

# Chemical Shift Anisotropy of Organometallic Carbon

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Principal values of  $^{13}\text{C}$  chemical shift tensors have been measured in 19 compounds containing carbon  $\sigma$ -bonded to transition metals, namely,  $\text{PtMe}_2(\text{cod})$ ,  $\text{PtMe}_2(\text{nbd})$ ,  $\text{PtMe}_2(\text{bpy})$ ,  $\text{PtMe}_2(\text{tmeda})$ ,  $\text{cis-PtMe}_2(\text{dmsO})_2$ ,  $\text{PtClMe}(\text{cod})$ ,  $\text{PtClMe}(\text{bpy})$ ,  $\text{Pt}(\text{CH}_2\text{SiMe}_3)_2(\text{cod})$ ,  $\text{Pt}(\text{CH}_2\text{SiMe}_3)_2(\text{nbd})$ ,  $\text{cis-Pt}(\text{CH}_2\text{SiMe}_3)_2(\text{dmsO})_2$ ,  $\text{Pt}(\text{C}\equiv\text{C}-t\text{Bu})_2(\text{cod})$ ,  $\text{Pt}(4-t\text{Bu-phenyl})_2(\text{nbd})$ ,  $[\text{Me}_3\text{PtI}]_4$ ,  $[\text{Me}_3\text{PtOH}]_4$ ,  $(\text{Me}_3\text{Pt})_2\text{SO}_4$ ,  $\text{PdMe}_2(\text{tmeda})$ ,  $\text{Fe}(\text{Cp})(\text{CO})_2\text{Me}$ ,  $\text{Mo}(\text{Cp})(\text{CO})_3\text{Me}$ , and  $\text{Mo}(\text{Cp})(\text{CO})_3\text{Et}$ . A range of behaviours is observed, the most striking of which is a strong dependence of anisotropy on the nature of the other ligands in the complex. A very large anisotropy is induced by the presence of a chelating diolefin on the same metal center. The low-frequency isotropic shifts generally observed for metal-bound carbon are found to result mainly from a single low-frequency component.

## Introduction

Chemical shift is a tensorial property and, to first order, appears to be a symmetric second rank tensor.<sup>1</sup> The chemical shift is therefore represented by six parameters, which are conveniently taken as three principal values and three principal directions. In liquids, isotropic rotation of the molecules averages chemical shifts to their traces. In solids the anisotropic character of chemical shift is readily apparent. Determination of all six parameters generally requires single-crystal studies. However, the three principal values are readily determined in powder samples, either from the observation of powder patterns of static samples,<sup>1</sup> or from spinning sideband intensities under slow magic-angle spinning conditions.<sup>2,3</sup>

In recent years, much information has been collected on chemical shift anisotropy.<sup>4</sup> While carbon has been widely studied in a variety of chemical environments, there have been few studies of organometallic carbon. This is unfortunate, since, besides the intrinsic interest of such studies, the NMR of organometallic complexes is often used as a model in work involving species chemisorbed on metal surfaces.<sup>5–7</sup> For example, both isotropic shift and anisotropy for CO chemisorbed on Ru and Rh<sup>5</sup> agree with those of known carbonyl complexes. This leads to a high degree of confidence that the bonding is similar. Attempts<sup>6</sup> to argue from anisotropies of chemisorbed hydrocarbon fragments are rather speculative, because of the lack of data from known compounds. It would be of considerable assistance in

such studies if particular carbon–metal bonds were found to have characteristic anisotropies.

To date, there have been surveys of  $\pi$ -cyclopentadienyl complexes,<sup>8</sup> of  $\pi$ -complexed olefins,<sup>9,10</sup> and of carbonyls.<sup>4</sup> There have so far been only two studies of the anisotropy of carbon  $\sigma$ -bonded to transition metals. Kim and co-workers<sup>11</sup> observed an extremely large anisotropy for the bridging methylene in  $\text{cis}(\mu\text{-CH}_2)(\mu\text{-CO})[\text{FeCp}(\text{CO})]_2$ . Heyes and Dobson<sup>12</sup> measured anisotropies of the  $\sigma$ -bonded Cp carbons in  $\text{Ti}(\text{Cp})_4$  and obtained anisotropies in the range typical of  $\text{sp}^2$  carbon. Although the authors did not calculate anisotropies, the MAS spectrum of  $\text{Zr}(\text{Cp})_2(\text{CH}_3)_2$  published by Dahmen and co-workers<sup>13</sup> shows unusually large spinning sidebands for the methyl resonance. An approximate calculation based on this spectrum suggests that the methyl anisotropy<sup>14</sup> is in the vicinity of 90 ppm, much larger than for a typical organic methyl group.<sup>4</sup>

The above limited data suggest that there may indeed be some interesting features to be found in the chemical shift anisotropies of organometallic carbon. We have therefore determined, by low-speed MAS, the principal values of chemical shift for carbons  $\sigma$ -bonded to transition metals in some 19 compounds. Our results are reported below.

