Scheme I is operative. The low-resolution mass spectrometry data, however, do not allow clear analysis of lower molecular weight products (containing less deuterium), although their presence is determined by qualitative interpretation of the spectra.

Although there is a disparity between the high-resolution and GC mass spectrometry data, both sets of results indicate some production of hydrocarbons containing less deuterium than predicted by Schemes I and II. For the saturated products isolated before HCl addition, the excess hydrogen must come from either the starting methyl complex or the solvent. The results for ethane show approximately equal amounts of d_3 and d_2 products, both of which may be formed according to Scheme II, differeing only in the cleavage step. While the d_3 species may arise from borane cleavage of the ethyl complex, the d_2 product may be the result of an interaction between the ethyl complex and a second metal alkyl or hydride. For example, β-H elimination from $Mn(CD_2CH_3)(CO)_5$ or the less likely α-H elimination from $Mn(CH_2CH_3)(CO)_5$ would produce a metal hydride, thus supplying the final hydrogen in the alkane products.

The low-resolution mass spectrometry data on propylene indicate the d_1 species is important, even if not the only product as suggested by the high-resolution mass spectrum results. Formation of propylene-d_1, after HCl addition, may occur by a deviation of Scheme II in which the acid supplies the excess hydrogens. Insertion of CO into the metal carbene bond of an intermediate such as IV would produce a C_3 fragment containing only one borane hydrogen (deuterium).[37] Subsequent reaction with HCl would give propylene-d_1. Alternatively, any unsaturate has the potential to recoordinate and undergo H/D exchange at a Mn center, but this type of reaction is not likely to be specific to one product.

The results of the ^{13}CO experiment definitely show that the mechanisms proposed in Schemes I and II cannot account for all observed products. As predicted by an insertion–reduction mechanism the ethane contains no ^{13}C. However, the C_3 products do not conform quite as well. The isotopic distribution in propylene (68% $^{13}CC_2H_6$, 32% C_3H_6) is close to that expected (75% $^{13}CC_2H_6$, 25% C_3H_6); but the propane products show a much greater incorporation of ^{13}CO.

The reaction between $Mn(CH_3)(CO)_5$ and BF_3 forming cyclic adduct VII is very fast and can account for the C_2 products with no ^{13}C, but this initial interaction cannot be the chain building step responsible for propanes containing more than one ^{13}C. It is likely that several mechanisms are operative in the production of hydrocarbons. The intermediates VII and IX may offer possible routes to an enriched molecule either by labilizing the terminal carbonyls or by providing an open coordination site on the metal.

Acknowledgment. This research was supported by the NSF.

Registry No. $Mn(CH_3)(CO)_5$, 13601-24-6; $(\eta^5\text{-}C_5H_5)Fe(CH_3)(CO)_2$, 12080-06-7; B_2H_6, 19287-45-7.

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Alkyl and Hydride Derivatives of (Pentamethylcyclopentadienyl)zirconium(IV)[†]

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Received January 12, 1982

Cp*Li (Cp* = η^5-C_5Me_5) reacts with $ZrCl_4$ in toluene to form $(Cp^*ZrCl_3)_x$. The trialkyls Cp^*ZrR_3 (R = CH_3, CH_2Ph, Ph), the dialkyl $Cp^*ZrCl(CH_3)_2$, and the alkyls $(Cp^*ZrCl_2R)_x$ (R = CH_3, CH_2Ph) are prepared via the treatment of $(Cp^*ZrCl_3)_x$ with a stoichiometric amount of RMgX. $Cp^*Zr(BH_4)_3$, prepared from $(Cp^*ZrCl_3)_x$ and $LiBH_4$, is treated with $N(CH_3)_3$ to afford $[Cp^*Zr(H)(BH_4)(\mu\text{-}H)]_2$. "Mixed" ring complexes were also prepared: $Cp^*CpZrCl_2$, $Cp^*(MeInd)ZrCl_2$ (MeInd = 1-methylindenyl), $Cp^*Cp'ZrCl_2$ (Cp′ = 1,2,4-trimethylcyclopentadienyl), $Cp^*CpZr(CH_3)_2$, $Cp^*(MeInd)Zr(CH_3)_2$, $Cp^*Cp'Zr(CH_3)_2$, $(Cp^*CpZrH_2)_2$, and $Cp^*Cp'ZrH_2$.

Introduction

The chemistry of dicyclopentadienyl[1,2] and bis(pentamethylcyclopentadienyl) zirconium hydrides[3,4] and alkyls has been explored extensively, yet the corresponding reactivity of the cyclopentadienylzirconium moiety (CpZr) has thus far received little attention. Several complexes containing the CpZr unit have been synthesized, but virtually all of these contain Zr–O, Zr–N, or Zr–X (X = F, Cl, Br, I) bonds.[1] Few monocyclopentadienylzirconium complexes containing Zr–C or Zr–H bonds have been characterized, although tetraalkylzirconium species[5] and $Zr(BH_4)_4$[6] are well-known. In general, the aforementioned dicyclopentadienylzirconium compounds are conveniently prepared from the readily available dichloride Cp_2ZrCl_2. $CpZrCl_3$, a logical starting material for the preparation of

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[†] Contribution No. 6576.

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monocyclopentadienylzirconium hydrides and alkyls may be synthesized via the reaction of $ZrCl_4$ and Cp_2Mg in reasonable yield;[7] however, $CpZrCl_3$ is not yet commercially available, so that the development of its chemistry has been slower.

Recently Wengrovius and Schrock have reported (pentamethylcyclopentadienyl)zirconium trichloride $(Cp^*ZrCl_3)_x$ and neopentyl derivatives.[8] Concurrently, Blenkers, De Liefde Meijer, and Teuben have reported another covenient preparation of $(Cp^*ZrCl_3)_x$ and its tris(allyl) derivatives.[9] Reported in this article are a number of Cp*Zr derivatives and our synthesis of (pentamethylcyclopentadienyl)zirconium trichloride, a variant on that described by Blenkers et al.[9] Various alkyl complexes have been prepared by the reaction of **1** and alkylmagnesium halides. Tetrahydroborate and hydride derivatives of (pentamethylcyclopentadienyl)zirconium were also prepared, but attempts to generate $Cp^*ZrH_3L_2$ were unsuccessful. $(Cp^*ZrCl_3)_x$ is also a convenient starting material for the preparation of (pentamethylcyclopentadienyl)cyclopentadienylzirconium complexes.

Results

$Cp_2^*TiCl_2$ is known to stoichiometrically transfer one pentamethylcyclopentadienyl ligand to a molecule of $TiCl_4$ in virtually quantitative yield to form Cp^*TiCl_3.[10] Therefore, the analogous cyclopentadienyl–chloride exchange reaction between $Cp_2^*ZrCl_2$,[11] a readily available starting material, and $ZrCl_4$ was attempted. No indication of a monopentamethylcyclopentadienyl species was detected by ^1H NMR, however, even when this mixture was heated for prolonged periods in either THF or toluene.

