in both the dependent and independent variables.[21]

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Supplementary Material Available: Figures giving variable-temperature $^1H\{^{31}P\}$ NMR spectra of **1a** and their computer simulations and variable-temperature $^{13}C\{^1H\}$ NMR spectra of an equilibrium mixture of the isomers **1b** and **1c** (2 pages). Ordering information is given on any current masthead page.

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[21] Irvin, J. A.; Quickenden, T. I. *J. Chem. Educ.* **1983**, *60*, 712.

Solvolysis of Dimethylzirconocene by Trialkylaluminum Compounds

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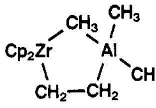
Liquid metal alkyls are strong Lewis acids and bases and useful solvents in which to conduct organometallic reactions. Cp_2ZrMe_2 undergoes rapid methyl exchange with pure Me_3Al but reacts with $EtAlMe_2$ in Me_3Al to form $Cp_2Zr(\mu\text{-}CH_3)(\mu\text{-}CH_2CH_2)AlMe_2$. Neat R_3Al reagents in which R has a hydrogen atom produce solvated Cp_2ZrH_2 derivatives. The gas-phase reaction of $Cp_2ZrCH_3^+$ with Me_3Al, studied by ion cyclotron resonance spectrometry, produces an ion formulated as $Cp_2Zr(\mu\text{-}CH_2)_2Al^+$.

Study of highly concentrated protic acids in which the conjugate bases are but weakly coordinated has been a highly productive area of chemistry. Notable is $HSO_3F{\cdot}SbF_5$, commonly known as magic acid.[1] In an analogous context, liquid metal alkyls such as Me_6Al_2, Me_3Ga, and Me_2Zn can serve both as powerful Lewis acids and bases as well as solvents. They are well suited to NMR experiments and, because of their high reactivity, are easily obtained free of dissolved oxygen and water; indeed, they are self-cleaning. The reactivity of alkyl derivatives of group IV metallocenes with aluminum alkyls is of interest on account of the ability of such systems to catalyze the polymerization of olefins.[2] We report here the reactions of Cp_2ZrMe_2 ($Cp = \eta^5\text{-}C_5H_5$) with some trialkylaluminum compounds, R_3Al, in fluid solution and discuss the effect of the structure of R on reactivity patterns. We also present complementary data on analogous gas-phase chemistry as studied by ion cyclotron resonance (ICR) spectrometry.

Solution-Phase Chemistry

^{13}C NMR spectroscopy shows that, in 0.3 M toluene solution, there occurs a facile ($\Delta G^{\ddagger}$ = 16.7 kcal mol^{-1}) statistical scrambling of $^{13}CH_3$ groups in $Cp_2Zr(^{13}CH_3)_2$ with the methyl groups in $(CH_3)_6Al_2$.[3] However, no new products or intermediates are detectable. We reasoned that these might be observed with the help of mass action if neat Me_3Al were used as both solvent and reactant. In fact, a new reaction has been detected but it is due to $EtAlMe_2$ present as an impurity at a 2.2 mol % level in commercial Me_3Al that is recognizable by its ^1H signals at 1.00 (t, CH_3) and -0.01 (q, CH_2) ppm.[4]

In neat Me_3Al, $EtAlMe_2$ slowly reacts with Cp_2ZrMe_2 to form $Cp_2Zr(\mu\text{-}CH_3)(\mu\text{-}CH_2CH_2)AlMe_2$ (**1**) and methane (identified by mass spectrometry). In hydrocarbon solvents, **1** decomposes too rapidly to permit growth of single crystals but its structure and composition can be deduced beyond cavil from spectroscopic and analytical data. The ^{13}C NMR spectrum of **1** exhibits a single Cp resonance at 107.2 ppm (J_{CH} = 173 Hz; $\delta(^1H)$ 5.30 ppm). The Zr-C-H_3-Al bridging methyl group is associated with a peak at -21.5 ppm (J_{CH} = 115 Hz; $\delta(^1H)$ -0.79 ppm). The high-field chemical shift is in accord with those observed in crystallographically characterized compounds known to contain a Zr-CH_3-Al bridge.[5] The Zr-CH_2 portion of the Zr-CH_2-CH_2-Al ethylene bridge gives rise to a ^{13}C resonance at 33.7 ppm (J_{CH} = 144 Hz; cf. Cp_2ZrMe_2, $\delta(^{13}C)$ 30.7, J_{CH} = 117 Hz), and the -CH_2-Al terminus is associated with a resonance at 1.39 ppm (J_{CH} = 127 Hz). The respective ^1H chemical shifts of the two types of CH_2 are 1.07 and -0.08 ppm. These protons, H_A and H_X, respectively, give rise to an AA'XX' multiplet, simulation of which yields $J_{XX'}$ = -12 Hz, J_{AX} = 13.2 Hz, and $J_{AX'}$ = 6.8 Hz. The proton spectrum provides evidence that the two methylene units are bonded to one another in the same molecule (vide infra). ^{13}C NMR measurements yield second-order rate constants for formation of **1** of 0.98 and



1

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[1] Olah, G. A. *Super Acid Chemistry*; Wiley: New York, 1985.