## Experimental Section

The following compounds<sup>15</sup> were prepared by literature methods:  $\text{PtMe}_2(\text{cod})$ ,<sup>16</sup>  $\text{PtMe}_2(\text{nbd})$ ,<sup>17</sup>  $\text{PtMe}_2(\text{bpy})$ ,<sup>18</sup>  $\text{cis-PtMe}_2(\text{dmsO})_2$ ,<sup>17</sup>  $\text{PtClMe}(\text{cod})$ ,<sup>16</sup>  $\text{PtClMe}(\text{bpy})$ ,<sup>16</sup>  $\text{Pt}(\text{CH}_2\text{SiMe}_3)_2(\text{cod})$ ,<sup>19</sup>

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(14) We adopt the convention that  $\delta_{11}$  is the highest frequency principal component of the chemical shift, and  $\delta_{33}$ , the lowest. We use the term "anisotropy" to indicate  $\delta_{11} - \delta_{33}$ .

Pt(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub>(nbd),<sup>19</sup> Pt(C≡C-<sup>t</sup>Bu)<sub>2</sub>(cod),<sup>20</sup> [Me<sub>3</sub>PtI]<sub>4</sub>,<sup>21</sup> [Me<sub>3</sub>-PtOH]<sub>4</sub>,<sup>22</sup> (Me<sub>3</sub>Pt)<sub>2</sub>SO<sub>4</sub>,<sup>23</sup> PdMe<sub>2</sub>(tmeda),<sup>24</sup> Fe(Cp)(CO)<sub>2</sub>Me,<sup>25</sup> Mo(Cp)(CO)<sub>3</sub>Me,<sup>25</sup> and Mo(Cp)(CO)<sub>3</sub>Et.<sup>25</sup> Pt(4-<sup>t</sup>Bu-phenyl)<sub>2</sub>(nbd),<sup>26</sup> PtMe<sub>2</sub>(tmeda),<sup>24</sup> and *cis*-Pt(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub>(dmsO),<sup>17</sup> were prepared by minor modifications of literature methods for closely related compounds. Adequate purity was verified in all cases by <sup>1</sup>H NMR in solution.

It will be noted that no phosphine complexes are included. A decision was made to exclude compounds involving uncoupled nuclei of high abundance and high gyromagnetic ratio—<sup>19</sup>F and <sup>31</sup>P. This avoids the complications inherent in the interactions between chemical shift and coupling anisotropies,<sup>27,28</sup> and makes the calculation of shift anisotropies from spinning sideband intensities relatively straightforward.

Solid-state NMR measurements were made on a Bruker MSL 300 instrument, with a resonance frequency of 75.47 MHz for <sup>13</sup>C. Excitation was by cross-polarization from protons, using matched rf fields of 50–60 kHz, with proton decoupling at the same field strength. Chemical shifts were determined relative to tetramethylsilane, using adamantane as a secondary standard, with an assumed value of 38.56 ppm for the shift of the high-frequency line. Assignments were made by delayed decoupling,<sup>29</sup> observation of Pt–C couplings where present, and comparison with liquid-phase <sup>13</sup>C spectra. Anisotropies were determined from analysis of sideband intensities under slow magic-angle spinning, rotational frequencies of 500–5000 Hz being used, depending on the magnitude of the anisotropy.

All measurements were made at room temperature, except for FeCp(CO)<sub>2</sub>Me and MoCp(CO)<sub>3</sub>Me. These molecules showed extensive motion in the solid at ambient temperature and had to be cooled to 150 and 170 K, respectively, before a normal carbonyl anisotropy indicated that motions had ceased (*vide infra*).

## Results

**Isotropic Spectra.** Although the main interest in this paper is in anisotropies, the majority of the compounds have not previously been studied by solid-state NMR. We therefore report the isotropic shifts, and where appropriate  $J_{\text{Pt-C}}$  for all compounds, in Table 1. In general these do not differ significantly from literature values obtained in solution, where those have been reported.<sup>16,17,19,24,30–33</sup>

(15) We use the following common abbreviations: cod, 1,5-cyclooctadiene; nbd, bicyclo[2.2.1]hepta-2,5-diene; bpy, 2,2'-bipyridyl; tmeda, *N,N,N',N'*-tetramethyl-1,2-ethanediamine; dmsO, dimethyl sulfoxide; Cp,  $\eta^5$ -cyclopentadienyl; Me, methyl; Et, ethyl; Bu, butyl.