A simple metathesis of either LiCp* or Cp*MgCl·THF and $ZrCl_4$ resulted in the preparation of Cp^*ZrCl_3 species in a variety of solvents. When ethereal solvents or small amounts of Lewis bases were present, the Cp^*ZrCl_3 moiety formed from the metathetical reactions was initially isolated as an adduct. Even when only one molecule of the THF per zirconium was present in the reaction in toluene of Cp*MgCl·THF and $ZrCl_4$, Cp^*ZrCl_3·THF was isolated from solution. The subsequent sublimation of this adduct at 160 °C in a dynamic vacuum (10^{-4} torr) still did not wholly free the Cp^*ZrCl_3 unit from the THF. When THF, dimethoxyethane, diethyl ether, or triethylamine were present, only weakly basic diethyl ether and bulky NEt_3 could be completely removed by sublimation, as was observed also by Wengrovious and Schrock.[8] The binding of these solvent molecules about the zirconium center may play an important role in preventing an additional attack by a second pentamethylcyclopentadiene ligand.

Since it was suspected that these strongly bound bases would interfere in ensuing reactions, an attempt was made to generate Cp^*ZrCl_3 in hydrocarbon solvents. Somewhat surprisingly, $(Cp^*ZrCl_3)_x$(**1**) was smoothly prepared by refluxing LiCp* and $ZrCl_4$ in toluene at 110 °C for 48 h, according to eq 1. The ^1H NMR of the crude reaction

$$\mathrm{LiCp^* + ZrCl_4 \rightarrow \underset{\mathbf{1}}{(Cp^*ZrCl_3)_x} + LiCl} \qquad (1)$$

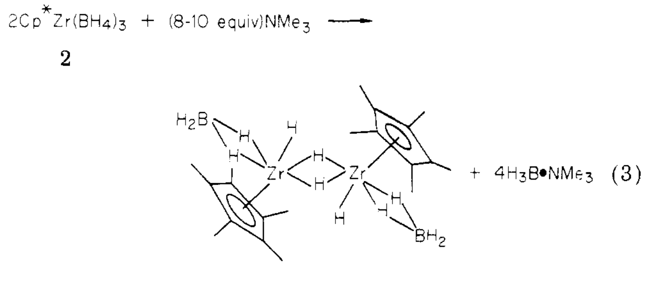
mixture reveals that virtually no $Cp_2^*ZrCl_2$ is obtained as a byproduct. Unlike soluble, monomeric Cp^*TiCl_3,[12] light yellow **1** is difficult to crystallize from hydrocarbon solvents and is thus formulated as an oligomer. Analytically pure $(Cp^*ZrCl_3)_x$ is obtained in 80% yield via sublimation of the crude material at 160 °C (10^{-4} torr). The "hard" Lewis acid behavior of this complex is indicated not only by its ability to form adducts with amines and ethers, but its inability to cleanly form adducts with "softer" ligands such as triphenylphosphine or bis(diphenylphosphino)ethane.

(Pentamethylcyclopentadienyl)zirconium trichloride (**1**) is sufficiently soluble in toluene to cleanly react with excess $LiBH_4$ (eq 2). The pure, white tris(tetrahydroborate)

$$\mathrm{\underset{\mathbf{1}}{(Cp^*ZrCl_3)_x} + LiBH_4\ (excess) \rightarrow \underset{\mathbf{2}}{Cp^*Zr(BH_4)_3} + 3LiCl} \qquad (2)$$

complex $Cp^*Zr(BH_4)_3$ (**2**) is isolated by crystallization from petroleum ether in 82% yield. The infrared spectrum of **2** (Table I) indicates that each tetrahydroborate is bound in a tridentate fashion about the zirconium.[13] A typical $^1J_{^{11}BH}$ coupling[13] of 86 Hz is observed for the quartet (12 H) of broad resonances centered at δ 1.39 in the ^1H NMR spectrum. The tris(tetrahydroborate) reacts with CO over a period of weeks at 80 °C to yield several unidentifiable products; none contain fragments that might be construed as occurring via a reduction of carbon monoxide.

Since the cleavage of BH_3 from tetrahydroborate complexes by suitable σ donors is a common route to transition metal hydride species,[14] **2** was treated with both $P(CH_3)_3$ and $N(CH_3)_3$. Although trimethylphosphine effectively cleaved BH_3 from **2**, none of the zirconium-containing products were cleanly isolable. When approximately 8–10 equiv of $N(CH_3)_3$ reacts with $Cp^*Zr(BH_4)_3$, dimer **3** is isolated from the toluene solution (eq 3). Repeated crystallizations from petroleum ether afforded $[Cp^*Zr(BH_4)H(\mu\text{-}H)]_2$ (**3**) in 40% yield as off-white prisms. The ^1H NMR and IR spectra for **3** are given in Table I. The IR spectrum clearly indicates the presence of a bidentate tetrahydroborate ligand,[13] one terminal hydride (ν(Zr–H) = 1628 cm^{-1}) and one bridging hydride (ν(Zr–H–Zr) $\approx$ 1450 cm^{-1}, partially obscured by Nujol). The broad hydride resonances[15] are evident in the ^1H NMR spectrum, but the tetrahydroborate is apparently missing. A closer inspection reveals a broad almost undetectable resonance centered near δ 1.3, which integrates as four hydrogens. The dimer **3** does not react with CO at 25 °C after 3 weeks, and, upon heating, merely decomposes to a multitude of products. $[Cp^*Zr(BH_4)H(\mu\text{-}H)]_2$ (**3**) appears to polymerize ethylene; however, the low rate of oligomerization may indicate trace impurities are responsible.



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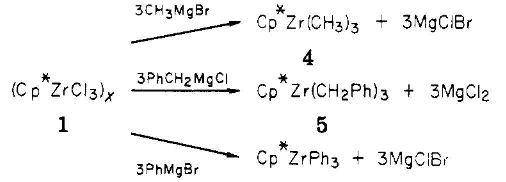
[15] In part, the broadness of these resonances is due to coupling between Zr–H_t and Zr–H_b, as confirmed by decoupling experiments. One cannot rule out possible ^{11}B broadening.

