where $k' = k_{-1}/k_2$ times the partition coefficient for the distribution of OH^- or OD^- between water and CCl_4. Axial ligand dissociation of I^- from Fe(TTP)I occurs to a sufficient extent in chloroform solution at room temperature that it provides a mechanism for inversion at the iron on the NMR time scale.[25] Although OH^- would be expected to bind more strongly than I^-, some dissociation is likely to occur as indicated in eq 1. Although one of the products of eq 2 is written as H^+, it is undoubtedly hydrated, so if there is 1 mol of water hydrogen bonded to the hydroxide of Fe(TTP)OH, formation of H_3O^+ would only require proton transfer from OH to water.

The concentration of Fe(TTP)OH as a function of time was calculated from the rate law as shown in Figure 3. The data for OH^- were fit with $k_1 = (1.4 \pm 0.2) \times 10^{-4}\ s^{-1}$ and $k'(H) = (0.2 \pm 0.15) \times 10^{-3}$. The data for OD^- were fit with $k_1 = (1.7 \pm 0.3) \times 10^{-4}\ s^{-1}$ and $k'(D) = (1.0 \pm 0.3) \times 10^{-3}$. Within experimental uncertainty the values of k_1 were the same for the data obtained with OH^- and OD^-. The secondary deuterium isotope effect on the dissociation of OH^- or OD^- would be expected to be less than the uncertainty in the data.[26] Therefore, the absence of a large deuterium isotope effect on k_1 is consistent with the proposal that k_1 is the rate of axial ligand dissociation. The values of k' were substantially different for OH^- and OD^-. The most likely source of an isotope effect on k' is the proton dissociation step described by k_2. If it is assumed that the isotope effect on k' was due entirely to changes in k_2, then $k_2(H)/k_2(D) = k'(D)/k'(H) = 5$. Since deuterium isotope effects between 4 and 9 have been reported for proton transfer from oxyacids to bases,[26] the magnitude of the observed isotope effect is consistent with the proposal that the second step of the reaction involves transfer of a proton from a bridging OH(D) to H_2O or D_2O.

Comparison with Dimerization of Other Iron Porphyrins

The equilibria between monomeric and dimeric iron(III) porphyrins have been studied extensively in aqueous solution. However, much less information has been obtained concerning the mechanism of dimerization. In an early report on the characterization of $(Fe(P))_2O$, Caughey and co-workers proposed that dimerization might occur by reaction of $Fe(P)^+$ and Fe(P)OH (pathway 1) or by reaction of 2 mol of Fe(P)OH to form a dihydroxy-bridged intermediate (pathway 2).[27] Both of these possibilities were found to occur in studies of the iron(III) complex of ethylenediamine-*N,N,N',N'*-tetraacetate (EDTA = L). It was shown that dimerization occurred about 100 times faster for $FeL(H_2O)$ + FeL(OH) (pathway 1) than for reaction of 2 mol of FeL(OH) (pathway 2).[28] It was proposed that the rate of reaction by pathway 1 might be controlled by the rate of water exchange. It would then be equivalent to Caughey's proposal of $Fe(P)^+$ + Fe(P)OH. On the basis of temperature-jump kinetics it was proposed that dimerization of the iron(III) complex of tetrasulfonated tetraphenylporphyrin proceeded by a dihydroxy-bridged intermediate (pathway 2) and there was no evidence of a contribution from pathway 1 in the pH range 6.1–7.5.[29] Temperature-jump studies of the dimerization of the iron(III) complex of deuterioporphyrin were only possible over a limited pH range. The data were consistent with pathway 1.[30] Thus, either pathway 1 or pathway 2 may be appropriate for iron porphyrins in aqueous solution. The preferred pathway is probably a function both of the porphyrin and of the pH of the solution. Our results clearly indicate that dimerization of Fe(TTP)OH in CCl_4 proceeds by pathway 1.