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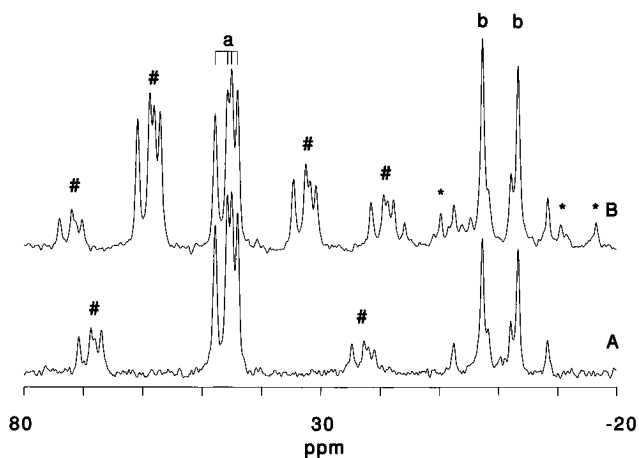
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**Table 1. Observed <sup>13</sup>C Isotropic Shifts (ppm) and One-Bond Platinum–Carbon Couplings (Hz)**

molecule	shift <sup>a</sup> ( $J_{\text{Pt-C}}$ )	assignt
Pt(CH <sub>3</sub> ) <sub>2</sub> (cod)	7.8 (778)	CH <sub>3</sub>
	28.0, 28.6, 33.8	CH <sub>2</sub>
	97.8, 98.2, 101.3,	olefin CH
	102.1	
Pt(CH <sub>3</sub> ) <sub>2</sub> (nbd)	6.4 (828)	CH <sub>3</sub>
	50.6	bridgehead CH
	76.1	CH <sub>2</sub>
	89.0	olefin CH
Pt(CH <sub>3</sub> ) <sub>2</sub> (bpy)	–13.9 (815)	CH <sub>3</sub>
	126.3, 134.5,	bpy
	142.8,* 155.4	
<i>cis</i> -Pt(CH <sub>3</sub> ) <sub>2</sub> (dmsO) <sub>2</sub>	–3.3 (756),	Pt–CH <sub>3</sub>
	2.8 (724)	
	44.0, 45.0,	S–CH <sub>3</sub>
	45.8, 47.8	
Pt(CH <sub>3</sub> ) <sub>2</sub> (tmeda)	–18.9 (804)	Pt–CH <sub>3</sub>
	48.3, 50.1, 53.4	N–CH <sub>3</sub>
	61.6	CH <sub>2</sub>
Pt(CH <sub>3</sub> )Cl(cod)	3.9 (635), 4.8 (635)	CH <sub>3</sub>
	25.8, 27.6, 30.3, 34.8	CH <sub>2</sub>
	85.6, 86.9, 88.1	olefin CH
		<i>cis</i> to Cl
Pt(CH <sub>3</sub> )Cl(bpy)	113.2, 114.7, 117.2	olefin CH
		<i>trans</i> to Cl
	–12.5 (735)	CH <sub>3</sub>
	126.9, 135.9, 138.8,	bpy
	143.6, 147.9,	
	152.6, 156.6	
Pt[CH <sub>2</sub> Si(CH <sub>3</sub> ) <sub>3</sub> ] <sub>2</sub> (cod)	4.8	Si–CH <sub>3</sub>
	12.3 (682)	Pt–CH <sub>2</sub>
	29.3, 31.9	C–CH <sub>2</sub>
	95.2, 95.6,	olefin
	100.7, 102.8	
Pt[CH <sub>2</sub> Si(CH <sub>3</sub> ) <sub>3</sub> ] <sub>2</sub> (nbd)	4.2, 5.1	Si–CH <sub>3</sub>
	19.4	Pt–CH <sub>2</sub>
	49.2	bridgehead CH
	73.3, 74.4	C–CH <sub>2</sub>
	83.3, 85.0, 88.3, 91.6	Olefin CH
	1.9	CH <sub>2</sub>
Pt(4- <sup>t</sup> Bu-phenyl) <sub>2</sub> (nbd)	4.1, 6.2	Si–CH <sub>3</sub>
	40.7, 44.4	S–CH <sub>3</sub>
	32.4	CH <sub>3</sub>
	35.5*	<i>t</i> -C <sub>4</sub> H <sub>9</sub>
	50.1	bridgehead CH
	77.2	CH <sub>2</sub>
	124.9, 134.6,	aromatic
	138.9, 146.2,*	
	152.6* (1192)	
Pt(C≡C- <sup>t</sup> Bu) <sub>2</sub> (cod)	27.2, 35.1	CH <sub>2</sub>
	29.4*	<i>t</i> -C <sub>4</sub> H <sub>9</sub>
	32.8, 33.1	CH <sub>3</sub>
	103.5, 106.6	olefin CH
	84.0* (1416), 85.5*	PtC≡
	(1514), 87.4*	
[(CH <sub>3</sub> ) <sub>3</sub> PtI] <sub>4</sub>	112.0*, 113.6* (357)	CC≡
	14.6	CH <sub>3</sub>
	–8.6 (755)	CH <sub>3</sub>
[(CH <sub>3</sub> ) <sub>3</sub> PtOH] <sub>4</sub>	–12.5 (795),	CH <sub>3</sub>
	–10.6 (804),	
[(CH <sub>3</sub> ) <sub>3</sub> Pt] <sub>2</sub> SO <sub>4</sub>	–10.1 (800)	
Pd(CH <sub>3</sub> ) <sub>2</sub> (tmeda)	–7.4, –5.8	Pd–CH <sub>3</sub>
	48.1, 49.2, 51.3	N–CH <sub>3</sub>
	60.9	CH <sub>2</sub>
Fe(Cp)(CO) <sub>2</sub> CH <sub>3</sub>	–22.2	CH <sub>3</sub>
	85.8	Cp
	218.2*	CO
Mo(Cp)(CO) <sub>3</sub> CH <sub>3</sub>	–23.2	CH <sub>3</sub>
	94.3	Cp
	231.4*	CO <i>cis</i> to CH <sub>3</sub>
	243.3*	CO <i>trans</i> to CH <sub>3</sub>
Mo(Cp)(CO) <sub>3</sub> C <sub>2</sub> H <sub>5</sub>	–3.5	CH <sub>2</sub>
	20.0	CH <sub>3</sub>
	94.5	Cp
	231.5*	CO <i>cis</i> to C <sub>2</sub> H <sub>5</sub>
	240.7*	CO <i>trans</i> to C <sub>2</sub> H <sub>5</sub>