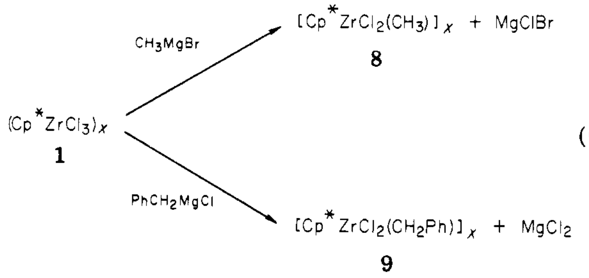
Compound 1 serves as a starting material for the synthesis of a number of (pentamethylcyclopentadienyl)zirconium trialkyl complexes. (Cp^*ZrCl_3)$_x$ (1) reacts cleanly with 3 equiv of CH_3MgBr, $PhCH_2MgCl$, or PhMgBr in diethyl ether to form the trialkyl derivatives Cp^*ZrR_3 according to eq 4. Whereas analytically pure $Cp^*Zr(CH_2Ph)_3$ (5) and $Cp^*Zr(Ph)_3$ (6) are obtained via crystallization from petroleum ether, $Cp^*Zr(CH_3)_3$ (4) is best purified by a room-temperature sublimation of the crude material onto a probe cooled to −20 °C.[16] Compound 4 is thermally unstable as a solid, at 25 °C even under pure N_2, yet may be kept at −20 °C under N_2 for months.



(4)

Alkyl and dialkyl derivatives are also easily prepared from (Cp^*ZrCl_3)$_x$ (1) and the appropriate Grignard reagents. Two equivalents of CH_3MgBr react with 1 to form $Cp^*ZrCl(CH_3)_2$ (7) as indicated by eq 5. Although light yellow 7 was crystallized from petroleum ether in good yield (68%), it too is unstable and could not be analyzed. (Cp^*ZrCl_3)$_x$ (1) also reacts with CH_3MgBr and $PhCH_2MgCl$ to form the monoalkyl complexes shown in eq 6. Both 8 and 9 are sparingly soluble in toluene and, as reacton 6 indicates, may be oligomers, although definitive molecular weight studies have not been undertaken. The benzyl complex 9 is crystallized from hot toluene, but the methyl derivative 8 could not be entirely freed from the magnesium dihalide via repeated crystallizations from hot benzene.[17]

$$\underset{1}{(Cp^*ZrCl_3)_x} + 2CH_3MgBr \xrightarrow{Et_2O} \underset{7}{Cp^*ZrCl(CH_3)_2} + 2MgClBr \quad (5)$$



(6)

By monitoring the disappearance of the pentamethylcyclopentadienyl singlet in the ^1H NMR, crude estimates of the relative thermal stabilities of the various alkyl complexes were determined. At both 25 and 80 °C, the order of stability for the trialkyl complexes is as follows: $5 \gg 6 \geq 4$.[18] [$Cp^*ZrCl_2(CH_3)$]$_x$ (8) is stable for days in solution at room temperature, while both $Cp^*Zr(CH_3)_3$ (4) and $Cp^*ZrCl(CH_3)_2$ (7) were partially decomposed after 24 h.[19] The only identifiable products (^1H NMR) from the decomposition of the various $Cp^*ZrCl_xR_{3-x}$ complexes are the corresponding hydrocarbons RH.

The trialkyl derivatives 4, 5, and 6 are easily hydrogenated;[18,20] again, the only identifiable products (^1H NMR) are the respective hydrocarbons: methane, benzene, and toluene. A large increase in the rate of decomposition is observed, yet the order of stability remains the same as in the thermal decompositions. Since no tractable zirconium-containing species are formed in these hydrogenations, phosphines were added in an attempt to trap and stabilize the intermediates. Trimethylphosphine ($P(CH_3)_3$) and bis(dimethylphosphino)ethane (dmpe) were added in the reaction of $Cp^*Zr(CH_3)_3$ (4) with dihydrogen in the (vain) hope that the presumed Cp^*ZrH_3 fragment might be stabilized as $Cp^*ZrH_3L_2$. Two equivalents of $P(CH_3)_3$ appear to bind to $Cp^*Zr(CH_3)_3$ (4) (^1H NMR) to form $Cp^*Zr(CH_3)_3(P(CH_3)_3)_2$ (10), yet the decomposition rate of this species under H_2 is barely slower than that of 4 alone. When dmpe is added to a solution of the trimethyl derivative 4, $Cp^*Zr(CH_3)_3$dmpe (11) is isolated by crystallization from petroleum ether. Although 11 is stable for hours at 25 °C under 3 atm of H_2, further heating results in decomposition.

Since it is conceivable that the concentration of H_2 in solution at 3 atm is too low to effectively trap intermediates present during the hdyrogenation of 11, the reaction was carried out under 95 atm of dihydrogen. Again, however, no soluble zirconium hydride species were evident upon workup of the high-pressure reaction mixture: only free dmpe was identified by ^1H NMR. An insoluble grayish precipitate was isolated, and its IR spectrum revealed the presence of a pentamethylcyclopentadienyl ring and a broad absorption ranging from 1350 to 1550 cm^{-1}. This absorption may correspond to a melange of zirconium–hydride stretches; thus the precipitate is formulated as (Cp^*ZrH_3)$_x$ (12).

Apparently, even dmpe cannot sufficiently stabilize the Cp^*ZrH_3 moiety with respect to oligomerization. When borohydride dimer 3 is treated with dmpe, the ^1H NMR spectrum shows that the dimeric unit surprisingly remains intact, and dmpe remains free in solution. Heating the reaction mixture with dmpe appears to effect cleavage of the remaining borohydride units of 3; however, a complex mixture of products results.

(Cp^*ZrCl_3)$_x$ (1) is also a convenient starting material for the synthesis of "mixed-ring" complexes of zirconium. (Pentamethylcyclopentadienyl)cyclopentadienylzirconium dichloride, $Cp^*CpZrCl_2$ (13), is isolated in 83% yield after 2 days' reflux in toluene of sodium cyclopentadienide and 1, according to eq 7. Lithium 1,2,4-trimethylcyclopentadienide (LiCp′) and lithium 1-methylindenide (LiMeInd)[21] also react cleanly with 1 to form the corresponding mixed-ring dichloride complexes 14 and 15 in good yield as indicated by eq 8. All of the zirconium dichlorides are converted to their dimethyl derivatives according to eq

$$\underset{1}{(Cp^*ZrCl_3)_x} + NaCp \rightarrow \underset{13}{Cp^*CpZrCl_2} + NaCl \quad (7)$$

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(16) $CpTi(CH_3)_3$ has been prepared in a similar fashion. Giannini, U.; Cesca, S. *Tetrahedron Lett.* **1960**, 19.

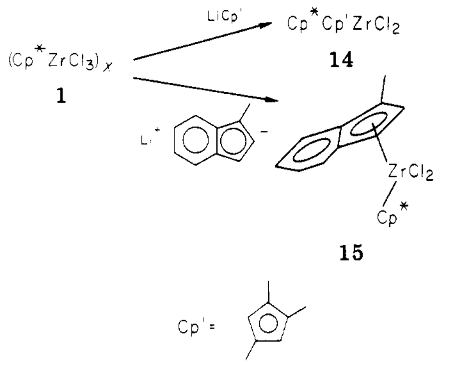
(17) The possibility of halogen exchange to form $Cp^*ZrCl_{2-x}Br_x(CH_3)$ cannot be ruled out.