The rates of these reactions suggested that it might be possible to isolate Fe(TTP)OH. The solvent was rapidly (2–3 min) removed from a 2 mM solution of Fe(TTP)OH in CCl_4. The solid was dried overnight and redissolved in CCl_4. The NMR spectra indicated that the porphyrin was about 10% Fe(TTP)OH and 90% $(Fe(TTP))_2O$. The conversion of Fe(TTP)OH to $(Fe(TTP))_2O$ is slower in the presence of OH^- than in the absence of OH^-. Therefore, another sample was dissolved in CCl_4 that had previously been shaken with 2 M NaOH. This sample contained about 30% Fe(TTP)OH and 70% $(Fe(TTP))_2O$. For both of the solutions the extent of conversion of Fe(TTP)OH to $(Fe(TTP))_2O$ was greater (for the short time that the Fe(TTP)OH was in solution) than can be explained by the rates obtained for pathway 1. Thus, other mechanisms of reaction to form $(Fe(TTP))_2O$ must occur during precipitation or in the solid state.

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Notes

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Synthesis and Study of (Dimethylamino)benzyl and (Diphenylphosphino)benzyl Compounds of Early-Transition-Metal Metallocenes and Their M(III) Derivatives

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Monoalkylated derivatives of dicyclopentadienyl group 4[20] metal dichlorides $Cp_2M(Cl)R'$, where M = Ti, Zr and R′ is a group attached through an alkyl linkage, have attracted attention as intermediates in CO insertion reactions[1-4] and other organic syntheses.[5-8] Furthermore, their compounds with alkyl-bound benzyl ligands containing tertiary nitrogen and phosphorus functionalities offer a number of interesting possibilities, such as the formation of heterobimetallic species through the bifunctional ligand, the stabilization of lower oxidation states of the metal through chelation by the alkyl and N (or P) functionalities, and the stabilization of reduced heterobimetallic species. For the

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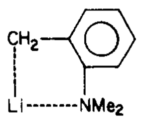
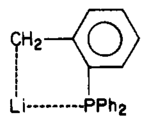
preparation of Zr and Hf compounds with alkyl-bound ligands with N or P functionalities, we have chosen the ligands obtained from the alkyllithium species Li(A) and Li(B). These ligands



Li(A)



Li(B)

have a reasonable bidentate "bite" size and the ability to form five-membered chelate rings and also have the synthetic advantage of directly forming stable complexes because they have no hydrogens to be lost by β elimination.

Recently, Manzer[9] has studied the reaction of ligand A with Cp_2MCl, where M = Sc, Ti, V, Cr, and isolated relatively stable M(III) compounds. While the bidentate capability of the ligand probably is of value in stabilizing the III state of these metals, it is, in any event, fairly common for them. However, isolable paramagnetic complexes of Zr(III) or Hf(III) are rare, and such bidentate ligation may be important. This is evident from the fact that Schore et al.[10] found a direct Zr(III)–P interaction in the product of reduction of $Cp_2Zr(Cl)CH_2P(C_6H_5)_2$. Our approach is to make the monoalkylated derivatives of the group 4 (Zr, Hf) elements from the metallocene dichlorides and the bulky, possibly bidentate ligands and to reduce them to stable paramagnetic compounds by removal of the remaining chloride. The potential value of this approach is clear from the reported incorporation of N_2 into Na(Hg)-reduced $Cp_2Zr(Cl)CH(SiMe_3)_2$.[11,12]

We report the preparation and characterization of $Cp_2M(Cl)R$ (M = Zr, Hf; R = ligands A and B) and Cp_2MR_2 (M = Zr, Hf; R = ligand A) and the reduction and ESR spectra of Na(Hg)-reduced $Cp_2Zr(A)_2$, $Cp_2Zr(Cl)(A)$, and $Cp_2Zr(Cl)(B)$.

Experimental Section

All synthetic procedures were carried out under N_2 or Ar. The solvents were dried over Na or distilled from sodium benzophenone ketyl and degassed. The Li salts of ligands A[9] and B[13] were prepared by reported methods. Cp_2ZrCl_2 and Cp_2HfCl_2 were obtained from Aldrich Chemical Co., Milwauke, WI. Infrared spectra were measured in the 50–4000-cm^{-1} region on Digilab FTS-15B and FTS-14 interferometers. The NMR spectra were measured on a Bruker WM-250, the mass spectra on a Perkin-Elmer 397, and the X-band ESR spectra on a Bruker ER-220D spectrometer equipped with a variable-temperature unit. Elemental analyses were done by Galbraith Laboratories, Knoxville, TN.