<sup>a</sup> An asterisk indicates a nonprotonated carbon.

It will be noted that in many cases the crystallographic symmetry is lower than the symmetry of the free molecule, and lines are split. For example, in the



**Figure 1.** Spectra of solid *cis*-PtMe<sub>2</sub>(dmsO)<sub>2</sub>: (A) magic-angle spinning at 1740 Hz; (B) spinning at 992 Hz. Identification of lines is as follows: a, S-CH<sub>3</sub> centerbands; b, Pt-CH<sub>3</sub> centerbands, #, S-CH<sub>3</sub> sidebands; \*, Pt-CH<sub>3</sub> sidebands.

spectrum of *cis*-PtMe<sub>2</sub>(dmsO)<sub>2</sub> (Figure 1), there are two Pt-Me lines and four S-Me lines, indicating that the asymmetric unit contains not less than one full molecule. In general, all crystallographically distinct resonances are not seen; in PtMe<sub>2</sub>(cod) the presence of four olefin lines again indicates one molecule in the asymmetric unit, but only three methylene lines and one methyl line are seen, rather than the crystallographically implied four and two. This means that the chemically identical but crystallographically distinct carbons have shift differences less than the resolution achievable in the solid-state experiment. In the case of [PtMe<sub>3</sub>]<sub>2</sub>SO<sub>4</sub>, the peak at -12.5 ppm is of about half the intensity of the other two. This compound is not well-characterized in the literature, and there is some uncertainty as to its degree of hydration.<sup>23,34,35</sup> We have followed the preparative procedure of Ivanova *et al.*,<sup>23</sup> and it may be that this produces a mixture of different hydrated forms. For Pt(C≡C-*t*Bu)<sub>2</sub>(cod), the peaks at 85.5, 87.4, and 112.0 ppm have about one-quarter of the intensity of the main acetylenic peaks at 84.0 and 113.6 ppm. Since the solution NMR spectrum does not show any significant impurities, this suggests either a complicated asymmetric unit or possibly a mixture of polymorphs.

**Anisotropies.** Chemical shift anisotropies have been determined by observing spectra at spinning speeds sufficiently slow to produce spinning sidebands. Where feasible, two or three different spinning speeds have been used for each compound. All observed sidebands were simultaneously least-squares fitted to the theoretical intensities<sup>2</sup> using a Levenberg-Marquardt algorithm. The reported results are based on fits to sideband heights. In several examples where peaks were well-separated we compared these with fits based on areas. Differences are in all cases within the quoted uncertainties.

A nonlinear least-squares fit requires rapid and accurate evaluation of the model function. To this end, our program calculates theoretical sideband intensities by several strategies. For values of  $\mu$  less than 8.0, the series expansion, eq 38 of ref 2 is used (this necessitated

recalculation of the coefficients of Table 3 of this reference to higher indices and higher accuracy). For  $8 \leq \mu < 20$ , we use linear interpolation in a precomputed table of  $I/I_0$  values, computed at a spacing of 0.2 in  $\mu$  and 0.04 in  $\rho$ , using eqs 24 and 33 of ref 2. On the rare occasions when a value for  $\mu \geq 20$  is required, the program evaluates eqs 24 and 33 directly. Finally  $\sum((I/I_0)_{\text{exp}} - (I/I_0)_{\text{calc}})^2$  is minimized with respect to  $\Delta\nu \equiv \mu\nu_{\text{rot}}$  and  $\rho$ , the summation extending over all sidebands observed at all spinning speeds. The three shift components are then derived from  $\Delta\nu$ ,  $\rho$ , and the isotropic shift, in the obvious manner. Our program has been tested on several samples of known anisotropy and found to give correct results in all cases.