(18) Defining $t_{1/2}$ as the time at which the Cp* resonance is half the integral value $t = 0$, at 25 °C $t_{1/2} \approx 25$ h (4), 30 h (6), and indefinite (5). Under 3 atm of H_2, at 25 °C $t_{1/2} \approx 10$ min (4), 20 min (10), and 10 min (4 + 2N(CH_3)$_3$ and at 80 °C $t_{1/2} \approx 4$ h (5).

(19) These stabilities are similar to those of $R_{4-x}Cl_xTi$ (R· = $(CH_3)_3SiCH_2$) observed by: Beilin, S. I.; Boudarenko, G. N.; Vdorin, V. M.; Dolgoplosk, B. A.; Markevich, I. N.; Nametkin, N. S.; Poletaev, V. A.; Svergun, V. I.; Sergeeva, M. B. *Dokl. Akad. Nauk SSSR* **1974**, *218*, 1347. However, they are opposite to those of $R_{4-x}Cl_xZr$ (R = CH_2Ph). See: Zucchini, U.; Albizzati, E.; Giannini, U. *J. Organomet. Chem.* **1971**, *26*, 357.

(20) (a) Weigold, H.; Bell, A. P.; Willing, R. I. *J. Organomet. Chem.* **1974**, *73*, C23. (b) Couterier, S.; Gautheron, B. *Ibid.* **1978**, *157*, C61. (c) Gell, K. I.; Schwartz, J. *J. Am. Chem. Soc.* **1977**, *100*, 3246.

(21) Bis(indenyl) complexes are well known. See: Samuel, E.; Setton, R. *J. Organomet. Chem.* **1965**, *4*, 156. Samuel, E. *Bull. Soc. Chim. Fr.* **1966**, 3548.



(8)

9–11. $Cp^*CpZrCl_2$ (**13**) reacts with 2 equiv of CH_3MgBr

$$\underset{\mathbf{13}}{Cp^*CpZrCl_2} + 2CH_3MgBr \rightarrow \underset{\mathbf{16}}{Cp^*CpZr(CH_3)_2} + 2MgClBr \quad (9)$$

$$\underset{\mathbf{14}}{Cp^*Cp'ZrCl_2} + 2CH_3Li \rightarrow \underset{\mathbf{17}}{Cp^*Cp'Zr(CH_3)_2} + 2LiCl \quad (10)$$

$$\underset{\mathbf{15}}{(MeInd)Cp^*ZrCl_2} + 2CH_3Li \rightarrow \underset{\mathbf{18}}{(MeInd)Cp^*Zr(CH_3)_2} + 2LiCl \quad (11)$$

in diethyl ether to form $Cp^*CpZr(CH_3)_2$ (**16**) in 89% yield. Both **14** and **15** were treated with 2 equiv of CH_3Li, and the corresponding dimethyl complexes **17** and **18** are obtained in 77 and 85% yields, respectively. The methylindenyl dimethyl compound **18** manifests its chirality via an inequivalence of the Zr–CH_3 resonances in the ^1H NMR.

Preparation of $(Cp^*CpZrH_2)_2$ (**19**) was carried out by treatment of $Cp^*CpZrCl_2$ with *n*-butyllithium in toluene under 1 atm of H_2 (eq 12). Molecular weight measure-

$$\underset{\mathbf{13}}{2Cp^*CpZrCl_2} \xrightarrow[H_2]{LiC_4H_9} \underset{\mathbf{19}}{(Cp^*CpZrH_2)_2} \quad (12)$$

ments and IR data (ν(Zr–H) at 1540 and 1270 cm^{-1}) are indicative of a dimeric structure entirely analogous to that established by Jones and Petersen for $[(C_5H_4Me)_2ZrH_2]_2$.[22] $Cp^*Cp'ZrH_2$ (**20**) was prepared by treatment of $Cp^*Cp'Zr(CH_3)_2$ (**17**) with H_2 (80 atm) and isolated as a yellow microcrystalline material from toluene in 70% yield. In neither case could the Zr–*H* resonance be identified in ^1H NMR spectra at room temperature. Presumably bridge–terminal exchange is occurring at intermediate rates for **19**, and an equilibrium between monomer and dimer is established in concentrated solutions for **20**. These features have not yet been examined in detail, however.

Discussion

The convenient syntheses of $(Cp^*ZrCl_3)_x$ (**1**) reported here and elsewhere[8,9] provide an inroad into the previously unexplored chemistry of various mono(pentamethylcyclopentadienyl)zirconium complexes. The ease of this synthesis concomitant with the solubility and stability properties inherent to compounds containing the pentamethylcyclopentadienyl ring[3,4] suggest that the chemistry associated with **1** may be more promising than that of $CpZrCl_3$. Whereas $Zr(CH_3)_4$[23] and $Zr(Ph)_4$[24] are unisolable, decomposing rapidly above 0 °C, $Cp^*Zr(CH_3)_3$ (**4**) and Cp^*ZrPh_3 (**6**) are stable at 25 °C, thus allowing isolation and purification. Although zirconium tetraalkyls containing sterically encumbering groups such as benzyl,[25] neopentyl, (trimethylsilyl)methyl,[26] and 1-norbornyl[27] have been isolated, the addition of the pentamethylcyclopentadienyl group undoubtedly contributes a great deal of stability to the coordinatively unsaturated polyalkyls herein described (Cp^*ZrR_3, R = CH_3 (**4**), CH_2Ph (**5**), Ph (**6**)).

The preparation of $[Cp^*Zr(BH_4)H(\mu\text{-}H)]_2$ (**3**) is apparently the first synthesis of a zirconium hydride complex containing less than two cyclopentadienyl ligands. Unfortunately, the ensuing reaction chemistry of this species appears to be minimal. The Zr–H bonds of **3** are hydridic as expected, yet **3** fails to effect the reduction of carbon monoxide, contrary to the chemistry observed for $Cp_2^*ZrH_2$,[3] $(Cp_2ZrHCl)_x$,[28] $Cp_2ZrH(\mu\text{-}H)_2(AlCH_2CH(CH_3)_2)_2(\mu\text{-}Cl)$,[29] and Cp_2^*ZrHF.[30] A plausible explanation for this lack of reactivity may lie in the inability of the tetrahydroborate dimer **3** to effectively bind CO. The extremely "hard" Lewis acid zirconium center of **3** may be inappropriate for a strong σ donation from CO, and the geometry of its hydride ligands may prevent the back-bonding believed to be operative for $Cp_2^*ZrH_2(CO)$.[31] The ligation of CO by d^0 zirconium complexes may be a key step in the aforementioned reductions of carbon monoxide.