Preparation of $Cp_2Zr(Cl)(CH_2C_6H_4$-*o*-$NMe_2)$ (1). To a stirred suspension of Cp_2ZrCl_2 (3.74 mmol) in 30 mL diethyl ether was added powdered $LiCH_2C_6H_4$-*o*-NMe_2 (soluble in ether) (3.74 mmol) in small increments ($\sim{}^1/_{100}$ at a time) over 1 h under Ar at 25 °C. The mixture was stirred for 45 min and filtered to yield an orange solution and a precipitate (LiCl plus some product). The precipitate was washed with benzene until it was colorless, and the washings and original solution were combined and reduced in volume. Following this, 30 mL of pentane was added and the solution was kept for ca. 12 h at 0 °C. Red crystals were obtained after the supernatant was decanted. They were washed with pentane and dried in vacuo at 25 °C for 3 h: yield 30%; dec pt 126 °C. Anal. Calcd (found): C, 58.36 (58.41); H, 5.67 (5.33); N, 3.58 (3.23); Cl, 9.07 (9.13).

Preparation of $Cp_2Hf(Cl)(CH_2C_6H_4$-*o*-$NMe_2)$ (2). This was prepared and purified similarly to the Zr analogue except that the combination of reactants was carried out at 0 °C and yielded a bright yellow solid product: yield 91%; dec pt 127 °C. Anal. Calcd (found): C, 47.71 (47.03); H, 4.64 (4.49); N, 2.93 (2.69); Cl, 7.41 (8.01).

Preparation of $Cp_2Zr(Cl)(CH_2C_6H_4$-*o*-$PPh_2)$ (3). To a stirred solution of Cp_2ZrCl_2 (2.57 mmol) in 15 mL of THF was added powdered $LiCH_2C_6H_4$-*o*-PPh_2 (2.57 mmol) in small increments over 3 h at −77 °C. After the solvent was stripped off, the resulting yellow solid mixture was dried in vacuo for 10 min. The solid was extracted with 15 mL of toluene, leaving a colorless solid (LiCl). After addition of 20 mL of pentane, the solution was held at −42 °C for 4 h. After the supernatant was decanted, a solid yellow product was obtained, washed with pentane, and dried in vacuo: yield 48%; dec pt 124 °C. Anal. Calcd (found): C, 65.45 (64.98); H, 4.92 (5.12); Cl, 6.68 (6.48).

Preparation of $Cp_2Hf(Cl)(CH_2C_6H_4$-*o*-$PPh_2)$ (4). To a stirred solution of Cp_2HfCl_2 (1.77 mmol) in 20 mL of THF was added solid $LiCH_2C_6H_4$-*o*-PPh_2 (1.77 mmol) in small increments over 1 h at −77 °C. The solution was warmed to 0 °C and held there for 0.5 h. After the solid was filtered it was washed with a minimum amount of cold (0 °C) benzene to yield a yellow solution, which was reduced in volume. Following addition of 20 mL of pentane, the solution was held at 0 °C for 12 h. The product was obtained as a yellow powder by decanting the supernatant and was washed with pentane and dried in vacuo: yield 92%; dec pt 132 °C. Anal. Calcd (found): C, 56.23 (57.65); H, 4.23 (4.46); P, 4.99 (5.23).

Preparation of $Cp_2Zr(CH_2C_6H_4$-*o*-$NMe_2)_2$ (5). Powdered $LiCH_2C_6H_4$-*o*-NMe_2 (1.77 mmol) was added slowly in small increments at 25 °C to a stirred suspension of Cp_2ZrCl_2 (0.885 mmol) in 20 mL of ether. The solution turned orange immediately. The reaction mixture was stirred for 12 h and then filtered to remove the solid. A small amount of benzene was added to the liquid, and the volume was reduced by rotary evaporation. Then 20 mL of pentane was added and this solution kept at 0 °C for 12 h. The product was obtained as a yellow, air-sensitive liquid by decantation and was desolvated in vacuo: yield approximately 25%; viscous liquid at 25 °C. Anal. Calcd (found): C, 68.66 (68.55); H, 6.99 (6.76). MS: parent ion *m/e* 490.