The results are presented as the three principal values of the chemical shift tensor, measured with respect to tetramethylsilane, with positive values corresponding to higher resonance frequencies.

We have carried out this procedure for all of the metal-bound carbons. The results for  $\sigma$ -bonded carbons are presented in Table 2 and shown schematically in Figure 2. Table 3 gives our results for  $\pi$ -bonded olefins, cyclopentadienyls, and carbonyls. In some cases it has not been feasible to obtain as many sidebands as desirable. This occurs when a line of low anisotropy has a large width, limiting the lowest spinning speed that can be used (*e.g.* [CH<sub>3</sub>PtI]<sub>4</sub>), or when another group in the molecule generates large numbers of interfering sidebands, due to its much larger anisotropy (*e.g.* for the methyl resonances of PtX(CH<sub>3</sub>)(bpy), sidebands of bpy are troublesome). The number of sidebands used in each case is shown in Tables 2 and 3. Uncertainty estimates given in the tables are standard deviations from the least-squares fitting procedure, when more than 5 sidebands were available. When fewer bands were used, uncertainty limits were estimated by repeating the least-squares fit several times with input data varying from the measured values by amounts commensurate with the noise level in the spectrum. The quoted limits are sufficient to encompass all results obtained in this perturbed fitting procedure.

In some cases crystallographic splittings of chemically equivalent carbons are not sufficient to permit accurate measurements of both sets of sideband intensities. In these cases, the split lines are considered as a composite, and average anisotropies are determined. Such cases are marked with a C in Tables 2 and 3.

**Motions.** As mentioned above, significant molecular motion is present at room temperature in solid FeCp(CO)<sub>2</sub>CH<sub>3</sub> and MoCp(CO)<sub>3</sub>CH<sub>3</sub>. *A priori*, the most likely motions would seem to be rotation of either the Cp ring or of the M(CO)<sub>x</sub>CH<sub>3</sub> unit about the axis joining the metal to the center of the Cp ring. Rapid Cp rotation should cause the Cp carbons to appear axially symmetric, with an anisotropy of the order of 100 ppm.<sup>8</sup> Rotation of M(CO)<sub>x</sub>CH<sub>3</sub> should have a substantial effect on the apparent anisotropy of the carbonyls, which could approach zero if the CO axis makes an angle close to 54.7° with the rotation axis.

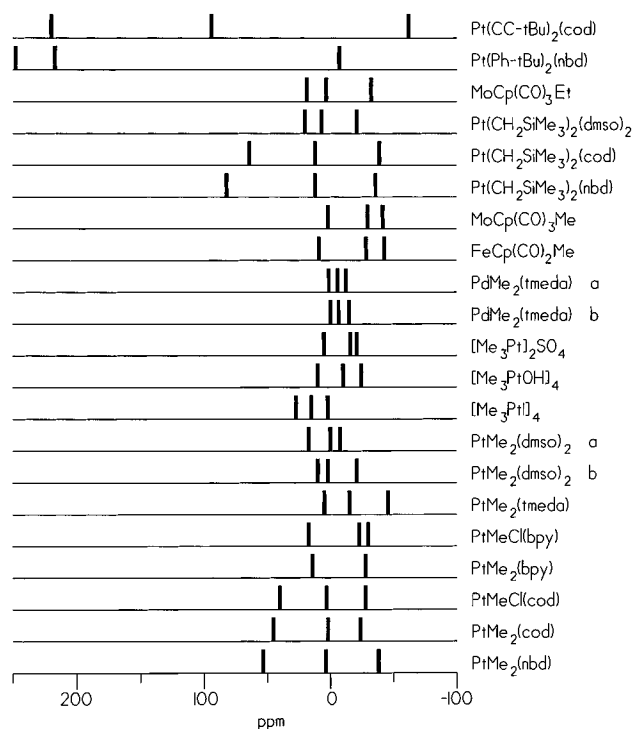
Our room-temperature MAS spectrum of solid FeCp(CO)<sub>2</sub>CH<sub>3</sub> appears nearly isotropic. It is essentially identical to the spectrum published by Toscano and Marks<sup>36</sup> and shows no spinning sidebands. Indeed, a static spectrum at room temperature shows symmetrical lines for all groups, with full widths at half-height of