Ethylene was not directly observed to insert into the Zr–H bonds of $[Cp^*Zr(BH_4)H(\mu\text{-}H)]_2$ (**3**); no zirconium–ethyl species were evident in the ^1H NMR. Since the dimer **3** may be considered as a coordinatively unsaturated 16 e^- complex, a pathway for the formation of any ethyl derivative is undoubtedly available. Therefore, the thermodynamics of such an insertion could be assumed to be surprisingly unfavorable. This finding is in contrast to the observed reactivities of $(Cp_2ZrHCl)_x$,[2] Cp_2^*ZrHF,[32] and $Cp_2^*ZrH_2$.[33]

Regrettably, Cp^*ZrH_3dmpe could not be synthesized, although a similar complex, Cp^*TaH_4 dmpe, can be prepared by the hydrogenation of $Cp^*Ta(CH_3)_4$[34] in the presence of dmpe. The propensity of zirconium hydride compounds to oligomerize has been well established.[1,2] Indeed, only one multiple hydride, $Cp_2^*ZrH_2$, has been shown to be monomeric.[4] This tendency to oligomerize may be primarily responsible for the unsuccessful attempts to synthesize Cp^*ZrH_3dmpe. The strongly basic, bidentate dmpe ligand is unable to overcome the bridging nature of the Zr–H bond, although it is known to stabilize high oxidation state hydrides of group 5, as indicated via the preparations of $NbH_5(dmpe)_2$[35] and $TaH_5(dmpe)_2$.[36] The combined steric bulk of the Cp* and dmpe ligands is less than that of two pentamethylcyclopentadienyl ligands of $Cp_2^*ZrH_2$, which presumably prevent its oligomerization. The mixed-ring dihydride derivatives $(Cp^*CpZrH_2)_2$ and

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Table I. ^{1}H Nuclear Magnetic Resonance and IR Data (cm^{-1})

compd	solvent	chem shift, δ		
$(Cp^*ZrCl_3)_x$ (1)	benzene-d_6	$C_5(CH_3)_5$	s	1.94
$Cp^*Zr(BH_4)_3$ (2)	benzene-d_6	$C_5(CH_3)_5$	s	1.76
$\nu(Zr-(BH_4)_3)$ = 2509, 2355, 2330, 2166, 2113 cm^{-1}		$(BH_4)_3$	q	1.39 ($^1J_{^{11}BH}$ = 86 Hz)
$[Cp^*Zr(BH_4)H(\mu\text{-}H)]_2$ (3)	benzene-d_6	$C_5(CH_3)_5$	s	2.14
$\nu(Zr-BH_4)$ = 2448, 2408, 2239, 2112, 2052, 1980 cm^{-1}		(BH_4)	br	3.0–0.0
$\nu(Zr-H_t)$ = 1628		$Zr-H_t$	s	3.91
$\nu(Zr-H_b)$ = 1350–1500 (br)		$Zr-H_b$	s	1.31
$Cp^*Zr(CH_3)_3$ (4)	benzene-d_6	$C_5(CH_3)_5$	s	1.76
		$(CH_3)_3$	s	0.23
$Cp^*Zr(CH_2Ph)_3$ (5)	benzene-d_6	$C_5(CH_3)_5$	s	1.68
		$Zr(CH_2Ph)_3$	s	1.64
		Ph_3	m (6 H)	6.52
			m (9 H)	7.52
Cp^*ZrPh_3 (6)	benzene-d_6	$C_5(CH_3)_5$	s	1.86
		Ph_3	m (9 H)	7.13
			m (6 H)	7.76
$Cp^*ZrCl(CH_3)_2$ (7)	benzene-d_6	$C_5(CH_3)_5$	s	1.78
		$(CH_3)_2$	s	0.47
$[Cp^*ZrCl_2(CH_3)]_x$ (8)	benzene-d_6	$C_5(CH_3)_5$	s	1.87
		(CH_3)	s	0.88
$[Cp^*ZrCl_2(CH_2Ph)]$ (9)	benzene-d_6	$C_5(CH_3)_5$	s	1.80
		$Zr-CH_2Ph$	s	2.23
		Ph	m	7.10
$Cp^*Zr(CH_3)_3(P(CH_3)_3)_2$ (10)	benzene-d_6	$C_5CH_3)_5$	s	1.86
		$(CH_3)_3$	s	−0.04
		$(P(CH_3)_3)_2$	s	0.86
$Cp^*Zr(CH_3)_3((CH_3)_2PCH_2CH_2P(CH_3)_2)$ (11)	benzene-d_6	$C_5(CH_3)_5$	s	2.00
		$(CH_3)_3$	s	−0.68
		PCH_2CH_2P	d	1.39 ($J_{^{31}P}$ = 13 Hz)
		$(P(CH_3)_2)_2$	d	0.86 ($J_{^{31}P}$ = 4 Hz)
$Cp^*CpZrCl_2$ (13)	$CDCl_3$	$C_5(CH_3)_5$	s	2.02
		C_5H_5	s	6.21
$Cp^*(1,2,4\text{-}(CH_3)_3C_5H_2)ZrCl_2$ (14) ($Cp^*Cp'ZrCl_2$)	$CDCl_3$	$C_5(CH_3)_5$	s	2.04
		1,2-$(CH_3)_2$	s	1.98
		4-(CH_3)	s	2.01
		C_5H_2	s	5.96
$(MeInd)Cp^*ZrCl_2$ (15)	$CDCl_3$	$C_5(CH_3)_5$	s	2.02
		Ind-CH_3	s	2.36
		C_5 ring CH	d	5.91 (J = 1.5 Hz)
		C_5 ring CH	d	5.93 (J = 1.5 Hz)
		C_6 ring	m (1 H)	7.60
		C_6 ring	m (3 H)	7.23
$Cp^*CpZr(CH_3)_2$ (16)	benzene-d_6	$C(CH_3)_5$	s	1.68
		C_5H_5	s	5.72
		$Zr(CH_3)_2$	s	−0.38
$Cp^*(1,2,4\text{-}(CH_3)_3C_5H_2)Zr(CH_3)_2$ (17) $[Cp^*Cp'Zr(CH_3)_2]$	benzene-d_6	$C_5(CH_3)_5$	s	1.78
		1,2-$(CH_3)_2$	s	1.81
		4-$(CH_3)_2$	s	1.76
		C_5H_2	s	5.29
		$Zr(CH_3)_2$	s	−0.42
$(MeInd)Cp^*Zr(CH_3)_2$ (18)	benzene-d_6	$C_5(CH_3)_5$	s	1.72
		Ind-CH_3	s	2.20
		C_5 ring CH	d	5.14 (J = 3 Hz)
		C_5 ring CH	d	5.21 (J = 3 Hz)
		C_6 ring	m (1 H)	7.60
		C_6 ring	m (3 H)	7.17
		$Zr(CH_3)$	s	−0.50
		$Zr(CH_3)$	s	−1.43
$(Cp^*CpZrH_2)_2$ (19)	benzene-d_6	$C_5(CH_3)_5$	s	1.78
$\nu(Zr-H)$ = 1540, 1270 cm^{-1}		C_5H_5	s	5.71
		ZrH_2	not located	
$Cp^*Cp'ZrH_2$ (20)	benzene-d_6	$C_5(CH_3)_5$	s	2.00
$\nu(Zr-H)$ = 1585 cm^{-1}		$C_5H_2(CH_3)(CH_3)_2$	s	1.93
		$C_5H_2(CH_3)(CH_3)_2$	s	2.27
		$C_5H_2(CH_3)(CH_3)_2$	s	5.23
		ZrH_2	not located	

$Cp^*Cp'ZrH_2$ also attest to the stability of hydride bridges and the sensitivity of the degree of oligomerization to steric bulk of the cyclopentadienyl ligands for this class of compounds.