[2] (a) Kaminsky, W.; Hahnsen, H. U.S. Patent 4,544,762. (b) Kaminsky, W.; Miri, M. *J. Polym. Sci. Polym. Chem. Ed.* **1985**, *23*, 2151. (c) Kaminsky, W.; Kulper, K.; Brintzinger, H.-H.; Wild, F. R. W. P. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 507. (d) Sinn, H.; Kaminsky, W. *Angew. Chem., Int. Ed. Engl.* **1985**, *19*, 390.

[3] Siedle, A. R.; Newmark, R. A.; Lamanna, W. M.; Schroepfer, J. N. *Polyhedron* **1990**, *9*, 301.

[4] We write the chemical formula for dilute Et_3Al in Me_3Al as if it were a single compound, $EtAlMe_2$. In fact, it is likely a statistical mixture of dimers in which $(EtAlMe_2)_2$ is most abundant. Similarly, for simplicity, we write R_3Al as such, even though it may be predominantly a dimer in solution.

[5] Waymouth, R. M.; Santarsiero, B. D.; Coots, R. J.; Bronikowski, M. J.; Grubbs, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 1427.

0276-7333/91/2310-0400$02.50/0

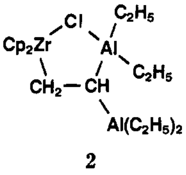
Table I. ^{13}C NMR Data

compd	$\delta(^{13}C)$ (J_{CH}, assignt)[a]
$Cp_2Zr(\mu\text{-}CH_2)(\mu\text{-}C_2H_4)\text{-}AlMe_2$ (**1**)	107.2 (173, Cp), 33.7 (144, Zr–CH_2), 1.39 (127, –CH_2Al, T_1 = 1.9 s), –4.6 CH_3Al), –21.52 (115, Zr–CH_3–Al, T_1 = 4.5 s)
$Cp_2Zr(\mu\text{-}CH_3)(\mu\text{-}C_2H_4)\text{-}Al(Me)Et$ (**3a**)	106.7 (Cp), 33.0 (Zr–CH_2), 10.23 (123, CH_2CH_3), 5.5 ($AlCH_2CH_3$), –0.82 (126, CH_2CH_2Al), –6.5 ($AlCH_3$), –23.69 (Zr–CH_3–Al, T_1 = 5.6 s)
$Cp_2Zr(\mu\text{-}CH_3)(\mu\text{-}C_2H_4)\text{-}AlEt_2$ (**3b**)	106.7 (Cp), 33.0 (Zr–CH_2), 10.05 (124, $AlCH_2CH_3$), 4.2 ($AlCH_2CH_3$), –2.71 (126, CH_2CH_2Al), –25.37 (114, Zr–CH_3–Al, T_1 = 5.1 s)
$Me_2Si(C_5H_4)_2Zr(\mu\text{-}CH_3)\text{-}(\mu\text{-}C_2H_4)AlMe_2$ (**4**)	121.6, 116.8, 109.2, 100.5 (Cp), 98.2 (Cp ipso), 34.9 (Zr–CH_2), 0.9 (–CH_2Al), –4.1, –5.8 ($SiCH_3$), –23.0 (Zr–CH_3–Al)
$Cp_2Hf(Me)Et$ (**7**)	106.3 (Cp), 49.3 (CH_2), 36.8 ($HfCH_3$), 16.2 (CH_2CH_3)
Cp_2HfEt_2 (**8**)	106.3 (Cp), 50.0 (CH_2), 16.1 (CH_3)
Cp_2HfMe_2	106.3 (Cp), 36.5 (CH_3)

[a] In toluene solution, with chemical shifts in ppm and coupling constants in Hz.

8.60×10^{-4} L s^{-1} mol^{-1} at 22 and 44 °C, respectively. The corresponding free energies of activation at both temperatures are 22.7 ± 0.1 kcal mol^{-1}, indicating that the entropy of activation is quite low. In toluene solution, **1** does not react with ethylene. However, in the course of a mechanistic study of ethylene polymerization catalyzed by Cp_2ZrMe_2–$(MeAlO)_x$, we have observed in the ^{13}C NMR spectra of aged, deactivated catalysts high-field resonances that are characteristic of the Zr–CH_3–Al bridge moiety in **1**.

