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Effects of Trifluoromethyl Substituents in a Tris(pyrazolyl)borate Ligand: A Structural and Spectroscopic Study of Analogous Platinum(IV) Trimethyl Complexes

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To gain insight into how fluorination of the popular hydridotris(pyrazolyl)borate (Tp) ligands modifies the properties of organometallic compounds containing metal-bound alkyls, the novel Pt(IV) complex $Tp^{(CF_3)_2}PtMe_3$ (**1**; $Tp^{(CF_3)_2}$ = hydridotris(3,5-bis(trifluoromethyl)pyrazolyl)borate) was synthesized and fully characterized. X-ray crystallographic studies were carried out on **1** and on the nonfluorinated analogue $Tp^{Me_2}PtMe_3$ (**2**; Tp^{Me_2} = hydridotris(3,5-dimethylpyrazolyl)borate). The structural and NMR spectral data for the complexes are compared and provide strong evidence for substantially weaker coordination of the fluorinated Tp ligand. The Pt–N bonds are significantly longer and the $Pt-CH_3$ bonds are slightly shorter in the fluorinated complex. These structural features are echoed in the relative magnitudes of the J_{Pt-H} and J_{Pt-C} coupling constants for the two complexes. The close spatial contact between the protons of the $Pt^{IV}-CH_3$ group and fluorines of the 3-CF_3 group of the *cis*-pyrazole ring results in a formal $^6J_{H-F} = 1.8$ Hz. The nature of this coupling with the possible contribution of intramolecular hydrogen bonding is discussed.

Introduction

The fluorination of "classical" ligands is a powerful tool for the modification of the coordination sphere of inorganic and organometallic complexes. Both the physical and chemical properties of metal complexes can be dramatically altered by incorporating fluorines into the ligands. For example, the solubility properties of catalysts with fluorinated ligands have led to the novel and promising concept of fluorous phase catalysis, which greatly facilitates the separation of catalyst from product.[1] The electronic properties of fluorinated ligands also differ significantly from those of nonfluorinated ligands, such that the donor ability of a ligand can be substantially modified by the incorporation of fluorines. In addition, increased thermal and oxidative stability of some transition-metal complexes, greater compatibility with acidic media, and other reactivity distinctly different from that of the nonfluorinated analogues can be achieved.[2,3]

Although a variety of fluorinated ligands and their metal complexes have been investigated, fluorination of the popular hydridotris(pyrazolyl)borate class of ligands,[4] has only recently received attention.[3,5] The synthesis of potassium hydridotris(3,5-bis(trifluoromethyl)pyrazolyl)borate ($KTp^{(CF_3)_2}$, isolated as an adduct of dimethylacetamide, $KTp^{(CF_3)_2}\cdot DMAC$) was reported in 1995 by Dias and co-workers.[5a] However, the use of this ligand in transition-metal organometallic chemistry has been limited. For example, while metal carbonyl, alkene, alkyne, and arene complexes of this ligand have been reported, metal alkyl complexes containing this fluorinated Tp ligand have been conspicuously absent.[5]

In this contribution, we report the synthesis and full characterization (including an X-ray crystal structure) of the Pt(IV) trimethyl complex of hydridotris(3,5-bis(trifluoromethyl)pyrazolyl)borate), $Tp^{(CF_3)_2}PtMe_3$ (**1**). To properly evaluate the effect of fluorination of the "classic" Tp^{R_2} (hydridotris(3,5-dialkylpyrazolyl)borate) ligand on the structural and spectroscopic properties of the organometallic fragment, we have also characterized the known nonfluorinated analogue $Tp^{Me_2}PtMe_3$ (**2**; Tp^{Me_2}

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= hydridotris(3,5-dimethylpyrazolyl)borate)[6] by X-ray crystallography and NMR spectroscopy. A detailed examination and comparison of the structural and spectroscopic properties of compounds **1** and **2** are presented.

Results and Discussion

Preparation of the Fluorinated Tp$^{(CF_3)_2}$ Ligand and the Pt(IV) Complexes 1 and 2. The potassium salt of the fluorinated ligand hydridotris(3,5-bis(trifluoromethyl)pyrazolyl)borate (KTp$^{(CF_3)_2}$) was prepared from a melt of 3,5-bis(trifluoromethyl)pyrazole and KBH_4 at 170 °C and isolated in 57% yield. This is a significantly higher yield than reported in a published procedure for the potassium salt, in which anhydrous dimethylacetamide (DMAC) was used as the solvent (21% yield of KTp$^{(CF_3)_2}$·DMAC).[5a] However, it should be noted that high-yield syntheses (67% and 76%) of the sodium salt NaTp$^{(CF_3)_2}$, using either benzene or kerosene, respectively, as a solvent have been previously reported.[5b,j] In addition, sodium salts of other fluorinated alkyl Tp derivatives have been prepared using a "melt" procedure similar to that reported here for the potassium salt.[5e]

The Pt(IV) complexes Tp$^{(CF_3)_2}$PtMe$_3$ (**1**) and Tp^{Me_2}PtMe$_3$ (**2**)[6] were synthesized by the reaction of the Pt(IV) trimethyl triflate tetramer $[PtMe_3(OSO_2CF_3)]_4$[7] with KTp$^{(CF_3)_2}$ or KTp^{Me_2}, respectively, in acetone. Compound **1** was isolated by sublimation from the residue remaining after the solvent was removed from the reaction. X-ray quality crystals of **1** were grown by slow evaporation from an acetone solution at room temperature. Compound **2** was isolated by crystallization directly from the reaction mixture.

Molecular Structures of 1 and 2. Although hydridotris(pyrazolyl)borate ligands are very common in organometallic chemistry,[4] there are only a few examples of crystallographically characterized Pt complexes of these ligands.[8,9] Structures of perhaps the simplest Pt(IV) alkyl complexes of the popular Tp and Tp^{Me_2} ligands, TpPtMe$_3$ (Tp = hydridotris(pyrazolyl)borate) and Tp^{Me_2}PtMe$_3$ (**2**, Tp^{Me_2} = hydridotris(3,5-dimethylpyrazolyl)borate), have not yet been reported. A recent article which included X-ray structural data for the related tris(indazol-1-yl)borate complex [(ind)$_3$BH]PtMe$_3$[9d] was limited to a comparison of the structural data with those *calculated* (SCF level) for $[(H_2C{=}NNH)_3BH]PtMe_3$,[10] a model for TpPtMe$_3$.