Preparation of $Cp_2Hf(CH_2C_6H_4$-*o*-$NMe_2)_2$ (6). This compound was prepared analogously to **5** and was isolated as a yellow liquid in approximately the same yield.

Preparation of $Cp_2Zr(CH_2C_6H_4$-*o*-$NMe_2)_2^-$ (8). Upon addition of 0.15 mmol of $Cp_2Zr(CH_2C_6H_4$-*o*-$NMe_2)_2$ in 5 mL of THF to an equal molar quantity of sodium naphthalenide in 5 mL of THF, a dark green solution was obtained. The product was not isolated, but the solution was transferred to an ESR tube for further study.

Preparation of $Cp_2Zr(CH_2C_6H_4$-*o*-$NMe_2)$ (9). To an amalgam (1% Na in Hg) in 15 mL of toluene was added 0.21 mmol of $Cp_2Zr(Cl)(CH_2C_6H_4$-*o*-$NMe_2)$, and the mixture was stirred for 1.5 h. The resulting dark green solution was decanted, the volume reduced, 20 mL of pentane added at 0 °C, and the mixture held at 0 °C for 12 h. After filtration of the resulting solid, it was freed of solvent in vacuo, and THF was added to make a solution for ESR study.

Preparation of $Cp_2Zr(CH_2C_6H_4$-*o*-$PPh_2)$ (10). This product and its THF solution for ESR study were obtained analogously to $Cp_2Zr(CH_2C_6H_4$-*o*-$NMe_2)$.

Results and Discussion

The general preparation of the monosubstituted derivatives of dicyclopentadienyl group 4 metal dihalides proceeds through reactions between Cp_2MCl_2 (M = Zr, Hf) and a molar equivalent amount of the lithium salts of ligands A and B:

$$Cp_2MCl_2 + LiCH_2C_6H_4\text{-}o\text{-}ER_2 \rightarrow Cp_2M(Cl)CH_2C_6H_4\text{-}o\text{-}ER_2 + LiCl$$

The details of the preparations given above reflect the fact that it is important to control the stoichiometry of the product by keeping the concentration of the ligand relatively low throughout the reaction and by controlling the reaction temperature.

The stoichiometries of the monosubstituted products were confirmed by elemental analysis and by observation of the parent ion peak in the mass spectrum of each. The parent ion masses, the 250-MHz ^1H NMR chemical shifts, and the key infrared features of these products, from which their structures were deduced, are presented in Table I. The mass spectrum of **1** contains the parent ion peak and shows the fragmentation route to involve first the loss of Cl and then the loss of one Cp. The mass spectra of **2**, **3**, and **4** are analogous; in none is there is a significant peak for an $[M - Cp]^+$ ion. The ^1H NMR spectrum of **1** in $CDCl_3$ at 250 MHz and 25 °C exhibits one signal for Cp at δ 6.12, typical of a monoalkyl $Cp_2Zr(Cl)R$,[10,14,15] and bands for equivalent $N(CH_3)_2$, methylene, and aromatic (C_6H_4) hydrogens. The infrared spectra of **1** and **2** contain bands typical of ortho-substituted

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Table I. Spectroscopic Data for Group 4 Complexes