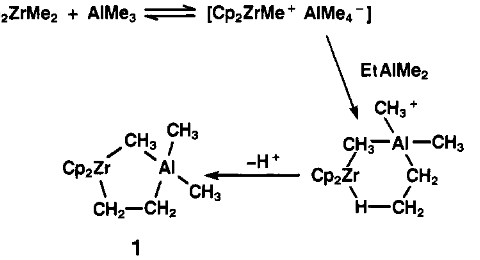
The yield of **1** is limited by the amount of adventitious $EtAlMe_2$ present in the neat Me_3Al solvent. However, if additional Et_3Al is added so that the Zr:Et ratio is 1:1, the yield exceeds 90%; **1** may then be isolated by evaporation of the trimethylaluminum and purified by rapid recrystallization from toluene–hexane. The compound gives good microanalytical and molecular weight data. The ^{27}Al NMR spectrum of pure **1** in toluene comprises a broad ($w/2$ = 1900 Hz) peak at 185 ppm. Although further detailed interpretation of the NMR data are not warranted, we note that J_{CH} for the Zr–CH_3–Al bridge is rather small (and invariant between +25 and –85 °C), possibly due to the effect of the electronegative substituents on carbon, and that J_{CH} for the CH_2 fragment adjacent to zirconium in the ethylene bridge, 144 Hz, is rather large. The latter feature has also been observed in **2** and may be associated with an acute Zr–CH_2–CH angle.[6]



2

Reaction of Cp_2ZrMe_2 with 0.33 mol of Et_3Al in toluene (i.e. Zr:Et = 1:1 with Me_3Al being omitted) gives rise to a statistical mixture containing **1** and the two other possible $Cp_2Zr(\mu\text{-}CH_3)(\mu\text{-}CH_2CH_2)AlRR'$ species (R = Me, R' = Et, **3a**; R,R' = Et, **3b**; cf. Table I). Significantly, the ^1H undecoupled high-field ^{13}C resonances of these compounds are all quartets; i.e., no Zr–$CH_2(CH_3)$–Al compounds are detected. Use of more concentrated Et_3Al solutions leads to different chemistry that is described below.

Scheme I



1

The Cp carbon atoms in **1** are all equivalent, presumably because of rapid ring rotation about the Zr–centroid axis. Reaction of the silicon-bridged compound $Me_2Si(C_5H_4)_2ZrMe_2$ with $EtAlMe_2$ produces an analogue of **1**, $Me_2Si(C_5H_4)_2Zr(\mu\text{-}CH_3)(\mu\text{-}CH_2CH_2)AlMe_2$ (**4**). In the ^{13}C NMR spectrum of this, the nonequivalent $SiCH_3$ groups appear at –4.1 and –5.8 ppm. The intra-ring cyclopentadienyl carbons are now all nonequivalent because of the rigidity imposed by the $SiMe_2$ bridge; cf. Table I. The shifts of the Zr–CH_3–Al, Zr–CH_2–CH_2–Al, and Zr–CH_2–CH_2–Al carbons demonstrate that **1** and **4** have similar structures.

One possible mechanism by which **1** could form is shown in Scheme I. We postulate that Cp_2ZrMe_2 and Me_3Al react to give Cp_2ZrMe^+ and $AlMe_4^-$; the reverse of this reaction leads to the observed scrambling of Zr–CH_3 and Al–CH_3 groups (vide supra). The electron-deficient Cp_2ZrMe^+ carbon is thought to be solvated by Me_3Al, as it is by Lewis bases such as THF and CH_3CN.[7] We believe, on the basis of gas-phase experiments described below, that this solvation involves a simple Zr–CH_3–Al bridge and an agostic Zr–H–CH_2–Al bridge. The latter bridging arrangement is stable, for the intermediate leads to no new compounds and, indeed, $(Me_5Cp)_2Zr(Me)(CF_3SO_3)$, which arguably contains an incipient cationic zirconium species, is simply methylated by Me_3Al to form $(Me_5Cp)_2ZrMe_2$.[8] In the case of $EtAlMe_2$, additional chemistry involving the Zr–H–CH_2–CH_2–Al bridge transpires. An M–*H*–CH_2 agostic interaction is known to render the hydrogen atom attached to the metal more acidic,[9] and its removal as H^+ by Me_3Al (or possibly also by $AlMe_4$) generates **1**. In accord with this scheme, **1** prepared from $Cp_2Zr(^{13}CH_3)_2$ contains the ^{13}C label only in the Zr–CH_3–Al position. Thus, Me_3Al acts as a Lewis acid (CH_3^- acceptor) and a base (H^+ acceptor). A similar dual functionality of R_3Al has been observed by Grubbs et al. in a study of the reaction of Cp_2TiCl_2 with Me_3Al.[10] With respect to both structure and means of formation, **1** deserves comment in relation to titanium chemistry.