Table 1. Crystal Data and Structure Refinement Details for Tp^{Me_2}PtMe$_3$ (2) and Tp$^{(CF_3)_2}$PtMe$_3$ (1)

	Tp^{Me_2}PtMe$_3$ (**2**)	Tp$^{(CF_3)_2}$PtMe$_3$ (**1**)
formula	$C_{18}H_{31}BN_6Pt$	$C_{18}H_{13}BF_{18}N_6Pt$
fw	537.39	861.24
temp (K)	161(2)	161(2)
wavelength (Å)	0.710 70	0.710 70
cryst descripn	colorless prism	colorless prism
crystal system	monoclinic	monoclinic
space group	$P2_1/m$ (No. 11)	$P2_1/c$ (No. 14)
a (Å)	8.0426(3)	14.6933(2)
b (Å)	13.7242(9)	15.7491(3)
c (Å)	9.5916(5)	11.5643(2)
α (deg)	90	90
β (deg)	101.613(3)	111.3290(10)
γ (deg)	90	90
V (Å^3)	1037.03(10)	2492.76(7)
Z	2	4
d_{calcd} (g cm^{-3})	1.721	2.295
μ (mm^{-1})	6.779	5.787
$F(000)$	528	1632
cryst size (mm)	0.23 × 0.03 × 0.03	0.09 × 0.09 × 0.06
θ range (deg)	$2.17 \le \theta \le 30.49$	$2.29 \le \theta \le 30.50$
index ranges	$-8 \le h \le 8$, $-11 \le k \le 19$, $-13 \le l \le 13$	$-20 \le h \le 20$, $-22 \le k \le 19$, $-16 \le l \le 15$
no. of rflns collected/unique	14 068/2782	59 890/7539
abs cor	SCALEPACK	
refinement method	full-matrix least-squares on F^2	
no. of data/restraints/params	2782/0/133	7539/0/400
goodness of fit on F^2	1.054	0.940
R1 ($I > 2\sigma(I)$)	0.0434	0.0382
wR2[a] (all data)	0.1336	0.0829

[a] $w = 1/[\sigma^2(F_o^2) + (aP)^2]$, where $P = (F_o^2 + 2F_c^2)/3$ and $a = 0.0798$ for **2** and 0.0336 for **1**.

We were able to prepare X-ray quality crystals of Tp^{Me_2}PtMe$_3$ (**2**) and have determined the crystal structure of this compound. The crystal data and details of structure refinement are summarized in Table 1 with selected interatomic distances and angles provided in Table 2. The molecular structure of compound **2** is shown in Figure 1. A slightly distorted octahedral geometry is observed about Pt with N−Pt−N angles of 86.0(3) and 87.2(2)° and C−Pt−C angles of 88.3(5) and 87.8(3)°. The Pt−N distances of 2.175(6) and 2.180(9) Å fall between the experimental values reported for the [(ind)$_3$BH]PtMe$_3$ analogue (2.13−2.17 Å; average 2.14 Å)[9d] and the calculated value for the TpPtMe$_3$ model complex (2.24 Å).[10] The Pt−C bond lengths of 2.065(11) and 2.047(8) Å are also very similar to the [(ind)$_3$BH]-

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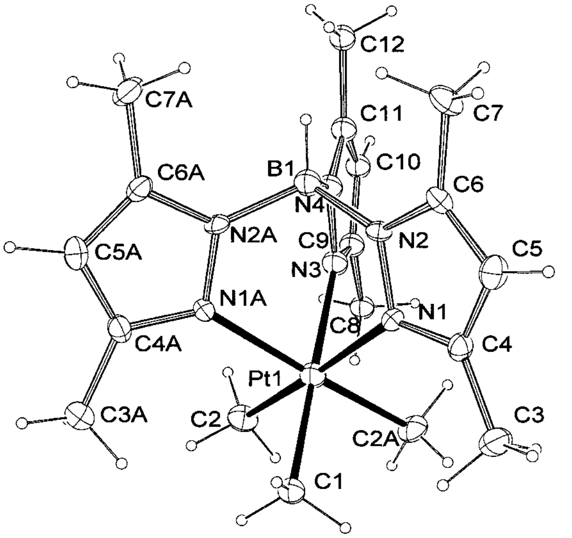

Figure 1. View of the molecular structure of **2**. Heavy atoms are shown as thermal ellipsoids (30% probability) and hydrogen atoms as spheres of arbitrary radius.

Table 2. Selected Interatomic Distances (Å) and Angles (deg) for $Tp^{Me_2}PtMe_3$ (2) and $Tp^{(CF_3)_2}PtMe_3$ (1)

	$Tp^{Me_2}PtMe_3$ (**2**)	$Tp^{(CF_3)_2}PtMe_3$ (**1**)
	Bond Distances	
Pt−N	2.175(6) (N_1, N_{1A}) 2.180(9) (N_3)	2.263(4) (N_1) 2.260(4) (N_3) 2.237(3) (N_5)
Pt−C	2.065(11) (C_1) 2.047(8) (C_2, C_{2A})	2.037(5) (C_1) 2.033(5) (C_2) 2.024(5) (C_3)
	Bond Angles	
C−Pt−C	88.3(5) (C_2−Pt−C_{2A}) 87.8(3) (C_2−Pt−C_1)	89.1(2) (C_2−Pt−C_3) 89.4(2) (C_3−Pt−C_1) 88.1(2) (C_2−Pt−C_1)
N−Pt−N	86.0(3) (N_1−Pt−N_{1A}) 87.2(2) (N_1−Pt−N_3)	84.89(13) (N_5−Pt−N_3) 84.44(12) (N_5−Pt−N_1) 89.63(13) (N_3−Pt−N_1)
	Nonbonded Distances	
N- - -N	3.004(10) (N_1- - -N_3) 2.967(8) (N_1- - -N_{1A})	3.189(5) (N_1- - -N_3) 3.025(5) (N_1- - -N_5) 3.036(5) (N_3- - -N_5)
C- - -F		3.058(7) (C_1−F_2) 3.018(8) (C_1−F_{14}) 3.448(7) (C_1−F_3) 3.100(7) (C_2−F_3) 2.963(6) (C_2−F_9) 3.232(6) (C_3−F_9) 3.243(6) (C_3−F_7) 3.042(8) (C_3−F_{13})
	Interplanar Angles for Pyrazole Planes	
	120.0 ({$N_1N_2C_4C_5C_6$}/{$N_{1A}N_{2A}C_{4A}C_{5A}C_{6A}$}) 120.0 ({$N_3N_4C_9C_{10}C_{11}$}/{$N_1N_2C_4C_5C_6$})	112.2 ({$N_5N_6C_{15}C_{16}C_{17}$}/{$N_1N_2C_5C_6C_7$}) 126.7 ({$N_3N_4C_{10}C_{11}C_{12}$}/$N_1N_2C_5C_6C_7$}) 117.2 ({$N_3N_4C_{10}C_{11}C_{12}$}/{$N_5N_6C_{15}C_{16}C_{17}$})

