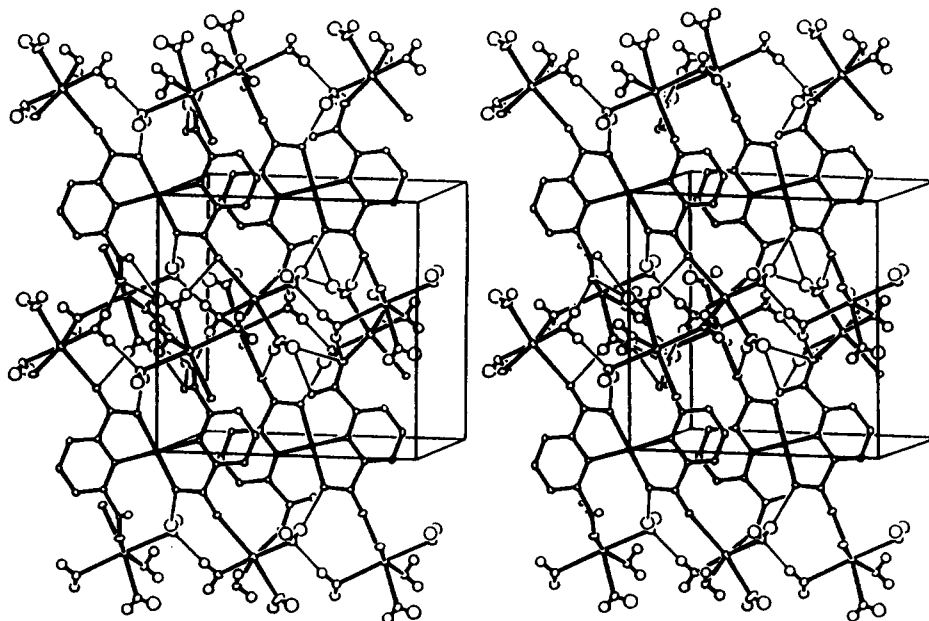


**Table IV.** Comparison of Bonding Parameters (Å and deg) in dipic Complexes<sup>a</sup>

complex	N-M	O1-M	C1-O1	C1-O2	N-M-O1	C1-N-M	C2-C1-N	O1-C2-C1	M-O1-C1	dihed <sup>b</sup>
[Pt(dipic) <sub>2</sub> ] <sup>2-</sup>	2.016	2.013	1.299	1.225	80.5	111.6	114.6	114.6	114.3	51.6
[Pt(dipic)Cl] <sup>-</sup>	1.88-1.91	2.01-2.05	1.28-1.32	1.19-1.23	80.7-81.9	117.5-119.3 <sup>c</sup>	110-113	114-116	113.6-116	
Pt(pic)(dmsO)Cl <sup>d</sup>	2.032	1.994	1.285	1.232	80.6	112.7	114.8	116.7	115.0	
Ru(dipicH) <sub>2</sub> Cl <sub>2</sub>	2.086	2.023	1.304	1.222	79.5	112.3	115.0	115.1	116.4	66.9 <sup>e</sup>
dipicH <sub>2</sub> <sup>f</sup>			1.288-1.315	1.181-1.217			115.3-118.4	110.8-116.2		0.5-0.8

<sup>a</sup> See Figure 1 for atom labels and see text for references. <sup>b</sup> Dihedral angle between the plane determined by the metal, coordinated carboxylate, and pyridine ring and the plane of the noncoordinated carboxylate. <sup>c</sup> Parameters not given in the original paper; recalculated from atom positions. <sup>d</sup> pic = 2-pyridinecarboxylate. <sup>e</sup> O1 is taken to be the protonated oxygen atom.

**Figure 2.** ORTEP stereoview of the crystal packing, with aromatic hydrogen atoms omitted and hydrogen bonds drawn in.

by chelate ring strain. Selected structural parameters are listed in Table III.

Comparisons of several key parameters with related species—the tridentate dipic-Pt complex,<sup>2</sup> a Pt complex of bidentate pyridine-2-carboxylate,<sup>7</sup> the aforementioned Ru-dipicH complex,<sup>3</sup> and free dipicH<sub>2</sub><sup>8</sup>—are given in Table IV. In all the complexes the intrachelate O-Pt-N angle (here 80.5 (7)°) is considerably below 90°, and the strained five-membered ring imposes additional constraints upon angles. For example, both M-N-C2 and N-C2-C1 are around 112-115° instead of the "natural" 120°; the only exception is M-N-C2 in [Pt(η<sup>3</sup>-dipic-O,N,O)Cl]<sup>-</sup>, which must be nearer 120° since both carboxylates are coordinated.