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(6) (a) Kopf, J.; Kaminsky, W.; Vollmer, H.-J. *Cryst. Struct. Commun.* **1980**, *9*, 197. See also: (b) Kaminsky, W.; Kopf, J.; Sinn, H.; Vollmer, H.-J. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 629. (c) Kaminsky, W.; Kopf, J.; Thirase, G. *Justus Liebigs Ann. Chem.* **1974**, 1531. (d) Kopf, J.; Vollmer, H.-J.; Kaminsky, W. *Cryst. Struct. Commun.* **1980**, *9*, 271. (e) Kopf, J.; Vollmer, H.-J.; Kaminsky, W. *Cryst. Struct. Commun.* **1980**, *9*, 985. (f) Kaminsky, W.; Sinn, H. *Justus Liebigs Ann. Chem.* **1975**, 424. (g) Sinn, H.; Kolk, E. *J. Organomet. Chem.* **1966**, *6*, 373. (h) Kaminsky, W.; Vollmer, H.-J. *Justus Liebigs Ann. Chem.* **1975**, 438.

(7) (a) Jordan, R. F. *J. Chem. Educ.* **1988**, *65*, 285. (b) Jordan, R. F.; Bajgur, C. S.; Willett, R.; Scott, B. *J. Am. Chem. Soc.* **1986**, *108*, 7410. (c) Jordan, R. F.; LaPointe, R. E.; Bajgur, C. S.; Echols, S. F.; Willett, R. *J. Am. Chem. Soc.* **1987**, *109*, 4111. (d) Jordan, R. F.; Echols, S. F. *Inorg. Chem.* **1987**, *26*, 383. (e) Jordan, R. F.; Bejgur, C. S.; Dasher, W. E.; Rheingold, A. L. *Organometallics* **1987**, *6*, 1041. (f) Jordan, R. F.; Dasher, W. E.; Echols, S. F. *J. Am. Chem. Soc.* **1986**, *108*, 1718. (g) Gassman, P. G.; Callstrom, M. R. *J. Am. Chem. Soc.* **1987**, *109*, 7875.

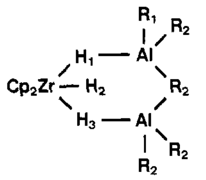
(8) Turner, H. W. U.S. *Patent* 4,752,597, June 21, 1988.

(9) Brookhart, M.; Green, M. L. H.; Wong, L.-L. *Prog. Inorg. Chem.* **1988**, *36*, 1.

(10) Ott, K. C.; deBoer, E. J. M.; Grubbs, R. H. *Organometallics* **1984**, *3*, 223.

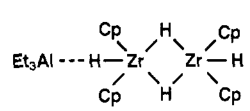
Tebbe observed that Cp_2TiMe_2 and $AlMe_3$ form the μ-methylene compound $Cp_2Ti(\mu\text{-}CH_2)(\mu\text{-}CH_3)AlMe_2$.[11] For nonobvious reasons, the zirconium (and hafnium, vide infra) analogues of Tebbe's compounds have never been reported.[12] In tantalum chemistry, a compound considered to be $[Cp_2TaMe_2][AlMe_4]$ is reported to eliminate methane to form $Cp_2Ta(Me)[CH_2AlMe_3]$.[13] Our data indicate that, in the Cp_2ZrMe_2–Me_2AlR system, methane loss and formation of Zr–hydrocarbyl–Al bridges as found in **1** occur only when R = ethyl.[14]

In the reactions described above, Me_3Al is both a solvent and a reactant. The products obtained from Cp_2ZrMe_2 and neat R_3Al at room temperature vary greatly with the nature of R. Rapid exchange of alkyl groups leads initially to Cp_2ZrR_2. This alkyl-exchange reaction appears not to have been previously described explicitly.[15] The Cp_2ZrR_2 compounds formed by alkyl exchange may then undergo β-elimination to form zirconium hydride species that may react further.[16] A solution of Cp_2ZrMe_2 in neat Et_3Al exhibits ^1H signals at δ 5.31 (s, 10 H, Cp), 1.30 (located by ^1H COSY, Zr-*H*-Zr), and −0.89 (d, 1 H, J_{HH}, 9 Hz, Zr-*H*-Al). We consider that these resonances may be due to $[Cp_2Zr(\mu\text{-}H)H\text{-}AlEt_3]_2$ (**5**), which is analogous to the complex of Cp_2ZrH_2 with Me_3Al reported earlier.[17] In mixtures of trialkylaluminums, as the Et_3Al:Me_3Al ratio decreases, less **5** and more **1** is produced.