$PtMe_3$ analogue (2.02−2.06 Å; average 2.06 Å)[9d] and the calculated values for $[(H_2C{=}NNH)_3BH]PtMe_3$ (2.06 Å).[10]

The fluorinated Tp analogue of **2**, $Tp^{(CF_3)_2}PtMe_3$ (**1**), has also been characterized by X-ray crystallography. The details of data collection and crystal data are summarized in Table 1, selected interatomic distances and angles are provided in Table 2, and the molecular structure of **1** is shown in Figure 2. In comparing the structural data presented for compounds **1** and **2**, it should be noted that the octahedral geometry of **1** (with N−Pt−N angles of 84.44(12)−89.63(13)°) is somewhat more distorted than that of **2**. The Pt−N bond lengths are also observed to lengthen significantly on fluorination of the Tp ligand, with the mean Pt−N distance increasing by 0.075 Å. This is similar to the 0.05 Å increase observed by Dias et al. in comparing the Mn−N bond lengths of $Tp^{Me_2}Mn(CO)_3$ and $Tp^{(CF_3)_2}Mn(CO)_3$.[5g] These differences between the M−N bonds of $Tp^{(CF_3)_2}$ and Tp^{Me_2} complexes are attributed to reduced donor ability of the ligand containing the electron-withdrawing fluorine substituents.

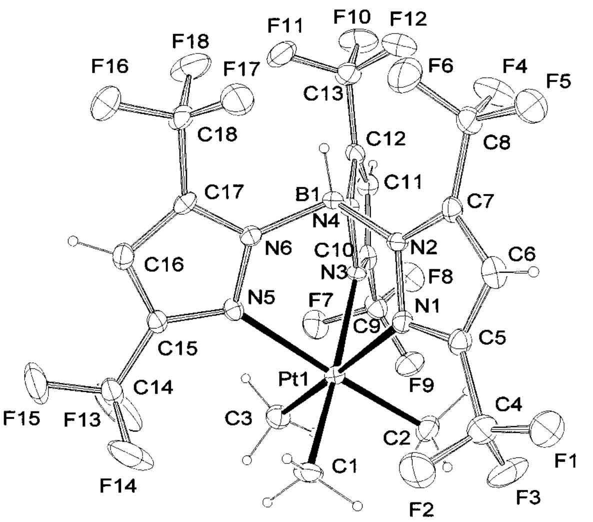

Figure 2. View of the molecular structure of **1**. Heavy atoms are shown as thermal ellipsoids (30% probability) and hydrogen atoms as spheres of arbitrary radius.

In contrast, with respect to the $PtMe_3$ substructure, the differences between complexes **1** and **2** are less profound. The Pt−C distances are slightly shorter in **1** (average 2.03 Å) than in **2** (average 2.06 Å), but not significantly so when the estimated standard deviations are considered. However, as discussed below, the Pt−H and Pt−C coupling constants observed by NMR are also supportive of longer Pt−C bonds in **2**. It is also interesting to compare the Pt−C bond lengths in **1** and **2** to those in other "N_3"$PtMe_3$ complexes in which a typical bond length appears to be about 2.06 Å (see Table S1 in the Supporting Information).[9d,11−14] However, the average Pt−C bonds in analogous Pt(IV) trimethyl complexes with tripodal oxygen donor ligands are in general shorter (2.00−2.04 Å, Table S1).[7,15−18] These differences between the Pt−C bond lengths in the nitrogen-ligated and oxygen-ligated complexes listed are

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Table 3. NMR Data for 1 and 2[a]

		NMR data, δ	
nucleus	assignment/integral	$Tp^{Me_2}PtMe_3$ (**2**)	$Tp^{(CF_3)_2}PtMe_3$ (**1**)
^1H	C−H of ligand/3 H	s, 5.82 ($^4J_{Pt-H} = 6$ Hz)	s, 7.59 ($^4J_{Pt-H} = 3$ Hz)
^1H	CH_3 of ligand/18 H	s, 2.38; s, 2.27	
^1H	CH_3 bound to Pt/9 H	s, 1.30 ($^2J_{Pt-H} = 70.0$ Hz)	septet, 1.58 ($^6J_{F-H} = 1.8$ Hz, $^2J_{Pt-H} = 75.4$ Hz)
^{19}F	3-CF_3		septet, −57.0 ($^6J_{F-H} = 1.8$ Hz)
^{19}F	5-CF_3		d, −58.8 ($^5J_{F-H} = 3.4$ Hz)
$^{13}C\{^1H\}$,[b] [^{13}C]	CH_3 or CF_3 (ligand)	s, 13.1 [q, $^1J_{H-C} = 128$ Hz]; s, 12.8 [q, $^1J_{H-C} = 128$ Hz]	q, 118.8 ($^1J_{F-C} = 271.3$ Hz); q, 119.4 ($^1J_{F-C} = 271.3$ Hz)
$^{13}C\{^1H\}$,[b] [^{13}C]	C(−CF_3 or −CH_3)	s, 149.2; s, 143.0	q, 144.4 ($^2J_{F-C} = 41.4$ Hz); q, 141.0 ($^2J_{F-C} = 41.1$ Hz)
$^{13}C\{^1H\}$,[b] [^{13}C]	C−H	s, 107.6 [d, $^1J_{H-C} = 173$ Hz]	s, 110.7 [d, $^1J_{H-C} = 187$ Hz]
$^{13}C\{^1H\}$,[b] [^{13}C]	CH_3 bound to Pt	s, −10.5 ($^1J_{Pt-C} = 686$ Hz) [q, $^1J_{H-C} = 131$ Hz]	septet, −4.9, ($^5J_{F-C} = 3.9$ Hz, $^1J_{Pt-C} = 712$ Hz) [q, $^1J_{H-C} = 137$ Hz]
^{11}B	B	d, −9.89 ($J_{B-H} = 89$ Hz)[b]	br, −5.00