The difference between the coordinated (C1-O1) and noncoordinated (C1-O2) C=O bond lengths of the carboxylate group involved in bonding to Pt is pronounced, as is the case with the related complexes in Table IV, while C7-O3 and C7-O4 are nearly equal. (Note though that all these oxygens are involved in further interactions, either coordinated to Na or hydrogen bonded; see below.) The noncoordinated carboxylate group is twisted out of the pyridine/coordination plane, as is also the case for the previous η<sup>2</sup>-dipic structure (Table IV)<sup>3</sup> but *not* for the free acid, where both carboxyl groups are essentially coplanar with the pyridine ring.<sup>8</sup>

**Coordination about Na and Three-Dimensional Structure.** The overall structure, shown in Figures 1 and 2, consists of alternating, interlinked layers of Pt complex anions and Na cations. Each Na is octahedrally coordinated, with two (cis) positions each occupied by an oxygen of the dipic carboxylate groups. One of these comes from a carboxylate that is *not* involved in bonding to Pt, while the other is the "free C=O" of a Pt-coordinated

carboxylate. The remaining four coordination sites are occupied by water molecules; of these, two bridge to adjacent sodium ions. The structure is further cross-linked by hydrogen bonding between all the hydrogen atoms and neighboring water or carboxylate oxygen centers. Presumably this extended structure is responsible for the facile crystallization of this hydrated sodium salt.

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**Supplementary Material Available:** Tables V-IX, listing crystal and intensity collection data, anisotropic displacement parameters, final hydrogen parameters, hydrogen bonds, and complete distances and angles (5 pages); Table X, listing observed and calculated structure factors (12 pages). Ordering information is given on any current masthead page.

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#### NMR Assignments of Alkylcyclopentadienyl Ligands in Zirconium and Platinum Complexes

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#### Introduction

We have been investigating organometallic complexes of both zirconium and platinum containing alkyl-substituted cyclopentadienyl (Cp = η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>) ligands. Assignment of the protons

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**Table I.** Chemical Shifts (ppm) and Coupling Constants (Hz) for (Alkylcyclopentadienyl)platinum and -zirconium Compounds<sup>a</sup>

		$\delta(H_\alpha)$	$J(HH)^b$	$\delta(H_\beta)$	$J(HH)^b$	$\delta(CCH_3)$	$\delta(MCH_3)$
1	(MeCp)PtMe <sub>3</sub>	5.26	tq, 2.2, 0.45	5.52	t, 2.2	1.99	0.86
2	(MeCp) <sub>2</sub> Zr(CD <sub>3</sub> ) <sub>2</sub>	5.64	tq, 2.6, 0.55	5.45	t, 2.6	2.00	-0.36
3	(EtCp) <sub>2</sub> ZrCl <sub>2</sub>	6.21	tt, 2.7, 0.52	6.31	t, 2.7		
4	(Me <sub>3</sub> SiCp) <sub>2</sub> ZrCl <sub>2</sub>	6.67	t, 2.5	6.50	t, 2.5	0.29	
5	(Me <sub>2</sub> SiCp <sub>2</sub> )ZrMe <sub>2</sub>	6.65	t, 2.3	5.38	t, 2.3	0.16	-0.12
		$\delta(C_\alpha)$	$^1J(CH)$	other $J$ 's <sup>c</sup>	$\delta(C_\beta)$	$^1J(CH)$	other $J$ 's <sup>c</sup>
1 <sup>d</sup>		91.41	174.3	qq, 6.3, 4.0	95.67	175.3	t, 7.0, d, 5.9
2		112.07	170.0	tdq, 6.2, 7.6, 4.0	107.60	171.4	t, 6.6, d, 5.1
3		115.76	172.9	multiplet	112.21	174.1	t, 6.9, d, 5.2
4		125.74	173.8	ddd, 6.4, 7.1, 8.7	115.83	173.4	t, 7.1, d, 6.0
5		120.93			112.45		
		$\delta(ipso)$	$J$ 's	$\delta(CH_3)$	$^1J(CH)$	other $J$ 's	$\delta(MCH_3)$
1		114.15	tq, 7.3, 5.8	11.87	127.6	t, 1.7	-18.08
2		122.85		14.98	127.0	tt, 0.7, 1.7	28.71
3		136.64	m				
4		126.22	m	-0.14	119.7	heptet, 2.1	
5		101.30		-5.31			29.97