$R_1 = CH_3$
$R_2 = i\text{-}Bu$

5



6

Reaction of Cp_2ZrMe_2 with neat $(i\text{-}Bu)_3Al$ yields isobutene and **6**. The ^{13}C NMR spectrum of **6** comprises a singlet at 104.3 ppm, the various alkyl resonances being obscured by $(i\text{-}Bu)_3Al$. The ^1H NMR spectrum demonstrates peaks at δ 5.71 (s, Cp), −2.23 (br s, 1 H, H_1 or H_3), −1.75 (br s, 1 H, H_3 or H_1), and −1.22 (t, 1 H, $J_{H2\text{-}H1,3}$ = 6 Hz, H_2). Splitting of H_2 by coupling to $H_{1,3}$ is presumably obscured by the large line width associated with neighboring quadrupolar nuclei (^{27}Al, $I = {}^3/_2$; ^{91}Zr, $I = {}^5/_2$) but the expected coupling was verified by a ^1H COSY experiment. Broadening of the $H_{1,3}$ (but not H_2) signals occurs at 50 °C. The NMR parameters of **6** bear a close resemblance to those of a zirconium hydride–triisobutylaluminum complex reported by Schwartz,[18] and this is the basis for the structure proposed.

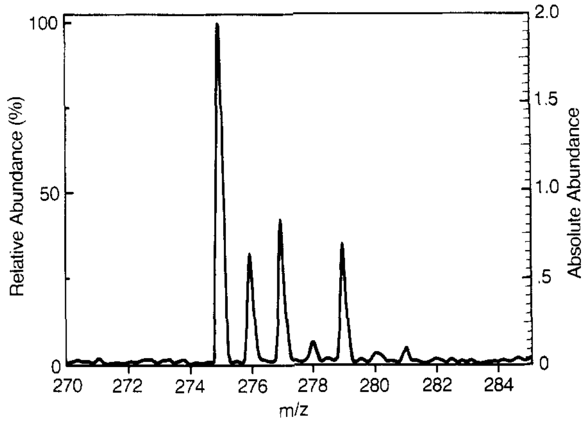


Figure 1. FT MS spectrum of ions produced from $Cp_2ZrCH_3^+$ and $Al(CH_3)_3$.

Exchange Reactions in Related Systems

Although $(Me_5Cp)_2ZrMe_2$ undergoes degenerate exchange of Zr-methyl groups with Me_3Al, no exchange (or any other reaction) with Et_3Al is detectable at 25 °C in toluene solution. Likewise, no alkyl exchange (or other reaction) is observed between Cp_2ZrMe_2 and the less acidic organometallics Et_3B and Me_3Ga. Dialkylzincs comprise a special case.

Cp_2ZrMe_2 and Me_2Zn undergo rapid methyl exchange in toluene solution, and no new compounds are detectable by NMR spectroscopy. In contrast, Cp_2ZrMe_2 catalyzes the decomposition of Et_2Zn to form ethane, ethylene, and metallic zinc. This result can be rationalized as beginning with the now-familiar alkyl-exchange process, leading to ethyl-zirconocenes that decompose to ethylene and zirconocene hydrides. Subsequent exchange of Zr-*H* and Zn-*Et* produces unstable zinc hydrides that decompose to ethane and zinc metal. Schwartz has already described exchange of Zr-*H* and Al-*R*,[18] and were it not for the stability of the Al-H bond, a like decomposition of R_3Al to aluminum metal could occur.

Cp_2HfMe_2 reacts with 1 equiv of Et_3Al in toluene to form a statistical mixture containing $Cp_2Hf(Me)Et$ (**7**) and Cp_2HfEt_2 (**8**). These ethylhafnocene compounds are stable in solution for at least 1 week. The stability of the Hf–alkyl bond is in accord with the observations of Erker, who prepared stable ethyl- and hexylhafnocenes by hydrohafnation of alkenes.[19] The stability of the Hf–C(sp^3) bond in these compounds is presumably due to kinetic rather than thermodynamic effects.[20]

Gas-Phase Studies

The $Cp_2ZrCH_3^+$ cation has not yet been observed in solution in the absence of coordinated Lewis bases.[7] It is not obvious that this species would have a classical rather than an agostic structure.[21] It may, however, readily be

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[11] Tebbe, F. N.; Parshall, G. W.; Reddy, G. S. *J. Am. Chem. Soc.* **1978**, *100*, 3611. Note that, in $Cp_2Ti(\mu\text{-}CH_2)(\mu\text{-}CH_3)AlMe_2$, the $-CH_2$ group has $\delta(^{13}C)$ 204.