[a] δ values are referenced to internal TMS (^1H, ^{13}C) and $CFCl_3$ (^{19}F, measured against external, neat F_3CCOOH, reported relative to $CFCl_3$) and external $BF_3 \cdot OEt_2$ (^{11}B). The solvent is acetone-d_6 for ^1H and ^{19}F NMR and $CDCl_3$ for ^{13}C and ^{11}B NMR. [b] The $^{13}C\{^1H\}$ and ^{11}B values for $Tp^{Me_2}PtMe_3$ are from ref 6. Values in brackets are J_{C-H} values from an ^1H-coupled experiment (this work).

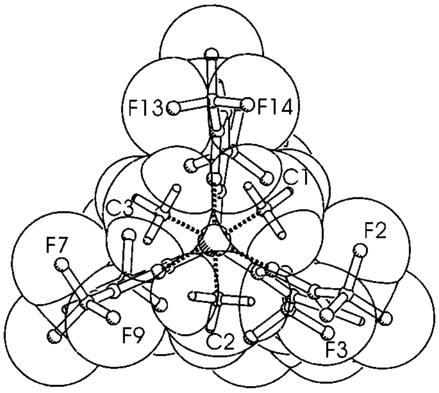

Figure 3. View (PLUTON) onto the $C_1-C_2-C_3$ (Pt−methyl) plane of $Tp^{(CF_3)_2}PtMe_3$ (**1**).

consistent with the differences in the expected *trans* influences of the ligands.[19] It is reasonable that the fluorination of the nitrogen-based hydridotris(dialkylpyrazolyl)borate ligand should reduce its donor ability and so lead to a reduction in its *trans* influence. Thus, the slightly shorter Pt−C bonds in complex **1** relative to **2** are then expected.

Beyond the modification of the Pt−N and Pt−C bond lengths, another interesting property of complex **1** can be seen from Figure 3. The van der Waals radii of the 3-CF_3 groups and the two *cis* CH_3 groups are in contact with each other in **1**, which gives rise to some steric congestion. This crowding may also contribute to the longer Pt−N bonds in **1**. The intramolecular close contacts of the hydrogens of the Pt−CH_3 group and the fluorines of the CF_3 group range from 2.26 to 2.83 Å with an average of 2.63 Å. This is within the sum of the van der Waals radii of H and F ($r_H + r_F = 2.5-2.7$ Å).[20] The heavy-atom distances (ca. 3 Å for C(methyl)−F(trifluoromethyl)) are listed in Table 2.

Apparently, less crowding occurs in complex **2** (space-filling plot in Figure S1 in the Supporting Information), since CH_3 groups are smaller than CF_3 groups.

NMR Spectroscopic Characterization of 1 and 2. The NMR (^1H, ^{19}F, ^{13}C, ^{11}B) spectroscopic data for compounds **1** and **2** are summarized in Table 3. In agreement with the structural data, the solution NMR data for these complexes also support that the fluorinated $Tp^{(CF_3)_2}$ ligand is less strongly bound to Pt(IV) than the Tp^{Me_2} ligand. The Pt−H coupling constant for the methine protons of the pyrazole rings is $^4J_{Pt-H} = 3$ Hz (δ 7.59) for **1** and $^4J_{Pt-H} = 6$ Hz (δ 5.82) for **2**. The significantly smaller platinum−hydrogen coupling constant for the methine proton in the $Tp^{(CF_3)_2}$ complex (**1**) compared to that in the Tp^{Me_2} complex (**2**) is consistent with the longer Pt−N distances (*vide supra*) in complex **1**.

The opposite situation is observed for the platinum−hydrogen coupling constants associated with the platinum-bound methyl groups. The value for **1** ($^2J_{Pt-H} = 75.4$ Hz) is significantly larger than that observed for the platinum-bound methyl groups in **2** ($^2J_{Pt-H} = 70.0$ Hz). This 75.4 Hz coupling constant observed for complex **1** is one of the largest reported for a "N_3"$PtMe_3$ complex ("N_3" = sets of three nitrogen donor ligands wherein the ligands are not necessarily identical or chelating, 28 examples).[9d,11,12,21,22,24a] The $^2J_{Pt-H}$ values in this group range from 65.8 to 72.2 Hz (average value of 69.2 Hz), with only two notable exceptions. For the tetrameric $Me_3Pt(\mu$-azide), where one nitrogen donor is shared by three platinum atoms, a $^2J_{Pt-H}$ value of 74.1 Hz is observed,[23] and $^2J_{Pt-H} = 76.3$ Hz is observed for the methyl group *trans* to the weak donor acetonitrile in (diimine)(MeCN)$PtMe_3^+$.[14] The latter value is the only one known to us that exceeds the coupling constant observed for **1**. Larger $^2J_{Pt-H}$ values are generally associated with more weakly bonded ligands *trans* to the methyl group.[24] The platinum−carbon coupling constant for the platinum-bound methyl group in **1** ($^1J_{Pt-C} = 712$ Hz) is also larger than that for **2** (686 Hz).

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[19] This appears to be somewhat general for $PtMe_3$ complexes comprising all-oxygen or all-nitrogen donor atom sets. However, in mixed-donor-atom complexes, especially where steric bulk is present, the situation is more complicated. For example, there is no significant difference in Pt−C bond length *trans* to nitrogen (2.039 Å) and *trans* to triflate (2.041 Å) in [(tmeda)(F_3CSO_3)$PtMe_3$]^7 (Cambridge Structural Database, refcode ROJPAH).