	^{1}H NMR chem shifts, δ^a				IR,^{b} cm^{-1}			mass spectrum parent ion $[M]^+$, m/e
compd	C_5H_5	NMe_2	MCH_2	C_6H_4, C_5H_5	ν(M–Cl)	ν(M–C)	ν(Cp)	
$Cp_2Zr(Cl)CH_2C_6H_4$-*o*-NMe_2 (**1**)	6.12 s	2.66 s	2.30 s	6.80–7.13 m	342	470	812	391
$Cp_2Hf(Cl)CH_2C_6H_4$-*o*-NMe_2 (**2**)	6.06 s	2.66 s	2.00 s	6.80–7.10 m	304	470	807	479
$Cp_2Zr(Cl)CH_2C_6H_4$-*o*-PPh_2 (**3**)	6.26 s		2.36 s	7.06–7.70 m	343	445	808	532
$Cp_2Hf(Cl)CH_2C_6H_4$-*o*-PPh_2 (**4**)	5.96 s		2.13 s	7.16–7.50 m	301, 302	443	820	519
$Cp_2Zr(CH_2C_6H_4$-*o*-$NMe_2)_2$ (**5**)	5.97 s	2.69 s	2.30 s	6.67–7.13 m		459	801	490
$Cp_2Hf(CH_2C_6H_4$-*o*-$NMe_2)_2$ (**6**)	5.85 s	2.60 s	2.00 s	6.67–7.10 m		460	797	N/A
$Cp_2Zr(CH_3)(CH_2C_6H_4$-*o*-$NMe_2)$ (**7**)	6.01 s	2.65 s	2.32 s	6.70–7.10 m, 0.17 s^c		451	800	N/A

^{a}In $CDCl_3$. ^{b}In Nujol. ^{c}CH_3. ^{d}All compounds gave correct relative peak areas upon integration.

benzene and ortho-substituted benzyl amine, respectively. A band in the 443–470-cm^{-1} region for each of the compounds **1**–**6** is assigned to the M–C(methylene) stretching mode.[15] The far-infrared spectra of **1** and **3** contain a very strong peak at 342 ± 2 cm^{-1}, assigned to ν(Zr–Cl), while **2** and **4** exhibit ν(Hf–Cl) at 302 ± 2 cm^{-1}.

The spectral properties of compounds **1** and **2** are qualitatively the same, and those of **3** and **4** are nearly as similar, as may be expected for Zr and Hf.[16] However, it is possible that the ligation of A and B could differ significantly. For example, the P atom of ligand B could have a bonding interaction at a site in an expanded Zr (or Hf) coordination. In $Cp_2Zr(Cl)(CH_2PPh_2)$ (**10**) the closest Zr–P distance is 3.75 Å, which is nonbonding, but the larger "bite" of the $CH_2C_6H_4PPh_2$ ligand makes such an interaction feasible. In those cases where there is P–M bnding to an MCp moiety, such as that containing the P–W–Cp linkage,[15,17] nuclear spin coupling is found between phosphorus and the protons of the Cp ring. In the 250-MHz ^{1}H NMR spectra of **3** and **4** the Cp protons give a singlet, which indicates that there is no direct P–Zr (or P–Hf) interaction. More direct evidence is available from the ^{31}P NMR spectrum of **3**. It shows one sharp singlet at 100.46 ppm (relative to $P(OCH_3)_3$), whereas several satellite peaks (or, more likely, a broadened resonance) would be expected from the coupling of the ^{31}P to the ^{91}Zr ($I = {}^5/_2$) nucleus. Thus, there is no significant Zr–P bonded interaction.

The fact that these ligands do not function as bidentates when the $Cp_2Zr(Cl)$ unit is intact presumably indicates that the 16-electron configuration is relatively stable and that the attraction of the P (or N) lone pair to Zr (or Hf) is not great enough to overcome the steric requirements of A (or B) and the energy required to rearrange the ligands around the metal. The chemistry of these complexes is consistent with this. They are thermally stable, they decompose in the presence of H_2O to yield a mixture of $(Cp_2MCl)_2O$ and either $CH_3C_6H_4$-*o*-NMe_2 or $CH_3C_6H_4$-*o*-PPh_2, and they react quantitatively with anhydrous HCl in diethyl ether to give Cp_2MCl_2 and $CH_3C_6H_4$-*o*-NMe_2 or $CH_3C_6H_4$-*o*-PPh_2. In addition, reaction of **1** with 1 molar equiv of $LiCH_3$ yielded a very air-sensitive, viscous yellow liquid, formulated as $Cp_2Zr(CH_3)(CH_2C_6H_4$-*o*-$NMe_2)$ (**7**). Compound **7** was thermally unstable and decomposed with evolution of CH_4. However, in striking contrast to the case of $Cp_2Zr(Cl)CH_2PPh_2$, which undergoes CO insertion under mild conditions,[3] **3** was inert to CO insertion under the same (130 psi of CO) conditions. Although this difference is not fully understood, it may be related to the difference in electron-donating properties of the moieties attached to the methylene (–CH_2–) bridge. With the molecules formulated as $Cp_2Zr(Cl)CH_2X$, CO insertion occurs with X = PPh_2 but not with X = $C_6H_4PPh_2$ under the same conditions. This reaction also does not proceed under these conditions with **1**, **2**, or **4**.