[12] Alkylidene-bridged Zr,Al complexes have been reported: (a) Hartner, F. M., Jr.; Clift, S. M.; Schwartz, J.; Tulip, T. H. *Organometallics* **1987**, *6*, 1346. (b) Hartner, F. M. Jr.; Schwartz, J.; Clift, S. M. *J. Am. Chem. Soc.* **1983**, *105*, 640.

[13] Schrock, R. R.; Sharp, P. R. *J. Am. Chem. Soc.* **1978**, *100*, 2389.

[14] (a) Sinn, H.; Oppermann, G. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 962. (b) Kaminsly, W.; Vollmer, H.-J. *Justus Liebigs Ann. Chem.* **1975**, 438.

[15] Zucchini, U.; Albizatti, E.; Gianinni, U. *J. Organomet. Chem.* **1971**, *26*, 367. These workers found that Et_3Al and $(PhCH_2)_4Ti$ produced C_2H_4 and C_2H_6, presumably by exchange reactions leading to form a EtTi compounds. $(PhCH_2)_3Al$ and $(PhCH_2)_4Ti$ were reported to form a *red* complex that partially dissociated in solution; ^1H NMR spectra were interpreted as showing no exchange of $PhCH_2$ groups. Alkyl-chloride exchange (with $AlCl_3$) has been reported by: Carr, D. B.; Schwartz, J. *J. Am. Chem. Soc.* **1979**, *101*, 3521.

[16] Negishi, E.; Cederbaum, F. E.; Takahashi, T. *Tetrahedron Lett.* **1986**, *27*, 2829.

[17] Wailes, P. C.; Weigold, H.; Bell, A. P. *J. Organomet. Chem.* **1972**, *43*, C29. For data on $[(MeCp)_2ZrH_2]_2$, see: Jones, S. B.; Peterson, J. L. *Inorg. Chem.* **1981**, *20*, 2889.

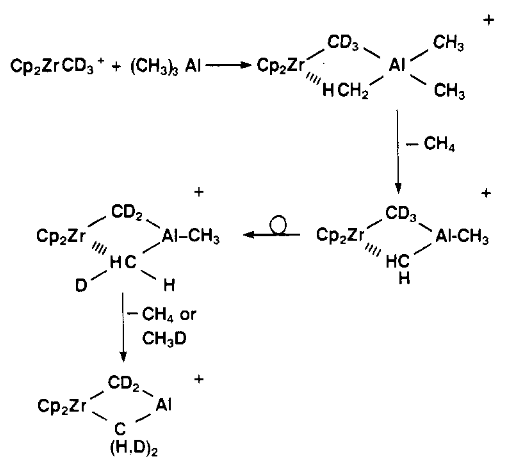
[18] Shoer, L. I.; Gell, K. I.; Schwartz, J. *J. Organomet. Chem.* **1977**, *136*, C19.

[19] Erker, G.; Schlung, R.; Kruger, C. *Organometallics* **1989**, *8*, 2349.

[20] (a) Schock, L.; Marks, T. J. *J. Am. Chem. Soc.* **1988**, *110*, 7701. (b) Bulls, A. R.; Bercaw, J. E.; Manriquez, J. M.; Thompson, M. E. *Polyhedron* **1988**, *7*, 1409.

[21] An agostic Zr-H-C interaction involving the ethyl group in $Cp_2Zr(Et)(Me_3P)^+$ has been demonstrated: Jordan, R. F.; Bradley, P. K.; Baenziger, N. C.; LaPointe, R. K. *J. Am. Chem. Soc.* **1990**, *112*, 1289.

Scheme II



generated in the gas phase by action of an 11-eV electron beam upon Cp_2ZrMe_2.[22] The interaction of Cp_2ZrMe^+ with Me_3Al has been studied by Fourier transform ion cyclotron resonance mass spectroscopy.[23]

Cp_2ZrMe^+ and Me_3Al yield, in the gas phase, a species that we suggest has the plausible dimetallacyclobutane structure $Cp_2Zr(\mu\text{-}CH_2)_2Al^+$ (m/z calcd for ${}^{12}C_{12}{}^{1}H_{14}{}^{27}Al^{90}Zr$ 274.9954, found 274.9949). Figure 1 shows the FT ICR mass spectrum of this reaction product. The cluster of ions is due to ${}^{90,91,92,94}Zr$, which have natural abundances of 51, 11, 17, and 17%, respectively. Although knowledge of exact mass conveys literally no structural or mechanistic information, we surmise that this ion arises by loss of 2 equiv of methane from the encounter complex $Cp_2Zr(\mu\text{-}CH_3)_2AlMe_2^+$. Such reactions in fluid solution are well-known and lead to the Tebbe class of compounds.[11]