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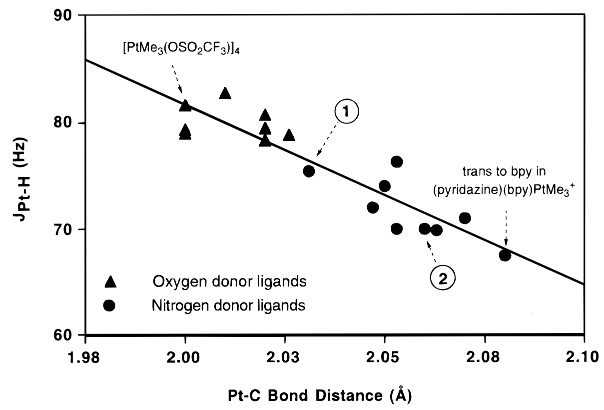

Figure 4. Data and regression line for the correlation between $^2J_{Pt-H(methyl)}$ and r_{Pt-C} for various "D_3"$PtMe_3$ complexes. "D_3" denotes a set of the same donor atoms (oxygen *or* nitrogen), but the ligands are not necessarily identical or chelating. Data for **1** and **2** are from this work, and the other data can be found in ref 7, 9d, 11−16, 17b, 18, and 24a.

These data are consistent with the slightly shorter Pt−C bond lengths in **1** and provide further support for $Tp^{(CF_3)_2}$ being a weaker *trans* influence ligand than Tp^{Me_2} (*vide supra*).

In contrast to the observations for the "N_3"$PtMe_3$ complexes, the Pt−Me coupling constants for "O_3"$PtMe_3$ complexes (11 examples) are generally higher, ranging from 75.7 to 81.6 Hz with an average value of 79.6 Hz.[7,15,16,17b,24a] As shown in Figure 4, there is a good correlation between the $^2J_{Pt-H}$ coupling constants and the crystallographically determined Pt^{IV}−C bond lengths for a series of "D_3"$PtMe_3$ complexes (D = donor group). As expected, it is an inverse relation such that longer Pt^{IV}−C bonds are associated with lower values of $^2J_{Pt-H}$. Complex **1**, with its fluorinated $Tp^{(CF_3)_2}$ ligand, occupies an intermediate position between that for nitrogen donors which do not contain electron-withdrawing substituents and the set of oxygen donor ligands. This nicely demonstrates an important effect of fluorination of a Tp ligand on a late transition-metal alkyl complex. The incorporation of electron-withdrawing groups into the Tp ligand reduces the donor strength of the ligand and so results in a weaker *trans* influence.

It is interesting to note that, in transition-metal carbonyl complexes, fluorination also leads to an increase in M−N bond length as was observed in the $PtMe_3$ case. However, the effect on the M−C bond lengths of the *trans* carbonyl ligands is in contrast to our observations with alkyl ligands. In a comparison of the Tp^{Me_2} and $Tp^{(CF_3)_2}$ complexes of $Mn(CO)_3$,[5g] the M−C bond length is observed to increase with fluorination of the ligand. This elongation is ascribed to a decrease in π-back-bonding to the carbonyl group when a more electron-withdrawing ligand is present. This reduction in the π-density available for back-donation more than compensates for the small expected opposite effect of the reduction in the σ-donor ability of the fluorinated ligand. In the Pt alkyl system, however, only the σ-donor effect is observed, since methyl groups have no π-acceptor properties.

Perhaps the most remarkable feature in the ^1H and ^{19}F NMR spectra of the $Tp^{(CF_3)_2}PtMe_3$ complex (**1**) is the observed long-range coupling between fluorines on the Tp ligand and the hydrogens of the platinum-bound methyl groups. The ^1H NMR signal for the platinum-bound methyl groups appears as a septet rather than as a singlet, as noted for $Tp^{Me_2}PtMe_3$ (**2**). The ^{19}F NMR signal for the 3-CF_3 groups (those attached to the carbons next to the N−Pt bonds) also appears as a septet. These septet signals in the ^1H and the ^{19}F NMR spectra, each with $J_{H-F} = 1.8$ Hz, are shown in Figure 5. Thus, each CH_3 group bonded to Pt is coupled to six fluorine atoms and each of the 3-CF_3 groups is coupled to six protons. The 5-CF_3 groups (those attached to the carbons next to the N−B bonds) do not couple to the protons of the platinum-bound methyl groups and show only a doublet ($J_{H-F} = 3.4$ Hz) in the ^{19}F NMR due to coupling to the hydrogen on the boron atom. This same coupling is observed in the free ligand.[5j]

It is notable that, of the three 3-CF_3 groups in the molecule, only two show coupling to each Pt−CH_3. These are the two CF_3 groups that are *cis* to each Pt−CH_3. For example, the trifluoromethyl group containing C14 couples to the methyl group hydrogens on C1 and C3 but not to those on C2 (Figure 2). Formally, the observed H−F coupling of 1.8 Hz should be described as $^6J_{H-F}$. However, an H−F coupling through *six* bonds is expected to be much smaller. In addition, the fact that the CF_3 group *trans* to the methyl group shows no coupling to that methyl group would argue against the concept of through-bond coupling and suggests that the coupling takes place through space. This suggestion is strongly supported by the X-ray structure discussed above, which exhibits H−F distances within the sum of the van der Waals radii (Figure 3). The complex appears symmetrical in solution at ambient temperature; all three methyl and all three 3-CF_3 groups are equivalent in the NMR spectra. This implies that both the methyl groups and the trifluoromethyl groups are free to rotate on the time scale of the NMR measurements.

Nature of the C−H- - -F−C Interactions. Long-range hydrogen−fluorine couplings (LRHF) were first observed almost 40 years ago.[25,26] Couplings over 6 or more bonds, however, are still relatively rare.[26,27] A variety of long-range couplings for F- - -X (X = Ag,[5j] P,[5j] Tl,[5m] H−(B)[5j,h]) have been observed in metal complexes of fluorinated hydridotris(pyrazolyl)borate ligands, but examples of LRHF couplings involving atoms on the Tp ligand and those contained in other ligands attached to the metal are uncommon. One previous example of such coupling was reported in the characterization of platinum(II) fluoroolefin complexes of hydridotris(pyrazolyl)borate, in which long-range J_{F-H} values of 2−3 Hz were observed.[8b,28] The coupling occurs between the fluorines on the olefin and the 3-H of the Tp pyrazolyl rings, and a through-space mechanism was proposed. The LRHF