The disubstituted compounds of Cp_2MCl_2 (M = Zr, Hf) with the $CH_2C_6H_4NMe_2$ ligand, compounds **5** and **6**, were isolated as pale yellow viscous liquids. Their mass spectra showed the parent ion peak, and their ^{1}H NMR and infrared properties are in accord with their formulas. However, the reaction of Cp_2MCl_2 (M = Zr, Hf) with 2 molar equiv of $LiCH_2C_6H_4PPh_2$ did not yield tractable products of the disubstituted stoichiometry. This presumably is due to the greater steric hindrance between two B ligands than between two A ligands. Interestingly, neither of the disubstituted compounds with ligand A, **5** and **6**, is found in the preparation of the monosubstituted analogues, **1** and **2**, although they would be readily distinguishable in the 250-MHz ^{1}H NMR spectra of the solutions from which **1** or **2** were isolated. Attempts to prepare mixed halides of the type Cp_2MXY typically result in statistical mixtures of Cp_2MX_2, Cp_2MXY, and Cp_2MY_2. Since **5** and **6** can be prepared, it appears that the synthesis of **1** and **2** requires both the limitation of the amount and dilution of the ligand and some energy barrier to distinguish **1** from **5** and **2** from **6**. The most likely possibility is that the Zr (or Hf) to ligand bond through the methylene is not kinetically labile.

Table II. ESR Parameters^a

species	$\langle g \rangle$	$\langle A^M \rangle$	$\langle A^H \rangle$	$\langle A^P \rangle$
$Cp_2Zr(CH_2C_6H_4$-*o*-$NMe_2)_2^-$	1.891	20.35	2.94 (4 H)	
$Cp_2Zr(CH_2C_6H_4$-*o*-$NMe_2)$	1.973	<10	6.07 (1 H)	
$Cp_2Zr(CH_2C_6H_4$-*o*-$PPh_2)$	1.984	6.70	5.49 (2 H)	19.09 (1 P)
$Cp_2Zr(CH_2Ph)_2^{-\,b}$	1.986	16.22	2.27 (4 H)	
$Cp_2Ti(CH_2C_6H_4$-*o*-$NMe_2)^c$	1.981	6.7(Ti)	4.7 (1 H)	
$Cp_2Zr(CH_2PPh_2)^d$	1.98	12.5		18.0 (1 P)

^{a}Hyperfine couplings in units of 10^{-4} cm^{-1}. ^{b}Reference 18. ^{c}Reference 9. ^{d}Reference 10.

ESR Studies. The radical anion of $Cp_2Zr(CH_2C_6H_4$-*o*-$NMe_2)_2$ (**8**) exhibited a well-resolved ESR spectrum (line widths ca. 1.4 G) showing coupling to four equivalent protons and to the 11.23% natural abundance of ^{91}Zr ($I = {}^5/_2$). The spectrum is readily analyzed to give the parameters shown in Table II. The ESR parameters are very similar to those reported by Lappert and co-workers[18] for $Cp_2Zr(CH_2Ph)_2^-$. A THF solution of $Cp_2Zr(CH_2C_6H_4$-*o*-$NMe_2)$ (**9**) gave a poorly resolved ESR spectrum (line widths ca. 7 G) that showed coupling to a single proton. No ^{91}Zr satellites could be detected.[19] The ESR spectrum of the THF solution of $Cp_2Zr(CH_2C_6H_4$-*o*-$PPh_2)$ (**10**) consists of a doublet and one pair of ^{91}Zr satellites (Figure 1A); the second-derivative spectrum (Figure 1B) shows further resolution to a doublet of triplets. We tentatively assign the doublet coupling to ^{31}P and the triplet to the two protons of the methylene group. However, it is not obvious from the experimental spectra that the triplet has intensity ratios 1:2:1 as expected for coupling to two equivalent protons. Attempts to verify this assignment by computer simulation of the spectrum led to some further insights.