<sup>a</sup> **1** and **4** in CDCl<sub>3</sub>; others in toluene-*d*<sub>8</sub>. <sup>b</sup> The triplets for the CH protons comprise an AA'XX' spin system in which the observed triplet splitting is  $0.5(J(AX) + J(AX'))$ . <sup>c</sup> Long-range coupling constants are estimated from first-order splittings. <sup>d</sup> (MeCp)PtMe<sub>3</sub>: CH<sub>3</sub>,  $J(Pt,H) = 81.6$  Hz,  $J(Pt,C) = 715.2$  Hz,  $J(CH) = 145.3$  Hz; Cp,  $J(Pt,C_\alpha) = 5.7$  Hz,  $J(Pt,C_\beta) = 5.1$  Hz,  $J(Pt,C_{ipso}) = 13.5$  Hz.

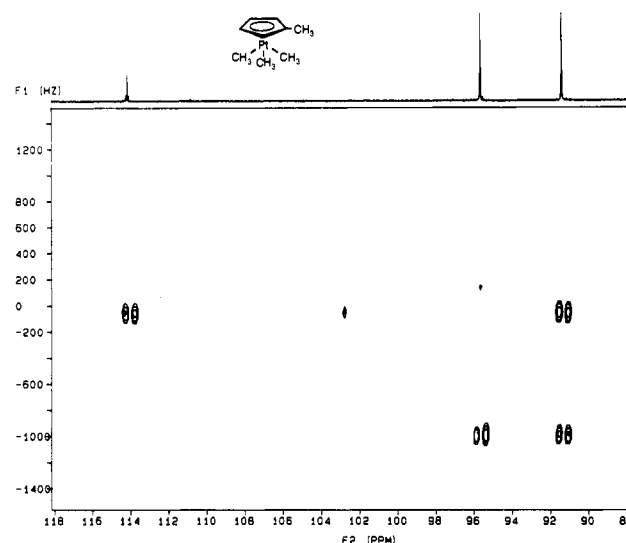
**Table II.** Proton Relaxation Times (s) in **1**, **2**, and **5**

proton	<b>1</b>		<b>2</b>	<b>5</b>
	$T_1$	$T_2$	$T_1$	$T_1$
H <sub>α</sub>	26	12	25	10
H <sub>β</sub>	28	12	24	10
MeCp	8.2	5.5		
MePt	8.9	8.9		

and carbons  $\alpha$  and  $\beta$  to the alkyl substituent in (alkylcyclopentadienyl)metal compounds is important for complete characterization of these materials and their derivatives. Recent publication of the NMR spectra of one of these compounds, **1** (MeCp)PtMe<sub>3</sub>, prompts us to publish methods for the unambiguous NMR assignment of alkyl-substituted Cp ligands. Assignment of the ring protons in RCp ligands had been made by assuming that the long-range coupling from R to the  $\alpha$  protons is greater than that to the  $\beta$  protons, that is,  $^4J(HH) > ^5J(HH)$ .<sup>2,3</sup> Although  $^4J(HH) > ^5J(HH)$  in alkyl-substituted benzenes, it is not clear that extrapolation to alkyl-substituted Cp ligands is valid, especially since  $^6J(HH) > ^5J(HH)$  in the benzene case.<sup>4</sup> Unambiguous assignment of the protons requires a technique independent of correlations to other types of compounds that may have different electron densities in the carbocyclic ligands. Observation of a nuclear Overhauser enhancement (NOE), in which the interaction is distance dependent, or carbon-carbon coupling in an INADEQUATE experiment meets these criteria.<sup>5,6</sup> We also describe the nontrivial syntheses of (RCp)<sub>2</sub>ZrCl<sub>2</sub> (R = Et, *n*-Pr, *n*-Bu). NMR parameters of these compounds have been reported previously,<sup>3</sup> but details of their preparation, usefully extensible to other (cyclopentadienyl)metal complexes, have not been published previously.