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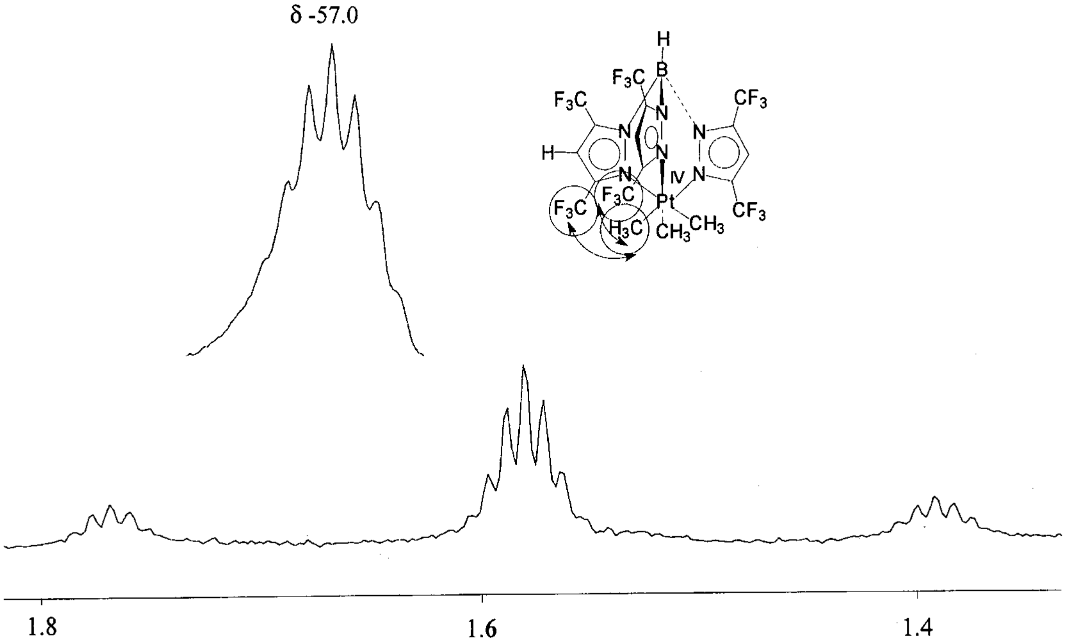

Figure 5. NMR spectra of $\mathrm{Tp^{(CF_3)_2}PtMe_3}$ (**1**) in acetone-d_6. The $\mathrm{CH_3}$–Pt region is shown (^{1}H, 200 MHz) along with the $\mathrm{CF_3}$ region (insert: ^{19}F, 188.3 MHz) for the $\mathrm{CF_3}$ group on the C next to the N–Pt bond. The spatial relation of the coupling groups is also shown.

coupling that is observed in **1** ($J_{\mathrm{F-H}} = 1.8$ Hz) occurs between the 3-$\mathrm{CF_3}$ fluorines on the $\mathrm{Tp^{(CF_3)_2}}$ and the hydrogens of the platinum-bound methyl groups. This is the first example of a formal $^6J_{\mathrm{F-H(-C)}}$ in complexes involving this class of ligands.

A through-space mechanism is most commonly proposed for LRHF coupling.[29] Although bond orientation effects are important for LRHF,[27b,30] Myhre has shown an empirical correlation between interatomic distance and $J_{\mathrm{H-F}}$.[29b] Using our observed coupling constant of 1.8 Hz, Myhre's correlation would predict an F- - -C nonbonded distance of ~2.8 Å. This agrees quite well with the ca. 3 Å distances that were observed for F- - -C close contacts in the crystal structure of **1**. Long-range carbon–fluorine coupling has also been observed in conjunction with LRHF coupling.[31] In our system, a formal $^5J_{\mathrm{C-F}} = 3.9$ Hz was found between the fluorines of the 3-$\mathrm{CF_3}$ groups and the carbons of the platinum-bound methyls. A proposal that carbon-centered orbitals can act to mediate LRHF coupling is supported by the observation of a strong carbon–fluorine coupling interaction.[30,32] The empirical relation for the relative magnitude of the coupling constants ($^5J_{\mathrm{Pt-C}} \approx 2 \times {}^6J_{\mathrm{Pt-H}}$) also holds in our case.[31]

The fact that in complex **1** the hydrogen atoms of the platinum-bound methyl groups are in such close proximity to the fluorine atoms of the $\mathrm{Tp^{(CF_3)_2}}$ ligand raises the question whether a solely van der Waals interaction or a stronger interaction, such as hydrogen bonding, is involved. Discussions of the significance of hydrogen bonding to organic fluorine (X–H- - -F–C interactions where X = O, N, C) have recently appeared in the literature.[33–35] While in a few cases there appears to be some evidence for hydrogen bonding to organic fluorine, a general opinion appears to be that "organic fluorine hardly ever accepts hydrogen bonds."[35] The less polarized C–H moiety is expected to be an even poorer hydrogen bond donor than O–H or N–H toward a C–F group. This expectation is supported by statistics on nonbonded contacts in X-ray structures and *ab initio* calculations.[36] The calculated interaction energy of only 0.85 kJ/mol for an $\mathrm{H_3CF}$- - -$\mathrm{HCH_3}$ model system is more consistent with a van der Waals interaction than a hydrogen bond.[36] However, evidence for weak CH- - -FC interactions both in solution and in the solid state have been reported.[27e,37]

Recently, evidence for CH- - -FC interaction energies on the order of 2.2 kJ/mol were obtained via microwave spectra for the $\mathrm{CH_2F_2}$ dimer in the gas phase.[38] An interesting aspect of this report was the blue shift of the C–H stretching frequency.[39] Red shifts are typically observed for O–H bonds in which the hydrogen acts as a hydrogen bond donor. However, calculations have shown that this blue shift along with the strengthening of the C–H bond is expected in the case of a $\mathrm{C_{sp^3}}$–H

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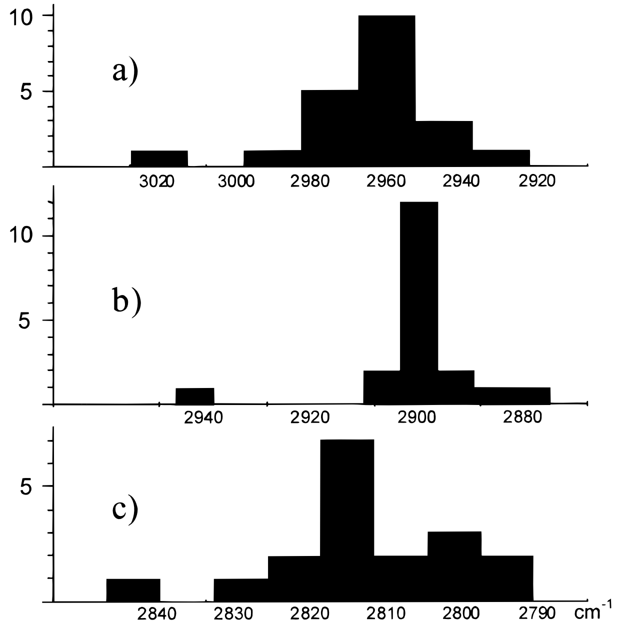

