3}$ SPt: C, 35.05%; H, 5.54%, N, 2.40%. Found: C, 35.25%; H, 5.56%; N, 2.12%. IR (KBr pellet, cm⁻¹): 3255 (s), 3224 (s), 3151 (s), 2972 (s), 2910 (s), 2823 (w), 1601 (m), 1510 (m), 1446 (s), 1377 (s), 1263 (vs), 1223 (vs), 1205 (s), 1188 (s), 1157 (vs), 1074 (w), 1032 (s), 931 (w), 893 (m), 831 (w), 752 (m), 638 (s), 573 (m), 542 (w), 517 (s), 447 (m), 440 (m). ¹H NMR $(CD_2Cl_2): \delta$ 1.84 ppm [s, 15 H { η^5 -C₅ $(CH_3)_5$ }, ${}^{3}J_{Pt-C} = 12 \text{ Hz}$]; δ 0.99 ppm [s, 6 H, 2 {CH₃}, ${}^{2}J_{Pt H}$ = 73 Hz]; δ 1.15 ppm [s, 9 H, {NH₂C(CH₃)₃}]; δ 3.94 ppm [br, 2 H, $\{NH_2C(CH_3)_3\}$]. ¹⁹F NMR (CD_2Cl_2) : -16.0 ppm [s]. ¹³C{¹H} NMR (CD_2Cl_2) : 3.3 ppm [s, 2 C, 2 { CH_3 }, ${}^1J_{Pt-C} = 671$ Hz]; 9.0 ppm [s, 5 C, { η^{5} -C₅(CH₃)₅}]; 107.3 ppm [s, 5 C, { η^{5} -C₅(CH₃)₅}, $^{1}J_{PI-C} = 25 \text{ Hz}$; 29.7 ppm [s, 3 C, {NH₂C(CH)₃}]; 56.3 ppm [s, 1 C, {NH₂C(CH₃)₃}]; 121.3 ppm [q, 1 C, $\{OSO_2CF_3\}, {}^1J_{C-F} = 321 \text{ Hz}].$

Cp*PtMe₂N₃

At -35° C, THF (3 ml) was added to a mixture of Cp*PtMe₂(OTf) (0.18 g, 0.35 mmol) and NaN₃ (0.12 g, 1.80 mmol). The mixture was stored at -35° C for 30 min. and then allowed to warm to room temperature and stirred for 20 min. The volatile components were removed in vacuo and the product was extracted from the solid residue into pentane (2×10) ml, 4×5 ml). The first extract was orange and the final extract was colorless. The extracts were filtered and combined. The filtrate was concentrated under reduced pressure so that the volume was approx. $\frac{1}{2}$ the original volume. The product, an orange crystalline solid, was crystallized from this concentrated pentane solution at -78° C, isolated by filtration, and dried in vacuo. Yield: 0.06 g (41%). Anal. Calc. for $C_{12}H_{21}N_3Pt$: C, 35.82%; H, 5.26%; N, 10.44%. Found: C, 35.42%; H, 5.23%; N, 9.99%. IR (KBr pellet, cm⁻¹): 2974 (s), 2960 (s), 2897 (s), 2812 (m), 2008 (vs), 1518 (s), 1446 (vs), 1431 (vs), 1381 (vs), 1354 (s), 1282 (vs), 1230 (s), 1205 (s), 1153 (s), 1095 (w), 1072 (m), 1028 (m), 951 (w), 837 (m), 798 (w),

619 (m), 582 (m), 548 (s). ¹H NMR (CD₂Cl₂): δ 1.78 ppm [s, 15 H, { η^{5} -C₅(CH₃)₅}, ³J_{Pt-H} = 13 Hz]; δ 0.96 ppm [s, 6 H, 2 {CH₃}, ²J_{Pt-H} = 77 Hz]. ¹³C{¹H} NMR (CD₂Cl₂): -0.3 ppm [s, 2 C, 2 {CH₃}, ¹J_{Pt-C} = 710 Hz]; 8.1 ppm [s, 5 C, η^{5} -C₅(CH₃)₅]; 106.0 ppm [s, 5 C, { η^{5} -C, { η^{5}

Cp*PtMe₂[S(p-tol)]