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(20) In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

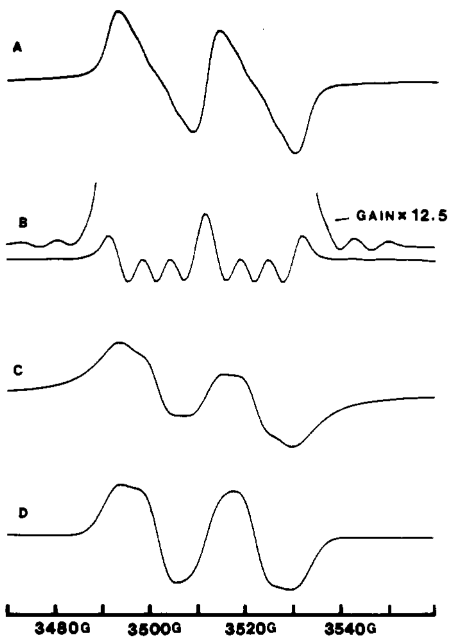

Figure 1. ESR spectra of $Cp_2Zr(CH_2C_6H_4\text{-}o\text{-}PPh_2)$: (a) experimental first-derivative spectrum; (b) experimental second-derivative spectrum showing ^{91}Zr satellites; (c) simulated first-derivative spectrum with Lorentzian line shapes and equal line widths; (d) simulated first-derivative spectrum with Gaussian line shapes and equal line widths.[19] An upper limit of about 10 G can be placed on the ^{91}Zr coupling constant. The ESR spectrum of this solution was also examined at 120 K. The frozen-solution spectrum showed the **g**-tensor anisotropy (1.938, 1.988, 2.001) expected for a $4d^1$ system, but no trace of hyperfine coupling was detectable.

In order to just lose resolution of a 1:2:1 triplet in a first-derivative spectrum, the Lorentzian component line width must be about 1.5 times the triplet splitting.[19] However, a simulated spectrum with 9-G line widths (Figure 1C) is a very poor match to the experimental spectrum. In particular, the wings of the simulated spectrum are much too broad. Indeed, the wings of the experimental spectrum closely approximate a Gaussian line shape, suggesting that the shape of the component lines is due largely to unresolved hyperfine coupling, probably to the protons of the benzene rings. Although a simulation with Gaussian line shapes (Figure 1D) substantially improves the fit of the wings of the spectrum, the central portions of the 1:2:1 multiplets are poorly reproduced. It appears that the central features of the triplets have substantially greater width (and hence smaller amplitudes) than the outer features. Simulations with a variety of arbitrary unresolved hyperfine patterns and Lorentzian line shapes have convinced us of the general validity of this conclusion.

It is well-known that the coupling constant of a methylene proton adjacent to a radical center depends on the dihedral angle. Thus in general, the two coupling constants are modulated out of phase by a rotation about the bond. When essentially free rotation is permitted, as in the propyl radical, the couplings are rapidly averaged and a 1:2:1 hyperfine pattern is obtained. When rotation is very slow or is stopped, a doublet of doublets is expected and often only the larger coupling is resolved. In intermediate cases, a triplet pattern may be observed, but with the central feature broadened.[19] Examples of all three cases are found in the ESR spectra reported here. Thus in **8** and $Cp_2Zr(CH_2Ph)_2$,[18] the ligands are freely rotating with apparently equivalent methylene protons. In **9** and $Cp_2Ti(CH_2C_6H_4\text{-}o\text{-}NMe_2)$,[9] rotation is slow and only one coupling is observed. In **10**, the chelate ring is sufficiently fluxional that the methylene proton couplings are nearly averaged but with broadening of the central feature of the triplet.