Figure 6. Histograms (counts vs wavenumber/cm^{-1}) for IR data on C−H frequencies in *fac*-trimethylplatinum(IV) compounds. The three bands associated with the CH_3 groups are: (a) ν_1(C−H), (b) ν_2(C−H), and (c) $2\delta(CH_3)$. The available literature covers a wide variety of compounds, including halide, oxygen, and nitrogen donors in *trans* positions and monomeric, dimeric, and tetrameric compounds. The single, significantly blue-shifted value for each band belongs to complex **1**. Data are from this work (**1**; reproduction of literature data for $TpPtMe_3$[21]) and from refs 7, 12, 16, 21, 23, 24b, 41, and 42.

group acting as a hydrogen bond donor.[40] It is then interesting to note that the three infrared bands associated with the CH_3 units in complex **1** (3016, 2944 (ν_{C-H}), 2842 ($2\delta_{CH_3}$) cm^{-1}) appear at higher wavenumbers than observed in other $Pt^{IV}Me_3$ complexes, as shown in Figure 6.[7,12,16,21,23,24b,41,42] Values reported for the two ν_{C-H} bands can serve as indicators of the relative C−H bond strengths. Electronic inductive effects of the ligands *trans* to methyl appear to be relatively small, as can be seen from the homologous series $[\{PtXMe_3\}_2(\mu\text{-pyridazine})]$ or $\{PtXMe_3\}_4$, where ν_{C-H} shows only small (and not apparently systematic) variations (3 and 14 cm^{-1}, respectively) on going from X = Cl to X = I.[41,42] While a direct comparison with ν_{C-H} for complex **2** is difficult due to the ambiguity in the assignments caused by the methyl groups of the Tp^{Me_2}, data have been collected for the analogous complex containing the nonmethylated ligand Tp (Tp = tris(pyrazolyl)borate); in appropriate agreement with the literature,[21] the values of 2951 and 2896 cm^{-1} were measured for ν_{C-H}. $2\delta_{CH_3}$ was observed at 2818 cm^{-1}. Thus, the high vibrational frequencies ν_{C-H} observed for **1** are likely due to the close contact with the trifluoromethyl groups. Additional evidence for slightly stronger C−H bonds in the $Pt-CH_3$ group of $Tp^{(CF_3)_2}PtMe_3$ (**1**) compared to $Tp^{Me_2}PtMe_3$ (**2**) is obtained from the larger $^1J_{H-C}$ coupling constant (Table 3). In general, the value of $^1J_{H-C}$, as measured for a variety of platinum(II)-bound methyl groups, appears to be fairly insensitive to the nature of the other ligands on platinum.[43,44] These observations regarding C−H bond strengthening (blue-shifting of ν_{C-H} and larger $^1J_{H-C}$) may be an indication of a weak hydrogen-bonding interaction between the $Pt-CH_3$ groups and the $3\text{-}CF_3$ moieties.

Conclusions

Examination of the structural and spectroscopic features of the Pt(IV) complex $Tp^{Me_2}PtMe_3$(**2**) and its fluorinated analogue $Tp^{(CF_3)_2}PtMe_3$ (**1**) has allowed a direct evaluation of the effects of Tp^{Me_2} fluorination on a late-metal alkyl complex. It is clear from both the X-ray and the NMR data for compounds **1** and **2** that the fluorination of the classical Tp^{Me_2} ligand leads to significantly weaker Pt−N bonds. This appears to result from both the inductive effect of the fluorines and steric crowding. A bond strengthening effect for the Pt−C bonds, a consequence of the weakening of the nitrogen donor in the *trans* position, is also indicated. In addition, evidence for very close nonbonded H- - -F contacts between the $Pt-CH_3$ and the $3\text{-}CF_3$ groups of the pyrazolyls in both the solid state and solution structures is provided by the X-ray data and the observed coupling between the nuclei in the NMR spectra. These interactions may be simple van der Waals interactions or possibly weak hydrogen-bonding interactions.

Experimental Section

General Procedures. Unless otherwise indicated, all chemicals were used as received (Aldrich). Reactions were carried out under inert conditions using high-vacuum/Schlenk or drybox techniques. Solvents were dried (acetone over anhydrous $CaSO_4$, benzene over Na/benzophenone) and vacuum-transferred into the vessel or NMR tube used. NMR spectra were acquired on a Bruker AC200, DPX 300, or DRX 400WB instrument, and the data are referenced as stated in Table 3. IR spectra were recorded on a Mattson Polaris FT-IR spectrophotometer. Melting points were measured using a digital melting point apparatus (Electrothermal Eng. Ltd.). 3,5-Bis(trifluoromethyl)pyrazole was prepared by a literature method[45] or purchased from Aldrich. $[PtMe_3(OSO_2CF_3)]_4$ was prepared by a literature method.[7]

Synthesis of $KTp^{(CF_3)_2}$ (Potassium Hydridotris(3,5-bis(trifluoromethyl)pyrazolyl)borate). 3,5-Bis(trifluoromethyl)pyrazole ($3,5\text{-}(CF_3)_2Pz\text{-}H$; 1.00 g, 4.9 mmol) and KBH_4 (66 mg, 1.2 mmol) were finely ground with a spatula under N_2 in a 25 mL Schlenk tube. The mixture was heated in an oil bath with stirring under an N_2 atmosphere. For safety, the use of a commercially available heat-stable silicone oil is recommended. The mixture melted at 100 °C. The temperature was increased to 140 °C over a period of 10 min. Many gas bubbles (hydrogen) emerged from the melt; the evolution of gas was

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[43] Large $^1J_{H-C}$ values (137−139 Hz) for Pt^{II}-bonded methyl groups have also been reported by Roddick et al. in complexes containing perfluoroethyl substituents on chelating bis-phosphine ligands.[2f] Examination of the X−ray structures (atomic coordinates from the Cambridge Structural Database) of these complexes (dfepe)PtMe(Me, OTf)[2b] show several Pt−C- - -F close contacts between 3.17 and 3.35 Å. Thus, although the high $^1J_{H-C}$ values were rationalized in terms of inductive effects transmitted through bonds, there may be a through-space influence of the perfluoroalkyl substituents on the C−H bonding of the platinum-bound methyl group.