At -35° C, THF (3 ml) was added to a mixture of Cp*PtMe₂OTf (0.18 g, 0.35 mmol) and KS(p-tol) (0.06 g, 0.37 mmol). The mixture was stored at -35° C for 30 min. and then allowed to warm to room temperature and stirred for 15 min. The volatile components were removed in vacuo and the product was extracted from the solid residue into pentane (3×10) ml, 2×5 ml). The first extract was red and the final extract was colorless. The extracts were filtered and combined. The filtrate was concentrated under reduced pressure so that the volume was approx. $\frac{2}{3}$ the original volume. The product, an orange crystalline solid, was crystallized from this concentrated pentane solution at -78° C, isolated by filtration, and dried in vacuo. Yield: 0.11 g (61%). Anal. Calc. for C₁₉H₂₈SPt: C, 47.19%; H, 5.84%. Found: C, 47.29%; H, 5.70%. IR (KBr pellet, cm⁻¹): 3059 (w), 2956 (m), 2895 (m), 2856 (m), 2812 (m), 1884 (w), 1630 (w), 1593 (w), 1514 (m), 1483 (s), 1444 (s), 1423 (s), 1383 (s), 1356 (m), 1259 (w), 1225 (m), 1211 (w), 1198 (m), 1176 (w), 1155 (m), 1101 (w), 1080 (s), 1016 (m), 951 (w), 933 (w), 847 (w), 829 (w), 806 (vs), 702 (w), 685 (w), 627 (m), 609 (m), 586 (w), 546 (m), 494 (vs), 465 (w), 449 (w), 440 (w), 417 (w). ¹H NMR (CD₂Cl₂): δ 1.73 ppm [s, 15 H, $(\eta^{5}-C_{5}(CH_{3})_{5}, {}^{3}J_{Pt-H} = 9 Hz]; \delta 0.78$ ppm [s, 6 H, 2 (CH₃), ${}^{2}J_{Pt-H} = 80$ Hz]; δ 2.21 ppm [s, 3 H, $\{SC_6H_4(CH_3)\}\}$; δ 6.84 ppm [d, 2 H, $\{SC_6H_4(CH_3)\}, \ {}^{3}J_{H-H} = 8 \ Hz]; \ \delta \ 7.08 \ ppm \ [d, 2 \ H,$ $\{SC_6H_4(C_3)\}, \quad {}^{3}J_{H-H} = 8 \quad Hz]. \quad {}^{13}C\{{}^{1}H\} \quad NMR$ $(CD_2Cl_2): -3.9 \text{ ppm} [s, 2 \text{ C}, 2 (CH_3), {}^1J_{Pt-C} = 690$ Hz]; 8.1 ppm [s, 5 C, $(\eta^{5}-C_{5}(CH_{3})_{5}]$; 132.9 ppm [s, 5 C, $(\eta^{5}-C_{5}(CH_{3})_{5}, {}^{1}J_{Pt-C} = 30 \text{ Hz}]$; 21.1 ppm [s, 1 C, SC₆H₄(CH₃)]; 105.7 ppm [s, 2 C, SC₆H₄(CH₃)]; 128.9 ppm [s, 2 C, $SC_6H_4(CH_3)$]; 133.5 ppm [s, 1 C, $SC_{6}H_{4}(CH_{3})$; 137.1 ppm [s, 1 C, $SC_{6}H_{4}(CH_{3})$].

Formation of Cp*PtMe₂[S(p-tol)] from Cp*PtMe₂I

THF-d₈ (1 ml) was added to a mixture of $Cp*PtMe_2I$ (0.006 g, 0.01 mmol) and KS(p-tol) (0.006 g, 0.04 mmol). ¹H NMR spectroscopy revealed the formation of $Cp*PtMe_2[S(p-tol)]$ to be complete within 30 min. at room temperature.

Reversibility of C₂H₄ coordination to Cp*PtMe₂(OTf)

A solution of $Cp*PtMe_2(C_2H_4)^+(OTf)^-$ (0.02 g, 0.04 mmol) in CH_2Cl_2 (5 ml) was magnetically stirred as the volatile components were slowly removed under

reduced pressure, leaving a yellowish orange solid. ¹H NMR analysis (CD_2Cl_2) revealed the solid to be a mixture of Cp*PtMe₂(C₂H₄)⁺(OTf)⁻ (76%) and Cp*PtMe₂(OTf) (24%).

Reactivity of Cp*PtMe2OTf toward SnMe4

SnMe₄ (2 μ l, 0.01 mmol) was added to a solution of Cp*PtMe₂OTf (0.007 g, 0.01 mmol) in CDCl₃ (1 ml). ¹H NMR spectroscopy revealed the formation of Cp*PtMe₃ to be complete within 5 min. at room temperature [17].

Reactivity of Cp*PtMe₂(OTf) toward Cp₂ZrMe₂

CDCl₃ (1 ml) was added to a mixture of Cp*PtMe₂-(OTf) (0.01 g, 0.02 mmol) and Cp₂ZrMe₂ (0.005 g, 0.02 mmol). ¹H NMR spectroscopy revealed the formation of Cp*PtMe₃ to be complete within 20 min. at room temperature [17].

Reactivity of Cp*PtMe2(OTf) toward MeI

MeI (1 μ l, 0.02 mmol) was added to a solution of Cp*PtMe₂(OTf) (0.006 g, 0.01 mmol) in C₆D₆ (1 ml). 'H NMR spectroscopy revealed the formation of Cp*PtMe₂I and MeOTf to be complete within 3 h at room temperature [18].

X-Ray Structure Determination of Cp*PtMe₂[S(p-tol)]

Crystal data and refinement parameters for $Cp*PtMe_2[S(p-tol)]$ are summarized in Table 2. An orange polyhedral crystal of Cp*PtMe₂[S(p-tol)] (approximate dimensions $0.12 \times 0.15 \times 0.27$ mm), obtained from a concentrated pentane solution at -35° C, was mounted on a glass fiber using Paratone N hydrocarbon oil. All measurements were made on a Siemens SMART diffractometer using graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å). Cell constants and an orientation matrix, obtained from a least-squares refinement using the measured positions of 5800 reflections with $I > 10\sigma(I)$ in the range $3.00 < 2\Theta < 45.00^{\circ}$, correspond to a primitive monoclinic cell. Systematic absences were uniquely consistent with the space group $P2_1/c$ (No. 14). The data were collected at a temperature of $-142 \pm 1^{\circ}$ C. Data were integrated using the program SAINT with box parameters of $1.6 \times 1.6 \times 0.6^{\circ}$ to a maximum 2 Θ value of 52.1°. The data were corrected for Lorentz and polarization effects. No decay correction was applied. Analysis of the data with XPREP indicated the space group and allowed for calculation of the absorption coefficient. The structure was solved by direct methods and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in idealized positions after location on a difference Fourier map, but not refined. All calculations were performed using the teXsan crystallographic software package of Molecular Structure Corporation.

Acknowledgements-Funding through NIH Grant No. GM-25459 is gratefully acknowledged. We thank Dr F. J. Hollander, Director of the UC Berkeley X-ray diffraction facility (CHEXRAY), for the structural characterization of Cp*PtMe₂[S(p-tol)].

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