The reported results merely hint at the breadth of chemistry available to the Cp*Zr moiety. Clearly, much further study needs to be undertaken, particularly with the potential Zr(II) chemistry which may evolve with the synthesis of species such as Cp^*ZrL_4R. Considering the wealth of reactivity mono(pentamethylcyclopentadienyl)tantalum[37] species exhibit, further exploration into the corresponding zirconium systems is undoubtedly warranted.

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Experimental Section

General Considerations. All manipulations were performed by using either glovebox or high vacuum line techniques. Solvent were purified by vacuum transfer first from $LiAlH_4$ and then from "titanocene".[38] NMR solvents, toluene-d_8 and benzene-d_6 (Stohler, Inc.), were also purified by transfer from "titanocene". Hydrogen was passed over MnO on vermiculite and activated 4-Å molecular sieves.[39] Carbon monoxide was used directly from the cylinder. The 1,2,4-trimethylcyclopentadiene, Cp′H, was prepared via a literature procedure.[40]

^1H NMR spectra were obtained by using Varian EM-390 and T-60 spectrometers. Infrared spectra were recorded on Perkin-Elmer 180 and Beckman 4240 spectrophotometers. Analyses and molecular weight measurements were performed by the Alfred Bernhardt Microanalytical Laboratory.

Reactions such as the hydrogen promoted decompositions were conducted in sealed NMR tubes and monitored by ^1H NMR spectroscopy. A typical example is the reaction of $Cp^*Zr(CH_3)_3$ (4), 2 equiv of $P(CH_3)_3$, and H_2: ca. 20 mg (0.074 mmol) of 4 were transferred to an NMR tube sealed to a ground-glass joint and fitted with a Teflon needle valve adapter. Benzene-d_6 (0.4 mL) and $P(CH_3)_3$ (0.15 mmol) were distilled into the tube at 77 K. At 77 K, 700 torr of H_2 was introduced and the tube was sealed with a torch.

Procedures. (1) $(Cp^*ZrCl_3)_x$ (1). $ZrCl_4$ (6.3 g, 27 mmol) and LiCp* (3.66 g, 25.7 mmol) were refluxed at 110 °C in toluene for 2 days. The toluene was pumped away, and the crude product was transferred to a sublimator, where 1 sublimed at 160 °C (10^{-4} torr) for 2 days. This material was then washed twice with 10-mL portions of cold toluene and dried to yield 6.85 g of 1 (80% yield). Anal. Calcd for $C_{10}H_{15}ZrCl_3$: C, 36.09, H, 4.54; Zr, 27.41. Found: C, 35.96; H, 4.69; Zr, 27.45.

(2) $Cp^*Zr(BH_4)_3$ (2). $(Cp^*ZrCl_3)_x$ (1) (1.00 g, 3.00 mmol) and $LiBH_4$ (220 mg, 10.1 mmol) were placed in a flask along with 35 mL of toluene. After being stirred at 25 °C for 24 h, the solution was filtered and the toluene stripped. Crystallization from cold petroleum ether yielded 670 mg of **2** (82% yield). Anal. Calcd for $C_{10}H_{27}B_3Zr$: C, 44.32; H, 10.01; Zr, 33.66. Found: C, 44.07; H, 9.95; Zr, 33.48.

(3) $[Cp^*Zr(BH_4)H(\mu\text{-}H)]_2$ (3). $Cp^*Zr(BH_4)_3$ (**2**) (360 mg, 2.32 mmol) was added to a flask with 30 mL of toluene. $N(CH_3)_3$ (19 mmol) was distilled in at −78 °C. After the solution was stirred at 25 °C for 2 days, the toluene was replaced with petroleum ether. The green-gray precipitate was filtered from the forest green solution and washed three times with 3-mL portions of cold petroleum ether. The solid was then pumped on for 4 h to remove residual $(CH_3)_3N{\cdot}BH_3$. The gray solid was then crystallized from hot benzene to yield the off-white $[Cp^*Zr(BH_4)H(\mu\text{-}H)]_2$ in 43% yield (286 mg). Anal. Calcd for $C_{20}H_{42}B_2Zr_2$: C, 49.37; H, 8.70; B, 4.44; Zr, 37.49. Found: C, 49.39; H, 8.11; B, 4.28; Zr, 37.48.

(4) $Cp^*Zr(CH_3)_3$ (4). The trichloride **1** (2 g, 6.00 mmol) was placed in a flask with 65 mL of diethyl ether. A 6.9 mL (20.7 mmol) portion of CH_3MgBr (3.0 M) in diethyl ether was syringed in at −78 °C. The reaction mixture was allowed to warm to 25 °C over a period of 4 h. After the brown solution was stirred for 2 h at 25 °C, the diethyl ether was removed and replaced with 60 mL of petroleum ether. The brown solution was filtered, and the precipitate was washed five times with 10-mL portions of petroleum ether. The solvent was removed, and the brown crystalline mass was transferred to a small sublimator. Pure white **4** sublimed at 25 °C (10^{-4} torr) completely within 12 h (1.26 g, 77% yield).

(5) $Cp^*Zr(CH_2Ph)_3$ (5). Procedure 4 was followed except 11 mL (19.8 mmol) of $PhCH_2MgCl$ (1.8 M in THF) was used. Crystallization from petroleum ether afforded 1.95 g of bright yellow **5** (65% yield). Anal. Calcd for $C_3H_{36}Zr$: C, 74.49; H, 7.26. Found: C, 74.24; H, 7.16.

(6) Cp^*ZrPh_3 (6). Procedure 4 was followed except 300 mg (0.90 mmol) of **1** and 1 mL (3.2 mmol) of PhMgBr (3.2 M in diethyl ether) were mixed in 25 mL of Et_2O. Crystallization from petroleum ether afforded 259 mg of white **6** (60% yield). Anal. Calcd for $C_{28}H_{30}Zr$: C, 73.46; H, 6.61. Found: C, 73.20; H, 6.73.

(7) $CpZrCl(CH_3)_2$ (7). Procedure 4 was followed except 1 g (3.0 mmol) of **1** and 2.2 mL (6.6 mmol) of CH_3MgBr (3.0 M in Et_2O) reacted in 40 mL of diethyl ether. Crystallization from petroleum ether afforded 550 mg of light yellow **7** (63% yield).