## Results

<sup>1</sup>H and <sup>13</sup>C chemical shifts and coupling constants for **1** and the four zirconocene complexes (MeCp)<sub>2</sub>Zr(CD<sub>3</sub>)<sub>2</sub> (**2**), (EtCp)<sub>2</sub>ZrCl<sub>2</sub> (**3**), (Me<sub>3</sub>SiCp)<sub>2</sub>ZrCl<sub>2</sub> (**4**), and (Me<sub>2</sub>SiCp<sub>2</sub>)ZrMe<sub>2</sub>

**Figure 1.** <sup>13</sup>C 2D INADEQUATE spectrum of 4.0 M (MeCp)PtMe<sub>3</sub> in CDCl<sub>3</sub>.

(**5**) are collected in Table I, and proton relaxation times in **1**, **2**, and **5** are reported in Table II. The <sup>1</sup>H and <sup>13</sup>C chemical shifts have not been previously reported for higher homologues of **2**, and data for (RCp)<sub>2</sub>Zr(CD<sub>3</sub>)<sub>2</sub> (R = Et, *n*-Pr, *n*-Bu) are given in Table III.

## Discussion

**NMR Assignment.** The <sup>13</sup>C NMR spectrum of **1** contains signals at 91.41 and 95.68 ppm due to the  $\alpha$  and  $\beta$  cyclopentadienyl CH carbon atoms. The ipso carbon, at 114.17 ppm, is readily identified by its low intensity relative to the two methines. The two-dimensional (2D) INADEQUATE pulse sequence uses double-quantum coherences to give connectivities between carbons.<sup>6</sup> This 2D experiment has 1% of the sensitivity of normal <sup>13</sup>C NMR experiments, since it requires observation of a <sup>13</sup>C adjacent to another <sup>13</sup>C nucleus. The correlations also depend on  $^1J(CC)$ , which were determined to be 46 Hz from observation of the <sup>13</sup>C satellites in the naturally abundant spectrum of the dilabeled isotopomer. Horizontal slices (along the double-quantum axis) in the INADEQUATE spectrum show doublets that correlate the coupled carbons. The INADEQUATE spectrum of **1** (Figure 1) thus shows coupling between the ipso carbon and the carbon at 91.41 ppm and, as expected, coupling between the two methine carbons. Therefore, the carbon resonance at 91.41 ppm is  $\alpha$  to the methyl substituent and the previous <sup>13</sup>C (and <sup>1</sup>H) spectroscopic assignments must be reversed.<sup>1</sup>

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**Table III.** Chemical Shifts (ppm) for Other (Alkylcyclopentadienyl)zirconium Compounds in Toluene- $d_8^a$ 

sample	chemical shifts						
	$^{13}\text{C}$				$^1\text{H}$		
	ipso	$\alpha$	$\beta$	Me	$\alpha$	$\beta$	Me
(EtCp) $_2$ Zr(CD $_3$ ) $_2^b$	129.64	110.22	107.69	28.88	5.67	5.50	-0.35
( <i>n</i> -PrCp) $_2$ Zr(CD $_3$ ) $_2^c$	128.12	111.07	107.75	29.06	5.67	5.50	-0.34
( <i>n</i> -BuCp) $_2$ Zr(CD $_3$ ) $_2^d$	127.83	110.53	107.23	28.58	5.69	5.52	-0.33

<sup>a</sup>  $^1\text{H}$  Me shifts determined from the CHD $_2$  isotopomer. <sup>b</sup> Et:  $^1\text{H}$ , 1.09 (CH $_3$ ) and 2.6 (CH $_2$ ) ppm;  $^{13}\text{C}$ , 15.64 (CH $_3$ ) and 3.14 (CH $_2$ ) ppm. <sup>c</sup> Pr:  $^1\text{H}$ , 0.90 (CH $_3$ ), 1.51 (CH $_2$ ), and 2.32 (CH $_2$ -Cp) ppm;  $^{13}\text{C}$ , 14.23 (CH $_3$ ), 25.2 (CH $_2$ ), and 32.52 (CH $_2$ -Cp) ppm. <sup>d</sup> Bu:  $^1\text{H}$ , 0.91 (CH $_3$ ), 1.29 (CH $_2$ -CH $_3$ ), 1.48 (CH $_2$ ), and 2.37 (CH $_2$ -Cp) ppm;  $^{13}\text{C}$ , 13.81 (CH $_3$ ), 22.4 (CH $_2$ -CH $_3$ ), 29.68 (CH $_2$ ), and 33.75 (CH $_2$ -Cp) ppm.