Conclusions. Compounds of the type $Cp_2Zr(Cl)(CH_2C_6H_4\text{-}o\text{-}ER_2)$ have been obtained with $ER_2 = NMe_2$ and PPh_2. Despite their size and potential chelating ability through the P of the PPh_2 moiety, the PPh_2-containing species do not bind significantly to Zr through the P atom. In the case of the smaller $(CH_2C_6H_4\text{-}o\text{-}NMe_2)$ ligand, two ligands can be attached to yield $Cp_2M(A)_2$ (M = Zr, Hf) compounds, but the larger $(CH_2C_6H_4\text{-}o\text{-}PPh_2)$ does not form analogous $Cp_2M(B)_2$ compounds by our methods. Although the $Cp_2M(A)_2$ species are accessible, the kinetic properties of $Cp_2M(Cl)(A)$ (kinetic stability of the M–C bond) do not lead to scrambling to form mixtures of Cp_2MCl_2, $Cp_2M(Cl)(A)$, and $Cp_2M(A)_2$. Upon reduction with Na(Hg) or the naphthalenide ion, M(III) compounds are formed. In the case of Zr-containing compounds, $Cp_2Zr(A)_2^-$ forms with freely rotating ligands and equivalent methylene protons, while $Cp_2Zr(A)$ and $Cp_2Zr(B)$ form with slower chelate ring fluctionality.

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Registry No. **1**, 96454-39-6; **2**, 96454-40-9; **3**, 96454-41-0; **4**, 96454-42-1; **5**, 96454-43-2; **6**, 96454-44-3; **7**, 96454-45-4; **8**, 96454-46-5; **9**, 96454-47-6; **10**, 96454-48-7; Cp_2ZrCl_2, 1291-32-3; Cp_2HfCl_2, 12116-66-4; $LiCH_2C_6H_4\text{-}o\text{-}NMe_2$, 96454-49-8; $LiCH_2C_6H_4\text{-}o\text{-}PPh_2$, 52891-06-2.

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Synthesis and Crystal Structure of a Simple Mononuclear Lithium Complex. Tetraethylammonium Bis(1,2-bis(2-hydroxyphenyl)-1,3-propanedionato)lithate

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As a part of a program to investigate synthesis-directing ligands such as 1,3-bis(2-hydroxyphenyl)-1,3-propanedione ($bhppH_3$),[1,2] we found that reaction of the zinc complex $Zn(bhppH_2)_2{\cdot}2CH_3OH$ with LiMeO surprisingly yielded a mononuclear lithium complex. Several lithium complexes have been reported in the literature. Most of them exhibit a dimeric or cluster structure.[3,4] A few are monomeric, but to our knowledge no one is as simple and symmetric as the one reported in this paper. We report here details of the isolation, characterization, and X-ray crystal structure of $NEt_4[Li(bhppH_2)_2]$. The need for bulky terminal groups in the β-diketone is believed to be necessary in order to get lithium complexation and isolation.

Experimental Section

Unless specifically mentioned, all operations were performed under nitrogen. Absolute ethanol and ethyl acetate were reagent grade and were used as received. Lithium methoxide/sodium methoxide had been prepared from lithium/sodium metal and methanol dried with magnesium. $Zn(bhppH_2){\cdot}2CH_3OH$[2] and $Zn(acac)_2{\cdot}H_2O$[5] were prepared by literature methods. Microanalyses (C, H, N) were performed in our analytical laboratory on a Perkin-Elmer 240-B, and lithium was determined by atomic absorption on a Perkin-Elmer 370-A. ^1H NMR spectra were run on a Bruker WP.80SY.

Synthesis of $NEt_4[Li(bhppH_2)_2]$. A solution containing 1.98 mmol of LiMeO in ethanol (10 mL) was slowly added to a suspension of $Zn(bhppH_2)_2{\cdot}2CH_3OH$ (0.2 g, 0.33 mmol) in ethanol (20 mL) at 0 °C.

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