(8) $[Cp^*ZrCl_2(CH_3)]_x$ (8). $(Cp^*ZrCl_3)_x$ (**1**; 1 g, 3.00 mmol) and CH_3MgBr (1.1 mL, 3.2 mmol of 2.9 M in Et_2O) were combined as in procedure 4. The diethyl ether was replaced with toluene, and the reaction mixture was filtered. The precipitate on the frit was washed four times with 10-mL portions of toluene, and the solvent was removed from the filtrate. The resulting crude **8** was taken up in toluene (or benzene) and filtered. Crystallization from toluene yielded 560 mg of yellow **8** (60% yield). The analysis indicated that the product still contained some magnesium salt, but a partial halogen exchange of Br for Cl could not be ruled out. Anal. Calcd for $C_{11}H_{18}Cl_2Zr$: C, 42.29; H, 5.81. Found: C, 37.89; H, 5.05.

(9) $[Cp^*ZrCl_2(CH_2Ph)]_x$ (9). Procedure 8 was followed except 500 mg of **1** (1.50 mmol) and 2.5 mL (1.55 mmol) of $PhCH_2MgCl$ (0.62 M in Et_2O) were stirred in 40 ml of diethyl ether. Crystallization from toluene yielded 355 mg of bright orange **9** (60% yield). Anal. Calcd for $C_{17}H_{22}Cl_2Zr$: C, 52.56; H, 5.71. Found: C, 52.36; H, 5.62.

(10) $Cp^*Zr(CH_3)_3$dmpe (11). $Cp^*Zr(CH_3)_3$ (**4**) (330 mg, 1.22 mmol) and 0.21 mL (185 mg, 1.25 mmol) of dmpe (density ≈ 0.9 g/mL) were combined in 20 mL of toluene. ^1H NMR shows that **11** forms quantitatively. The solution was stirred in a 150-mL glass bomb pressured with 3 atm of H_2. After 2 days the toluene was removed and replaced with petroleum ether. The solution was then filtered and concentrated to yield 103 mg of crystallized **11**. No products besides dmpe were identified by ^1H NMR of the filtrate. Anal. Calcd for $C_{19}H_{40}P_2Zr$: C, 54.11; H, 9.56. Found: C, 53.95; H, 9.42.

(11) Hydrogenation of 11 (95 atm). In a stainless-steel Parr high-pressure apparatus, 600 mg of $Cp^*Zr(CH_3)_3$ (**4**) (2.21 mmol) and dmpe (0.38 mL, 332 mg, 2.3 mmol) were combined in 45 mL of toluene. H_2 (95 atm) was then introduced, and the reaction mixture was vigorously stirred for 24 h (final pressure 83 atm). The bomb was depressurized and opened. The resulting clear yellow solution was transferred to a flask. As the transfer occurred, the solution turned dark green. As the toluene was removed, a gray material precipitated. Petroleum ether was then added, and the gray precipitate $(Cp^*ZrH_3)_x$ was collected. Anal. Calcd for $C_{10}H_{18}Zr$: C, 52.34; H, 7.91. Found: C, 52.20; H, 7.88. Free dmpe was identified in the filtrate.

(12) $Cp^*CpZrCl_2$ (13). $(Cp^*ZrCl_3)_x$ (**1**) (5 g, 15.02 mmol) and NaCp (1.52 g, 17.26 mmol) were placed in a flask with 45 mL of toluene and heated for 2 days at 110 °C. The toluene was then removed, and about 40 mL of CH_2Cl_2 was added along with 20 mL of 4 M HCl. The CH_2Cl_2 layer was separated and combined four times with 15-mL CH_2Cl_2 extracts of the aqueous layer. The CH_2Cl_2 solution was then dried over $MgSO_4$. Crystallization from CH_2Cl_2/petroleum ether afforded yellow **13** in 83% yield (4.55 g). Anal. Calcd for $C_{15}H_{20}Cl_2Zr$: C, 49.71; H, 5.56. Found: C, 49.83; H, 5.69.

(13) $Cp^*Cp'ZrCl_2$ (14). Procedure 12 was followed except LiCp′ (2 g, 17.5 mmol) was heated with **1** for 3.5 days. Crystallization from CH_2Cl_2/petroleum ether afforded 4.06 g of bright yellow **14** (67% yield). Anal. Calcd for $C_{18}H_{26}Cl_2Zr$: C, 53.44; H, 6.48. Found: C, 53.51; H, 6.39.

(14) 1-Methylindene. 1-Indanone (Aldrich, 5 g, 37.83 mmol) in 25 mL of Et_2O was added dropwise to 40 mmol of CH_3MgBr in 75 mL of Et_2O at 0 °C. Following a standard workup, 250 mg of *p*-toluenesulfonic acid was added to a 50 mL of diethyl ether solution containing 1-hydroxyl-1-methylindene. After the solution was stirred for 1 h and a standard workup was followed, 1-methylindene was distilled at 85–88 °C (10 torr) to yield 3.24 g of the pure indene (66% yield): ^1H NMR ($CDCl_3$) δ 2.13 (m, 3, CH_3), 3.23 (m, 2, CH_2), 6.13 (m, 1, $=CH$), 7.05–7.45 (m, 4, C_6H_4). All couplings were less than 2 Hz.

(15) (MeInd)Cp^*ZrCl_2 (15). Procedure 12 was followed except 5.88 g (17.66 mmol) of **1** was heated in toluene with 2.88 g (21.2 mmol) of Li(MeInd) for 5.5 days at 120 °C. Crystallization from CH_2Cl_2/petroleum ether afforded 3.86 g of **15** (51% yield). The

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workup of procedure 12 should be carried out quickly, as **15** is subject to hydrolysis.

(16) Cp*CpZr(CH$_3$)$_2$ (16). Cp*CpZrCl$_3$ (**13**) (1 g, 2.76 mmol) was placed in a flask with 40 mL of Et$_2$O. A 1.9-mL portion of 3.0 M CH$_3$MgBr (5.7 mmol) in Et$_2$O was syringed into the flask at −78 °C. The flask was warmed to 25 °C and stirred for 6 h. The diethyl ether was removed, and 30 mL of petroleum ether was added. The resulting slurry was filtered and the MgBrCl washed five times with 10 mL of cold petroleum ether. Crystallization from petroleum ether afforded 790 mg of white **16** (89% yield). Anal. Calcd for C$_{17}$H$_{26}$Zr: C, 63.49; H, 8.15. Found: C, 63.64; H, 8.06.

(17) Cp*Cp′Zr(CH$_3$)$_2$ (17). Procedure 16 was followed except that 1 g of Cp*Cp′ZrCl$_2$ (**14**) (2.47 mmol) and 3.1 mL (5.5 mmol) of 1.8 M CH$_3$Li were used. Crystallization from petroleum ether afforded 690 mg of white **17** (76% yield). Anal. Calcd for C$_{20}$H$_{32}$Zr: C, 66.05; H, 8.87. Found: C, 66.01; H, 8.71.