The spectrum is independently assigned by a proton NOE experiment. The NOE is proportional to the inverse sixth power of the distance between protons.<sup>5</sup> Saturation of the ring methyl protons yields a 9% increase in the intensity of the methine proton resonance at 5.26 ppm but no change in the intensity of that at 5.52 ppm, proving that the 5.26 ppm proton must be closer in space to the methyl group and is therefore H $_a$ . The single-frequency  $\{^1\text{H}\}^{13}\text{C}$ -decoupled spectrum completes the assignments, showing that the  $^1\text{H}$  at 5.26 ppm is coupled to the  $^{13}\text{C}$  at 91.41 ppm.

Spectra were also obtained for the (methylcyclopentadienyl)-zirconium complex (MeCp) $_2$ Zr(CD $_3$ ) $_2$  (**2**).<sup>7</sup> Homonuclear NOE spectra unambiguously assigned the  $\alpha$  and  $\beta$  protons in this sample; decoupling the ring methyl protons gave a 14% enhancement of the proton signal at 5.64 ppm but no enhancement of the upfield proton resonance at 5.45 ppm.

**Coupling Constants.** Because the INADEQUATE experiment is very insensitive and cannot be obtained routinely unless overnight blocks of spectrometer time are available and because NOE experiments are not trivially performed since carefully degassed solutions are necessary, alternative assignment techniques were explored. The results in Table I indicate that the long-range coupling constants  $^4J(\text{HH})$  and  $^3J(\text{CH})$  are readily observed in alkyl-substituted cyclopentadienyl ligands but that  $^4J(\text{CH})$ ,  $^5J(\text{HH})$ , and  $^5J(\text{CH})$  are less than 1 Hz and are not readily detectable. Spectra (Figures S1–S4) showing the long-range coupling in **1** are included in the supplementary material. These results thus provide an independent and much simpler method for the assignment of the  $\alpha$  and  $\beta$  nuclei. For **1**, 4.0-Hz quartets are observed for the upfield ( $\alpha$ ) carbon due to coupling to the methyl protons, but no quartets are detectable for the downfield ( $\beta$ ) absorption. The coupling from the ring carbons to the ring protons is more difficult to analyze due to magnetic inequivalence of the latter in their AA'MM' spin system. The two  $\beta$  protons are chemically equivalent, but have different couplings to an  $\alpha$  methine  $^{13}\text{C}$  nucleus. However,  $^3J(\text{HH})$  between the two equivalent  $\beta$  protons is large. As a consequence of virtual coupling,<sup>4</sup> the observed multiplet in the uncoupled spectrum appears as a triplet in which the splitting is the average coupling,  $0.5-[^2J(\text{C}_\alpha\text{H}_\beta) + ^3J(\text{C}_\alpha\text{H}_\beta)]$ . The  $^4J(\text{HH})$  couplings are more difficult to detect, but baseline splitting of the  $\alpha$  proton resonances into 0.45-Hz quartets from long-range coupling to the methyl is observable on resolution-enhanced spectra of degassed samples (Figure S2).

Similar long-range coupling constants are observed in ethyl-substituted Cp derivatives. The values for (EtCp) $_2$ ZrCl $_2$  (**3**) confirm the assignment given by Stucky et al.<sup>3</sup> Thus, observation of  $^4J(\text{HH})$  or  $^3J(\text{CH})$  in alkyl-substituted cyclopentadienyl compounds provides a simple and unambiguous assignment of the cyclopentadienyl protons and carbons.

Attempts to unambiguously assign the spectra of (Me $_2$ SiCp) $_2$ ZrCl $_2$  (**4**) by observation of analogous long-range coupling to silicon were unsuccessful. There was no detectable coupling of the proton or carbon of either methine to the methyl protons or silicon. However,  $^{13}\text{C}$  satellites are observed in the  $^{13}\text{C}$  spectrum due to the naturally abundant dilabeled  $^{13}\text{C}$  isotopomer present at the 0.01% level. The  $^{13}\text{C}$  satellites for the upfield absorption at 115.83 ppm are symmetrical about the monolabeled

$^{13}\text{C}$  isotopomer, whereas the  $^{13}\text{C}$  satellites for the ipso carbon at 126.22 ppm show a 1:2 ratio centered 7 Hz downfield from the monolabeled  $^{13}\text{C}$  isotopomer. This indicates that the ipso carbon is coupled to the carbon at 125.74 ppm, comprising an AB pattern with  $\Delta\nu = 52$  Hz and  $J(\text{AB}) = 46$  Hz in which the centers of the AB doublets are offset 7 Hz from the true chemical shifts due to second-order effects when  $\Delta\nu \approx J$ .<sup>4</sup> Thus, the 125.74 ppm carbon is  $\alpha$  and the 115.83 ppm carbon is  $\beta$ . In the alternative assignment, the  $^{13}\text{C}$  satellites would be of equal intensity and symmetrically located (except for a very small,  $\approx 1$  Hz,  $^{13}\text{C}^{12}\text{C}$  isotope shift) about the ipso carbon resonance, since the chemical shift difference would be much greater than the coupling constant.