When the reaction is conducted with $Cp_2Zr({}^{13}CH_3)^+$, the ratio of ion current from the two product ions $Cp_2Zr(\mu\text{-}{}^{12}CH_2)(\mu\text{-}{}^{13}CH_2)Al^+$ and $Cp_2Zr(\mu\text{-}{}^{12}CH_2)_2Al^+$ is 1.7:1. Thus, although some scrambling of methyl group does occur, the one originally attached to zirconium tends to be retained (in the putative bridge position) in the product cation *just as in the solution-phase reactions*; cf. Scheme II. The isotopomer distribution is invariant as the Me_3Al pressure is changed from 1.5×10^{-6} to 4.5×10^{-6} mm. The ${}^{13}C$-labeling experiment demonstrates that, at minimum, the product formed initially from Cp_2ZrMe^+ and Me_3Al is unlikely to have a single $Zr\text{-}CH_3\text{-}Al$ bridge, for then all the ${}^{13}C$ label would probably be retained. Further, it cannot have a symmetrical bis(methyl)-bridged structure, for then there is no reason to expect preferential retention of ${}^{13}C$ in the final ion product.

This gas-phase chemistry, too, is more complex than anticipated. The reaction of $Cp_2Zr(CD_3)^+$ with Me_3Al produces $Cp_2{}^{90}Zr({}^{12}C_2D_nH_{4-n})Al^+$, which contains 36% D_0, 0 ± 1% D_1, 13% D_2, 51% D_3, and no D_4. This isotopomer distribution is unchanged over the same Me_3Al pressure regime. A minimalist, but not necessarily unique, interpretation of the *striking absence of a D_1 species* and of the ${}^{13}C$-labeling experiment is that $Cp_2ZrCH_3^+$ reacts to form $Cp_2Zr(\mu\text{-}CH_3)_2AlMe_2^+$, in which the two bridging $Zr\text{-}CH_3\text{-}Al$ bridging groups are structurally different and have, therefore, intrinsically different chemical reactivity. We suggest that there occurs a 1,3-H(D) shift between the carbon atoms bridging Zr and Al following elimination of the first molecule of methane as shown in Scheme II. The observed D_2 and D_3 ions are then produced by subsequent elimination of CH_4 and CH_3D, respectively. Precedent for such a 1,3-shift is found in the rearrangement of $Cp_2Ti(\mu\text{-}{}^{12}CH_2)(\mu\text{-}{}^{13}CH_3)Rh(COD)$ to $Cp_2Ti(\mu\text{-}{}^{13}CH_2)(\mu\text{-}{}^{12}CH_3)Rh(COD)$.[24]

The gas-phase reactivity of $Cp_2ZrCH_3^+$ toward Me_3Ga parallels that of Me_3Al. According to Scheme II, the methane lost derives from a CH_3 group on Al (or Ga) and a hydrogen atom from the $\mu\text{-}CH_3$ groups. We expect that loss of only one molecule of methane from $Cp_2Zr(\mu\text{-}CH_3)_2ZnMe^+$ should occur. Accordingly, $Cp_2ZrCH_3^+$ and Me_2Zn produce an ion cluster whose masses correspond to isotopomers of $Cp_2Zr(\mu\text{-}CH_2)(\mu\text{-}CH_3)Zn^+$. Among these is m/z 312.9928 (calcd for ${}^{12}C_{12}{}^{1}H_{15}{}^{64}Zn^{90}Zr$ m/z 312.9526), the large (128 ppm) error being attributable to a low signal to noise ratio in the experiment. The collision-induced dissociation (CID) spectrum reveals peaks due to $M^+ - CH_2Zn$, $CpZr^+$, and CH_3Zn^+.

Thus, the gas-phase ICR experiments are consistent with and provide indirect support for the chemistry that occurs in liquid Me_3Al sketched in Scheme I. A critical feature in the steps that lead to $Cp_2Zr(\mu\text{-}CH_3)(\mu\text{-}CH_2CH_2)AlMe_2$ is an interaction between zirconium and the CH_3CH_2 hydrogen atoms in $EtAlMe_2$ that leads to loss of hydrogen as methane. We believe that, in both the gas and solution phases, this interaction involves an agostic interaction between a vacant orbital on zirconium and a filled C–H σ orbital in a $-CH_3$ group.