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**Table 2. Principal Components of Chemical Shift for  $\sigma$ -Bonded Carbons**

compd	isotropic shift (ppm)	no. of sidebands	principal values in ppm (uncertainty) <sup>a</sup>		
Pt(CH <sub>3</sub> ) <sub>2</sub> (cod)	7.8	10	45.0(0.7)	1.9(0.8)	-23.6(0.6)
Pt(CH <sub>3</sub> ) <sub>2</sub> (nbd)	6.4	15	53.3(0.9)	3.9(0.6)	-38.1(0.8)
Pt(CH <sub>3</sub> ) <sub>2</sub> (bpy)	-13.9	4	14(3)	-28(2)	-28(2)
<i>cis</i> -Pt(CH <sub>3</sub> ) <sub>2</sub> (dmsO) <sub>2</sub>	-3.3	7	9.7(1.1)	1.7(1.5)	-21.1(1.3)
	2.8	6	17(3)	0(3)	-8(2)
Pt(CH <sub>3</sub> ) <sub>2</sub> (tmeda)	-18.9	6	4.6(1.3)	-15.3(1.6)	-46.0(1.4)
Pt(CH <sub>3</sub> )Cl(cod)	4.4 C	8	40(2)	3(3)	-28(2)
Pt(CH <sub>3</sub> )Cl(bpy)	-12.5	2	17(3)	-23(5)	-30(5)
Pt[CH <sub>2</sub> Si(CH <sub>3</sub> ) <sub>3</sub> ] <sub>2</sub> (cod)	12.3	6	64(2)	12(2)	-39(2)
Pt[CH <sub>2</sub> Si(CH <sub>3</sub> ) <sub>3</sub> ] <sub>2</sub> (nbd)	19.4	6	82(7)	12(8)	-36(7)
Pt[CH <sub>2</sub> Si(CH <sub>3</sub> ) <sub>3</sub> ] <sub>2</sub> (dmsO) <sub>2</sub>	1.9	7	20(2)	7(3)	-21(2)
Pt(4- <sup>t</sup> Bu-phenyl) <sub>2</sub> (nbd)	152.6	18	248(6)	217(6)	-7(7)
Pt(C≡C- <sup>t</sup> Bu) <sub>2</sub> (cod)	84.0	8	220(4)	94(4)	-62(4)
[(CH <sub>3</sub> ) <sub>3</sub> PtI] <sub>4</sub>	14.6	2	27(4)	15(8)	2(5)
[(CH <sub>3</sub> ) <sub>3</sub> PtOH] <sub>4</sub>	-8.6	7	9.8(0.7)	-10.2(0.7)	-24.8(0.6)
[(CH <sub>3</sub> ) <sub>3</sub> Pt] <sub>2</sub> SO <sub>4</sub>	-10.3 C	4	5(1)	-16(2)	-21(2)
Pd(CH <sub>3</sub> ) <sub>2</sub> (tmeda)	-7.4	8	-0.4(0.6)	-6.7(0.9)	-15.1(0.7)
	-5.8	8	1.0(0.4)	-5.9(0.6)	-12.5(0.4)
Fe(Cp)(CO) <sub>2</sub> CH <sub>3</sub> (150 K)	-20.7	8	9.0(1.0)	-28.5(1.0)	-43.0(0.9)
Mo(Cp)(CO) <sub>3</sub> CH <sub>3</sub> (170 K)	-23.2	12	1.6(1.0)	-29.5(1.2)	-41.6(0.9)
Mo(Cp)(CO) <sub>3</sub> CH <sub>2</sub> CH <sub>3</sub>	-3.5	7	18.7(0.7)	3.2(1.0)	-32.4(0.8)

<sup>a</sup> See text.**Figure 2.** Schematic representation of the principal values of chemical shifts for carbons  $\sigma$ -bonded to metals.

only 4 ppm. This must indicate more profound motions than the single-axis rotation contemplated above. The effective disappearance of Cp anisotropy requires in addition a rotation of the whole molecule about an axis perpendicular to the Fe–Cp axis.

Upon cooling of FeCp(CO)<sub>2</sub>CH<sub>3</sub> to 200 K, the Cp carbons appear axially symmetric with an anisotropy of 87 ppm, while the carbonyl is invisible and a rather broad methyl line is observed. This is consistent with rapid axial rotation of the Cp, together with a slower axial rotation of the Fe(CO)<sub>2</sub>CH<sub>3</sub> unit, a rotational speed of the order of magnitude of the MAS rate (2 kHz) being required to destroy the coherent averaging of the anisotropy.

Finally at 150 K the carbonyl resonance is visible, with an anisotropy typical of static terminal iron carbonyls;<sup>37,38</sup> thus the carbonyls, and presumably the methyl, are motionless at this temperature. The Cp resonance shows deviation from axial symmetry, but the quality of the data fit is poor, suggesting that it may be undergoing slow motions.

MoCp(CO)<sub>3</sub>CH<sub>3</sub> shows less motion. At room temperature the Cp shows a substantial anisotropy and is possibly not axially symmetric, although the large uncertainties associated with the small data set preclude a definite statement. The carbonyls are visible, but broadened, and with little sideband intensity, indicative of slow motions. At 170 K carbonyl motion has ceased, and a typical static carbonyl anisotropy is observed.