**Relaxation Times.** The examples described above illustrate the necessity of performing NOE experiments on degassed solutions.<sup>5</sup> The spectra of **1** were first obtained on an undegassed solution in CDCl $_3$ . The proton relaxation times, 6 s, appeared long for a large organometallic molecule, but no NOE's were detectable. Degassing the solution gave a sample in which the relaxation times of the cyclopentadienyl ring protons were over 20 s (Table II) and permitted observation of the NOE by eliminating competitive relaxation by paramagnetic oxygen in the solvent. The relaxation times of the analogous zirconium complex **2** were similar (Table II). The observed relaxation times are typical of the ring protons in small inert molecules such as toluene, pyridine, or furan ( $T_1 = 22, 18,$  and  $40$  s, respectively),<sup>8–10</sup> whereas proton relaxation times in medium-size organic molecules are typically 1–5 s.<sup>5,6</sup> The long relaxation times for the Cp ring protons can be attributed to rapid spinning of the Cp ligand about the Pt–Cp axis,<sup>11</sup> giving relaxation times typical of the free ligand. In support of this interpretation, when free rotation of the Cp ligands is restricted, as in the dimethylsilyl-bridged species (Me $_2$ SiCp $_2$ )ZrMe $_2$  (**5**),<sup>7</sup> the relaxation time is reduced over 2-fold to 10 s. Long relaxation times contribute to excessive  $t_1$  noise that can be mistaken for evidence of cross coupling in normal 2D COSY experiments run with 1–2-s recycle times typical for medium-size organic molecules, which can render ambiguous assignments based solely on COSY spectra, such as the assignment of **1** in ref 1. Examples of COSY spectra of **1** for recycle delay times of 1.2 and 10.2 s are included in the supplementary material. A phase cycle to compensate for 2D recycle times much shorter than  $T_1$  has recently been published.<sup>12</sup>

It is interesting to note that the  $^{13}\text{C}$  methine relaxation times in **1**, 9 and 10 s for the  $\alpha$  and  $\beta$  carbons, respectively, are shorter than the proton relaxation times for the methine protons (Table II). This is contrary to the usual assumptions that carbon relaxation times are always long and that it is advantageous to use polarization transfer in order to take advantage of the shorter proton relaxation times.<sup>5,6</sup> This unusual result is easily rationalized in **1**, since intramolecular heteronuclear dipole–dipole relaxation is a function of the inverse sixth power of the distance between the nuclear dipoles but the square of the gyromagnetic ratio for each nucleus.<sup>13</sup> Considering the distances from the crystal

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structure of  $[(\text{MeCp})_2\text{ZrH}(\mu\text{-H})]_2^{14}$  as typical of the MeCp ligand, the methine protons in **1** are separated by over 2.6 Å whereas the carbon is only 0.92 Å from a proton. This ratio of 2.7 more than compensates for the 4-fold lower gyromagnetic ratio of carbon because the distance factor enters as the sixth power. The  $T_1$  for the ipso carbon, 56 s, is longer than any of the proton  $T_1$ 's. This carbon, unlike the methines, does not show a full NOE and its relaxation is not dominated by the dipole–dipole interaction.

$(\text{RCp})_2\text{Zr}(\text{CD}_3)_2$ . Proton and carbon-13 chemical shifts have not been previously reported for the higher homologues of **2**. The cyclopentadienyl chemical shifts (Table III) are not a function of the R substituent.