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almost complete within 10 min. The temperature was then raised to 170 °C over a 15 min period and was held at 170 °C for 1 h 45 min. Throughout the heating process, 3,5-$(CF_3)_2$-Pz-H sublimed and condensed at the cooler parts of the Schlenk tube. This material was melted back into the mixture using a heat gun. The completeness of the reaction and the purity of the products were determined by ^{1}H NMR (acetone-d_6): δ 7.26 (unreacted 3,5-$(CF_3)_2$Pz-H); 6.98 (KTp$^{(CF_3)_2}$ = K[HB-(3,5-$(CF_3)_2$Pz)$_3$]); 6.79 (intermediate, K[H_2B(3,5-$(CF_3)_2$Pz)$_2$]. After the reaction time given above, no K[H_2B(3,5-$(CF_3)_2$Pz)$_2$] remained. The excess 3,5-$(CF_3)_2$Pz-H was removed by sublimation (0.05 Torr, 90 °C, 1 h). KTp$^{(CF_3)_2}$ remained in the Schlenk tube. Yield: 459 mg, 57% based on KBH_4. Anal. Calcd for $K[C_{15}H_4BF_{18}N_6]\cdot H_2O$: C, 26.57; H, 0.89; N, 12.39. Found: C, 26.65; H, 0.52; N, 12.34. IR (KBr): 3162 (ν_{C-H}), 2605 (ν_{B-H}) cm^{-1}. The product can be used directly for the preparation of the platinum complex. If side products are formed (observed when the commercial 3,5-$(CF_3)_2$Pz-H from Aldrich was used), the product can be obtained in pure form by recrystallization from diethyl ether, followed by washing the white crystals with a minimum amount of dry toluene and drying under vacuum for 3 h.

Synthesis of Tp$^{(CF_3)_2}$PtMe$_3$ (1; Tp$^{(CF_3)_2}$ = Hydridotris-(3,5-bis(trifluoromethyl)pyrazolyl)borate). The compounds $[PtMe_3(OSO_2CF_3)]_4$ (164 mg, 0.105 mmol) and KTp$^{(CF_3)_2}$ (277 mg, 0.420 mmol) were dissolved in dry acetone in a sublimation apparatus. After 90 min, the acetone was removed under vacuum. The solid residue was sublimed at 64 °C for 1 day. The temperature was then raised to 90 °C, and the sublimation was continued for 2 days more. Total yield: 253 mg (70%). Anal. Calcd for $C_{18}H_{13}BF_{18}N_6Pt$: C, 25.10; H, 1.52; N, 9.76. Found: C, 25.34; H, 1.51; N, 9.60. Mp: 165−170 °C. IR (KBr): 3168 (ν_{C-H} of pyrazole), 3016, 2944 (ν_{C-H} methyl), 2842 ($2\delta_{C-H}$ methyl), 2651 (ν_{B-H}) cm^{-1}. ^{1}H, ^{19}F, ^{13}C, and ^{11}B NMR data are reported in Table 3.

Synthesis of Tp^{Me_2}PtMe$_3$ (2; Tp^{Me_2} = Hydridotris(3,5-bis(trimethyl)pyrazolyl)borate). This complex, synthesized previously from $[Me_3PtI]_4$,[6] was prepared in situ from [PtMe$_3$-(OSO$_2$CF$_3$)]$_4$ (2.0 mg, 1.3 μmol) and KTp^{Me_2} (1.7 mg, 5.0 μmol) in acetone-d_6 (0.2 mL) at ambient temperature. A ^{1}H NMR spectrum taken after 30 min indicated that the reaction had reached completion. The NMR spectroscopic data (Table 3) are in good agreement with those reported in the literature (^{1}H NMR ($CDCl_3$): δ 5.73 (3H, s, 4-Hpz); 2.34, 2.28 (each 9H, s, 3,5-Me$_2$pz); 1.32 (9H, $^2J_{Pt-H}$ = 70 Hz, Pt−Me)).[6] In addition to the published data, the $^4J_{Pt-H}$ coupling of the pyrazole C−H (6 Hz) was resolved (Table 3).

X-ray Crystal Structure Analyses of 1 and 2. Crystals of **1** were grown from a solution in acetone (2.5 mg/mL) at ambient temperature by means of slow evaporation over a period of 2 weeks. Crystals of **2** were obtained from the reaction mixture at −20 °C over a period of 2 weeks. Data were collected with a Nonius Kappa CCD diffractometer with φ-scans and 20 s exposures per frame for **1**. For **2**, a combination of φ- and ω-scans was used with 15 s exposures. The crystal-to-detector distance was 27 mm for both samples. Except for the treatment of the methyl hydrogen atoms, data for both structures were analyzed by the same methods. Data were reduced using DENZO.[46] The data were corrected by scaling and averaging using the program SCALEPACK.[46] The structure solution was carried out by direct methods using SIR92.[47] All non-hydrogen atoms were refined anisotropically by full-matrix least squares. For **2**, all hydrogen atoms were placed with ideal geometry and were refined with a riding model. Fixed isotropic displacement parameters were given such that they were 1.1 times the U_{eq} value of their parent atom and 1.5 times the U_{eq} value for for methyl hydrogens. Hydrogen atoms in **1** were treated in the same way except for methyl hydrogens, where the H−C−Pt−N torsion angles were refined, which adds an extra parameter per methyl group. SHELXL-97 was used for the refinement.[48] Plots were generated using ORTEP[49] and PLUTON.[50] Crystallographic data are summarized in Table 1, interatomic distances and angles are given in Table 2, and drawings are provided in Figures 1 and 2.

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Supporting Information Available: Tables of atom coordinates, thermal parameters, hydrogen atom parameters, bond distances, and angles for complexes **1** and **2**, a survey of Pt−C bond lengths in platinum(IV) trimethyl compounds, and a space-filling plot for complex **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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