## Discussion

We began this research with the hypothesis that there might exist a characteristic anisotropy for each type of metal–carbon bond. This proves not to be the case. Our most extensive set of data is for the square-planar L<sub>2</sub>PtR<sub>2</sub> complexes (where L<sub>2</sub> represents either a bidentate ligand or two unidentate ligands). It is quite clear from Table 2 that, for R = CH<sub>3</sub> or CH<sub>2</sub>SiMe<sub>3</sub>, the anisotropy observed for the metal-bound carbon in R is strongly dependent on the nature of L. The anisotropy is particularly large when L is a chelating diolefin. For R = CH<sub>3</sub> and L<sub>2</sub> = nbd, the anisotropy is 91 ppm, among the highest anisotropies ever observed for CH<sub>3</sub>,<sup>4</sup> while L = dmsO produces anisotropies of 25 and 31 ppm. The cod ligand also produces very large anisotropy, while bidentate N-donor ligands produce intermediate values.

The above effects are surprisingly large. A survey of the methyl anisotropies previously reported<sup>4</sup> shows that methyl bound to C has an average anisotropy of 33 ppm while methyl bound to O has an average anisotropy of 70 ppm. (The standard deviations from these averages are 13 and 8 ppm, respectively.) Thus changing the

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**Table 3. Principal Components of Chemical Shift for  $\pi$ -Olefins, Cp, and Carbonyls**

compd	isotropic shift (ppm)	no. of sidebands	principal values in ppm (uncertainty) <sup>a</sup>		
Pt(CH <sub>3</sub> ) <sub>2</sub> (cod)	98.0 C	8	179(1)	99(1)	15(1)
	101.7 C	7	185(3)	103(3)	17(2)
Pt(CH <sub>3</sub> ) <sub>2</sub> (nbd)	89.0	15	179.2(1.0)	77.0(0.7)	10.7(0.9)
	Pt(CH <sub>3</sub> )Cl(cod)	86.1 C	9	159(3)	88(2)
114.0 C		13	203(2)	115(1)	22(2)
Pt[CH <sub>2</sub> Si(CH <sub>3</sub> ) <sub>3</sub> ] <sub>2</sub> (cod)	117.2	13	208(2)	122(2)	22(2)
	95.4 C	15	170(3)	107(2)	9(4)
Pt[CH <sub>2</sub> Si(CH <sub>3</sub> ) <sub>3</sub> ] <sub>2</sub> (nbd)	100.7	15	188(4)	108(3)	7(5)
	102.8	15	187(5)	106(3)	15(5)
Pt[CH <sub>2</sub> Si(CH <sub>3</sub> ) <sub>3</sub> ] <sub>2</sub> (nbd)	83.3	9	171.8(1.2)	70.7(1.1)	7.4(1.1)
	85.0	9	178(3)	73(2)	4(2)
Pt(4- <i>t</i> -Bu-phenyl) <sub>2</sub> (nbd)	88.1	7	182(6)	76(5)	7(5)
	91.7	7	181.1(0.8)	81.6(0.7)	12.4(0.7)
Pt(C≡C- <i>t</i> -Bu) <sub>2</sub> (cod)	93.3	3	195(12)	73(18)	10(10)
	100.5	4	189(7)	102(6)	9(4)
Pt(C≡C- <i>t</i> -Bu) <sub>2</sub> (cod)	103.5	4	192(4)	102(5)	15(4)
	106.6	4	196(4)	113(5)	15(5)
Fe(Cp)(CO) <sub>2</sub> CH <sub>3</sub> (200 K)	87.2	6	116(1)	116(1)	29(2)
Fe(Cp)(CO) <sub>2</sub> CH <sub>3</sub> (150 K)	87.4	34	124(2)	112(2)	26(2)
Fe(Cp)(CO) <sub>2</sub> CH <sub>3</sub> (150 K)	218.2	11	368(2)	366(2)	-79(2)
Mo(Cp)(CO) <sub>3</sub> CH <sub>3</sub> (296 K)	94.3	5	137(7)	122(7)	22(3)
Mo(Cp)(CO) <sub>3</sub> CH <sub>3</sub> (170 K)	94.8	25	139.5(0.9)	121.5(1.1)	23.5(1.2)
Mo(Cp)(CO) <sub>3</sub> CH <sub>3</sub> (170 K)	231.4	12	382(8)	367(8)	-22(4)
Mo(Cp)(CO) <sub>3</sub> CH <sub>3</sub> (170 K)	243.3	7	370(20)	350(20)	12(10)
Mo(Cp)(CO) <sub>3</sub> C <sub>2</sub> H <sub>5</sub>	94.5	24	139.6(1.0)	122.7(1.3)	22.2(1.4)
	231.5	8	360(1)	358(1)	-24(2)
	240.7	8	357(1)	356(1)	9(2)

<sup>a</sup> See text.

ligand on Pt bound to CH<sub>3</sub> can have as large an effect as changing from a *directly bonded* C to an O. A change from *cis*-L<sub>2</sub>Pt(CH<sub>3</sub>)<sub>2</sub> to *cis*-L<sub>2</sub>Pt(CH<sub>3</sub>)Cl appears to have little effect on the methyl shift components.