### Experimental Section

NMR spectra were obtained on a Varian XL-400 spectrometer, operating at 400 MHz for  $^1\text{H}$ , on solutions in  $\text{CDCl}_3$  for **1** and **4** and in toluene- $d_8$  for all the other compounds. Proton chemical shifts are given relative to internal  $\text{Me}_4\text{Si}$ ; carbon chemical shifts were determined relative to  $\text{CDCl}_3$  (76.91 ppm) or the para CD of toluene- $d_8$  (125.2 ppm). Resolution-enhanced proton spectra were obtained with acquisition times in excess of 5 s and pseudoecho weighting of the free induction decay. Resolution-enhanced uncoupled carbon spectra were obtained with acquisition times exceeding 2.5 s and a delay, during which the decoupler was on for a time equal to the acquisition time. The proton–carbon correlations were determined by single-frequency decoupling of the proton resonances. 2D INADEQUATE spectra of **1** were obtained by using a 4.0 M solution to which sufficient  $\text{Cr}(\text{acac})_3$  was added to reduce the carbon relaxation times to less than 0.2 s. The spectra were acquired over 15 h with a 0.6-s repetition time, 3100-Hz spectral width, and 64 increments. The delays were optimized for  $J(\text{CC}) = 49$  Hz. Approximate values of  $J(\text{CC})$  were determined directly from the  $^{13}\text{C}$  satellites on spectra run for several hours with a 4.0-s acquisition time and 55° pulses (8  $\mu\text{s}$ ) on concentrated solutions (>1 M). Spin–lattice ( $T_1$ ) relaxation times were determined by using the inversion–recovery pulse sequence with at least eight values of  $\tau$ , typically between 1 and 16 s, and a delay exceeding  $4T_1$ . Spin–spin relaxation times were determined by using the Carr–Purcell–Meiboom–Gill pulse sequence with the same delay as for the  $T_1$  analyses. Proton  $T_1$  relaxation times for **1** ranged from 4.4 to 6.5 s on an undegassed solution; the values in Table II were obtained on a solution degassed via the freeze–pump–thaw technique. Proton homonuclear NOE experiments were performed with single-frequency decoupling on the methyl protons. The spectrum was quantitatively compared to a spectrum obtained under identical conditions, but with the decoupler offset 1000 Hz upfield. Sixteen transients, obtained with a 2-min recycle time, were accumulated with 90° pulses, alternating the decoupler frequency every four pulses. The proton homonuclear NOE's were attenuated by competitive relaxation by paramagnetic oxygen and were only 2% in the undegassed solution of **1**.

**Syntheses of  $(\text{RCp})_2\text{ZrCl}_2$ .** A generalized preparation of (alkylcyclopentadienyl)metal complexes requires generation of  $\text{RC}_5\text{H}_4^-$ . In contrast to ref 15, we find that this is difficult to achieve by alkylation in THF of NaCp by alkyl halides. This is presumably because an equilibrium mixture of  $\text{C}_5\text{H}_5^-$  and its mono- and dialkylated derivatives is produced, which, when treated with  $\text{ZrCl}_4$ , yields a complex mixture of products. A one-pot synthesis is possible when a highly reactive alkylating agent, such as ethyl trifluoromethanesulfonate, is used. Alternatively, NaCp in liquid ammonia can be cleanly alkylated by alkyl halides, a modification of the method of Alder and Ache.<sup>16</sup>

**$(\text{EtCp})_2\text{ZrCl}_2$ .** A solution of 3.0 g (40 mmol) of LiCp (Aldrich) in 40 mL of glyme (1,2-dimethoxyethane) was added under nitrogen and with stirring to 7.17 g (40 mmol) of ethyl trifluoromethanesulfonate (Aldrich) in 25 mL of the same solvent at 0 °C. This mixture was stirred for 1 h at room temperature, recooled to 0 °C, and treated with 16 mL of 2.5 M *n*-BuLi (40 mmol) in hexane. After 2 h, a solution of 4.6 g (20 mmol) of  $\text{ZrCl}_4$  in 40 mL of glyme was added. After overnight stirring, the mixture was filtered through celite and evaporated to dryness under vacuum. Recrystallization of the residue from hot hexane afforded 3.2 g (46%) of product as white needles, mp 106.5–107.0 °C. Anal. Calc (found): C, 44.4 (44.3); H, 5.6 (5.6). Use of glyme in this synthesis is preferred because some triflate salts can polymerize THF.