(18) (MeInd)Cp*Zr(CH$_3$)$_2$ (18). Procedure 16 was followed except that 1 g of (MeInd)Cp*ZrCl$_2$ (**15**) (2.34 mmol) and 3 mL (5.4 mmol) of 1.8 M CH$_3$Li were combined. Upon removal of the petroleum ether, 790 mg of oily yellow **18** crystallized (87% yield).

(19) (Cp*CpZrH$_2$)$_2$ (19). A 1.0-g sample of **13** in 20 mL of toluene was treated with 2.2 equiv of BuLi (1.6 M in hexane) at −80 °C under H$_2$ (1 atm). The mixture was stirred and allowed to warm to room temperature. After 2 h toluene was removed in vacuo, and 20 mL of petroleum ether distilled in. After filtration the solution was concentrated and cooled slowly to −80 °C. The white crystals were filtered off at −80 °C and washed with small portions of petroleum ether; yield 31%. Anal. Calcd for C$_{15}$H$_{22}$Zr: C, 61.37; H, 7.55. Found: C, 61.65; H, 7.40. Molecular weight (Bernhardt): 606; calculated for monomer, 294.

(20) Cp*Cp′ZrH$_2$ (20). To a stainless-steel Parr high-pressure apparatus, 500 mg of Cp*Cp′Zr(CH$_3$)$_2$ (**17**) (1.37 mmol) of 40 mL of toluene were added. H$_2$ (80 atm) was then introduced, and the reaction mixture was vigorously stirred for 24 h (final pressure 75 atm). The bomb was depressurized and opened. The yellow solution was then filtered, and the solvent was stripped. Petroleum ether was added, and 390 mg of pale yellow, microcrystalline **20** was collected on a frit (85% yield). Anal. Calcd for C$_{18}$H$_{28}$Zr: C, 64.41; H, 8.41. Found: C, 64.27; H, 8.32. Molecular weight (Bernhardt): 342; calculated for monomer, 336.

Acknowledgment. This work has been supported by the National Science Foundation (Grant No. CHE-8024869).

Registry No. **1**, 75181-07-6; **2**, 81476-62-2; **3**, 81476-63-3; **4**, 81476-64-4; **5**, 81476-65-5; **6**, 81476-66-6; **7**, 81476-67-7; **8**, 81476-68-8; **9**, 81476-69-9; **10**, 81476-70-2; **11**, 81476-71-3; **12**, 81476-72-4; **13**, 81476-73-5; **14**, 81476-74-6; **15**, 81476-75-7; **16**, 81476-76-8; **17**, 81496-91-5; **18**, 81476-77-9; **19**, 81476-78-0; **20**, 81496-92-6; ZrCl$_4$, 10026-11-6; CH$_3$Br, 74-83-9; PhCH$_2$Cl, 100-44-7; PhBr, 108-86-1; 1-methylindene, 767-59-9; 1-indanone, 83-33-0.

Synthesis, Characterization, and Structures of Aluminum Pentamethylcyclopentadienyl Complexes, [η^3-(CH$_3$)$_5$C$_5$Al(Cl)R]$_2$ (R = CH$_3$, C$_2$H$_5$, *i*-C$_4$H$_9$): Examples of η^3-Cyclopentadienyl Ligand Coordination

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Received October 21, 1982

The reactions of Li[(CH$_3$)$_5$C$_5$] and [(CH$_3$)$_5$C$_5$]MgCl with the alkyl aluminum halides [(CH$_3$)$_2$AlCl]$_2$, [(C$_2$H$_5$)$_2$AlCl]$_2$, [C$_2$H$_5$AlCl$_2$]$_2$, [(*i*-C$_4$H$_9$)$_2$AlCl]$_2$, and [(*i*-C$_4$H$_9$)AlCl$_2$]$_2$ are reported. The new compounds [(CH$_3$)$_5$C$_5$Al(Cl)R]$_2$ (R = CH$_3$, C$_2$H$_5$, and *i*-C$_4$H$_9$) have been isolated and characterized by mass, infrared, and ^{1}H and ^{13}C NMR spectroscopy. In addition, the complexes [(CH$_3$)$_5$C$_5$Al(Cl)CH$_3$]$_2$ and [(CH$_3$)$_5$C$_5$Al(Cl)(*i*-C$_4$H$_9$)]$_2$ have been subjected to single-crystal X-ray structural analysis. [(CH$_3$)$_5$C$_5$Al(Cl)CH$_3$]$_2$ (**1**) crystallizes in the monoclinic space group $P2_1/c$ with a = 8.550 (2) Å, b = 8.917 (3) Å, c = 16.012 (7) Å, β = 104.65 (2)°, Z = 2, V = 1181.1 (7) Å^3, and ρ = 1.20 g cm^{-3}. Data were collected at −65 °C by using Mo Kα radiation, and full-matrix least-squares refinement converged with final discrepancy indices R_F = 0.061 and R_{wF} = 0.092. The complex [(CH$_3$)$_5$C$_5$Al(Cl)(*i*-C$_4$H$_9$)]$_2$ (**3**) crystallizes in the monoclinic space group $P2_1/n$ with a = 13.040 (6) Å, b = 8.928 (2) Å, c = 13.083 (3) Å, β = 98.06 (3)°, Z = 2, V = 1508.3 (9) Å^3, and ρ = 1.12 g cm^{-3}. Data were collected at 27 °C by using Mo Kα radiation, and full-matrix least-squares refinement converged with final discrepancy indices R_F = 0.075 and R_{wF} = 0.095. The dimeric molecules possess C_i—$\bar{1}$ symmetry and nearly conform to C_{2h}—$2m$ symmetry. The structures reveal unusual planar, η^3-(CH$_3$)$_5$C$_5$ ring attachments to the central Al$_2$Cl$_2$ units. In **1**, the C$_5$ ring–Al interatomic distances are 2.100 (3), 2.252 (3), 2.282 (3), 2.499 (3), and 2.518 (3) Å. The last two distances are considered to be nonbonding distances. In **3**, the related distances are 2.096 (9), 2.359 (8), 2.243 (8), 2.616 (9), and 2.563 (9) Å. Several structural parameters suggest greater nonbonded or steric repulsions in **3** compared to **1** which result in a distortion toward an η^2 configuration. Nonparameterized molecular orbital calculations have been used to help clarify the bonding mode observed in these compounds.

Introduction

The structural chemistry of cyclopentadienide and cyclopentadienyl complexes of the transition metals has been extensively studied,[2] and metal atom–Cp ring bonding is well understood for the η^5 and η^1 coordination modes.[3-5] On the other hand, relatively little attention has been given to the synthesis and structural characterization of met-

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