Inspection of Table 2 shows that the generally large low-frequency isotropic shift associated with metal-bound CH<sub>3</sub> is largely the result of a single low-frequency component. Thus, all of the methyl groups, except in [Me<sub>3</sub>PtI]<sub>4</sub>, show a component between -15 and -45 ppm, whereas the typical organic methyl group<sup>4</sup> usually has no component below 0 ppm. The very large anisotropies in diolefin complexes reflect, in addition, a rather high frequency component, so that these, on the whole, show higher frequency isotropic shifts.

For all of the methyl groups where single-crystal NMR measurements have been reported in the literature, it is found that the lowest frequency shielding component lies approximately along the X-CH<sub>3</sub> bond axis and has a value in the range 0 ± 5 ppm. It would be interesting to have directional information for the present organometallic compounds. In the case of the Pt-containing compounds, it is in principle possible to analyze the spinning sideband intensities of the Pt-C coupling satellites to obtain the principal values of the Zilm and Grant T<sup>±</sup> tensors<sup>27</sup> and to determine the orientation of the bond in the principal axis system of the chemical shift tensor. As pointed out by these authors, the general problem is underdetermined. If one makes the reasonable approximations that in square-planar Pt(II) complexes the C-Pt-C plane is at least approximately a symmetry plane in the solid, and that the "scalar" (*J*) coupling is axially symmetric, with unique axis along the bond, the problem becomes more tractable. Exactly this approximate case is treated by Harris *et al.*<sup>28</sup> We have tried to apply the methods of these authors to our data for PtMe<sub>2</sub>(nbd), which is the compound for which we have the best coupling data. Unfortunately, our data are not sufficiently good to define the direction of the bond axis. Two possible

orientations give fits of the same quality: either the Pt-CH<sub>3</sub> bond lies along  $\delta_{22}$  or it lies perpendicular to  $\delta_{22}$  and at 50° to  $\delta_{11}$ . The former is in accord with the literature trend—a component between 0 and 5 ppm along the bond—but we cannot demonstrate this conclusively.

A large effect of diolefins on the anisotropy of CH<sub>2</sub> is also observed in Pt(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub>L<sub>2</sub> compounds. The methylene anisotropies of PtCH<sub>2</sub>SiMe<sub>3</sub>(cod) and its nbd analogue are larger than any heretofore reported, with the exception of the bridging methylene in *cis*-( $\mu$ -CH<sub>2</sub>)-(CO)[FeCp(CO)]<sub>2</sub>.<sup>11</sup> Replacement of the diolefin by (dmsO)<sub>2</sub> restores the anisotropy to a "normal" value.

Although we do not have a range of ligands for comparison, it appears that  $\sigma$ -bonded aromatics and acetylenes also have large anisotropies in the presence of chelating diolefins. The *ipso* ring carbon in Pt-[4-*t*-Bu-phenyl]<sub>2</sub>(nbd) has a larger anisotropy than any so far reported<sup>4</sup> for aromatic carbon bound to C or O. The Pt-bound acetylenic carbon in Pt[C≡C-*t*-Bu]<sub>2</sub>(cod) also has a large anisotropy compared to organic acetylenes, though not as large as found in ionic metal acetylides.<sup>39</sup>

It is interesting to ask how ligand changes may alter the anisotropy of a  $\sigma$ -bonded carbon. Twenty years ago, Evans and Norton<sup>40</sup> expressed scepticism regarding the possibility of realistic shift calculations in transition metal complexes. In spite of recent advances with the theory of first- and second-row elements, it remains the case that experiment outstrips theory for metal complexes.<sup>41</sup> Qualitatively one can understand how such effects are possible. There exist several approximate molecular orbital treatments<sup>42-44</sup> of the effects of metal

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d electrons on ligand shifts. In general these involve contributions to the Ramsey paramagnetic term resulting from mixing of d orbital excited states with the ground state. These contributions are anisotropic and may be quite large. Moreover, the possible modification of d-d splittings by ligand field effects, and of bond length or charge distribution by *trans* influences,<sup>45</sup> provides a mechanism for ligand dependence of the anisotropy.

There are literature examples of unusually large <sup>15</sup>N anisotropy in Pt(II) ammine compounds<sup>46</sup> and of substantial ligand<sup>47</sup> and geometry<sup>48</sup> effects on <sup>31</sup>P anisotropy in metal complexes. In addition, Challoner and

Sebald<sup>49</sup> have recently observed that certain combinations of ligands lead to unusually small <sup>195</sup>Pt anisotropies in Pt(II) complexes. It thus appears that our results may be part of a larger picture whose details will become more clear with future work.

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