**$(n\text{-BuCp})_2\text{ZrCl}_2$ .** Freshly distilled  $\text{C}_5\text{H}_6$  was added with stirring at –78 °C under nitrogen to 1.43 g (62 mmol) of Na in 100 mL of liquid  $\text{NH}_3$  until the blue color was discharged. Next, 11.4 g (62 mmol) of *n*- $\text{C}_4\text{H}_9\text{I}$  was added dropwise. The mixture was warmed to room tem-

perature overnight under a slow stream of  $\text{N}_2$ . Pentane, 20 mL, was added, and the liquid residue was decanted and evaporated at room temperature under water aspirator vacuum. There remained 5.8 g (77%) of a ca. 80% pure 1:1 mixture of 1- and 2- $(n\text{-C}_4\text{H}_9)\text{C}_5\text{H}_5$ ; the  $^1\text{H}$  NMR spectrum in  $\text{CDCl}_3$  showed  $\text{CH}_2$  multiplets at 2.95 and 2.90 ppm. This mixture need not be distilled or further purified. It was dissolved in THF and converted, by treatment with *n*-BuLi in hexane followed by  $\text{ZrCl}_4$  in glyme (vide supra), to  $(n\text{-BuCp})_2\text{ZrCl}_2$ , mp 93 °C, as thin needles from heptane (68% yield based on *n*- $\text{C}_4\text{H}_9\text{I}$ ). Anal. Calc (found): C, 53.5 (53.6); H, 6.4 (6.3).

$(n\text{-PrCp})_2\text{ZrCl}_2$ , mp 110–111 °C, was similarly prepared (74% yield). Anal. Calc (found): C, 51.1 (51.4); H, 5.9 (5.8).

The  $(\text{RCp})_2\text{ZrCl}_2$  compounds were converted to their  $(\text{RCp})_2\text{Zr}(\text{CD}_3)_2$  analogues by a literature method using  $\text{LiCD}_3$  in diethyl ether followed by quenching of unreacted  $\text{LiCD}_3$  by  $\text{Me}_3\text{SiCl}$ .<sup>17</sup> After removal of solvents, the products were isolated by extraction with hexane. The substituted dimethylzirconocenes are liquids or low-melting solids; purity was verified by NMR and mass spectroscopy.

**Supplementary Material Available:** Figures S1 and S2, showing  $^1\text{H}$ -resolved spectra of **1**, Figures S3 and S4, portraying uncoupled  $^{13}\text{C}$  NMR spectra of Cp multiplets of **1**, and Figures S5–S10, giving unsymmetrized and symmetrized COSY spectra of **1** with recycle delays of 1.2 and 10.2 s (10 pages). Ordering information is given on any current masthead page.

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### A New Tetranuclear Cr(III) Complex with a $[\text{Cr}_4\text{O}_2]$ Core: Synthesis, Structure, and Magnetic Properties of $[\text{Cr}_4\text{O}_2(\text{O}_2\text{CCH}_3)_7(\text{bpy})_2]\text{PF}_6$ (bpy = 2,2'-Bipyridine)

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### Introduction

Basic metal carboxylates with a  $[\text{M}_3\text{O}]^{n+}$  core, in which three metal atoms in an equilateral triangle are bridged by an oxo ligand, are common in the coordination chemistry of many transition metals.<sup>1</sup> Chromium(III) compounds containing the  $\{\text{Cr}_3\text{O}(\text{O}_2\text{CR})_6\}^+$  core were prepared a century ago, and their physical properties were extensively investigated in many laboratories. The  $[\text{Cr}_3\text{O}(\text{O}_2\text{CCH}_3)_6(\text{H}_2\text{O})_3]^+$  ion is the prototypical species for the study of antiferromagnetic interactions between the  $d^3$  chromium(III) ions.<sup>1</sup>

The structure of an unusual tetranuclear sulfur-centered chromium(III) complex,  $[\text{Cr}_4\text{S}(\text{O}_2\text{CCH}_3)_8(\text{H}_2\text{O})_4]^{2+}$ , was recently reported.<sup>2</sup> This complex, which is prepared by the reaction between chromium and sulfur in acetic acid, exhibits intramolecular ferromagnetic coupling with a ground state with spin  $S = 6$ .

A dinuclear, carboxylato-bridged, chromium(III) complex that results from the reaction of  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$  and formic acid,  $[\text{Cr}_2(\text{OH})(\text{O}_2\text{CH})_2(\text{H}_2\text{O})_6]^{3+}$ , was found to be an intermediate in the formation of trinuclear basic chromium carboxylates.<sup>3</sup> This complex consists of two octahedrally coordinated Cr(III) ions bridged by an hydroxo ligand and two bidentate formate groups. An antiferromagnetic exchange coupling exists between the two Cr(III) centers with  $J = -11.1$  (2)  $\text{cm}^{-1}$ .

Recently, research in Fe(III) and Mn(III) chemistry has revealed a new class of basic metal carboxylates containing a tet-

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