Experimental Section

Toluene and hexane were purified by distillation under nitrogen from $Na\text{-}Ph_2CO$-tetraglyme and Na–K alloy, respectively. Trialkylaluminum reagents, packaged in steel containers, were used as received from Aldrich. The compound $Me_2Si(C_5H_4)_2ZrMe_2$ was prepared by a literature method.[3] In NMR experiments, dimethylzirconocene and R_3Al were loaded in a drybox into 5-mm medium-wall NMR tubes; the organoaluminum compounds can be handled with well-dried syringes. Samples were then degassed and sealed under high vacuum with a torch. *Caution!* Trialkylaluminum compounds, both as the neat compounds and in solution, react violently with water and oxygen; suitable precautions should be observed. When not in use, filled sample tubes were stored in a can containing vermiculite. NMR spectra were obtained in toluene-d_8 solutions with a Varian XL-400 instrument whose ${}^{1}H$ operating frequency is 400 MHz. ${}^{1}H$, ${}^{13}C$, and ${}^{27}Al$ chemical shifts are expressed relative to internal $(CH_3)_4Si$ and external 1 M $Al(ClO_4)_3$ in D_2O. ICR experiments were conducted with a Nicolet Model 2000 Fourier transform mass spectrometer and associated software. Collision-induced-dissociation (CID) experiments were carried out with Ar buffer gas.

$Cp_2Zr(\mu\text{-}CH_3)(\mu\text{-}CH_2CH_2)AlMe_2$. To 0.5 g (2 mmol) of Cp_2ZrMe_2 dissolved in 10 mL of 2 M Me_3Al in toluene was added 0.175 mL of a 1.9 M solution of Et_3Al in toluene. After the mixture was stirred for 4 days under nitrogen, volatiles were removed by pumping on a high-vacuum line. These were collected in a removable trap, isolable by vacuum stopcocks, into which methanol could be condensed in order to destroy unreacted aluminum compounds. Pumping was continued for 36 h to ensure removal of $AlMe_3$. The residue was transferred to a drybox and extracted with 25 mL of hexane. The extract was filtered, concentrated, and cooled to obtain 0.35 g (55%) of 1 as yellow-orange microcrystals. Anal. Calcd (found) for $C_{15}H_{23}AlZr$: C, 56.1 (56.4); H, 7.2 (7.2); Al, 8.4 (8.6); Zr, 28.3 (27.9); mol wt 321 (306, osmometric in C_6H_6). The infrared spectrum contains strong bands at 1200, 1060, 1040, 1020, 910, 800, 700, 570, and 500 ± 5 cm^{-1} (Nujol mull). Fluoresence frustrated attempts to obtain a Raman spectrum. The compound was stored under nitrogen at −40 °C.

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[23] The 11-eV mass spectrum of Me_3Al shows Me_2Al^+ as the base peak; no dinuclear ions are apparent. Consequently, we discuss the gas-phase chemistry in terms of monomeric Me_3Al.

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Kinetic experiments were carried out with 0.6 M Cp_2ZrMe_2 and 0.23 M $EtAlMe_2$ in neat Me_3Al. Product formation was followed by ^{13}C NMR spectroscopy. The method of Levin and Eberhart[25] was used to calculate second-order rate constants. Integration of the rate equation gave excellent correlation coefficients with $R = 0.998$ at 22 °C and 0.996 at 40 °C. The rate is too fast at 60 °C for accurate measurements, and R decreased to 0.976.

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Preparation, Structure, and Formation Mechanism of *cis*-RuH(OAr)(PMe$_3$)$_4$ (Ar = C$_6$H$_5$, C$_6$H$_4$-*p*-Me) and *cis*-RuH(OC$_6$H$_4$-*p*-CN)(PMe$_3$)$_4$(HOC$_6$H$_4$-*p*-CN)

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Reactions of $RuH_2(PMe_3)_4$ with phenol, *p*-methylphenol, and *p*-cyanophenol give the hydrido–aryloxido complexes *cis*-$RuH(OPh)(PMe_3)_4$ (1), *cis*-$RuH(OC_6H_4\text{-}p\text{-}Me)(PMe_3)_4$ (2), and *cis*-$RuH(OC_6H_4\text{-}p\text{-}CN)(PMe_3)_4(HOC_6H_4\text{-}p\text{-}CN)$ (3-HOC_6H_4-*p*-CN), respectively. NMR spectra (^1H, ^{13}C, and ^{31}P) of these complexes are consistent with the cis structures. The ^1H NMR spectrum of complex 3-HOC_6H_4-*p*-CN at −40 °C in CD_2Cl_2 shows a signal due to the OH hydrogen of the associated *p*-cyanophenol at 16.3 ppm, indicating the presence of O–H···O hydrogen bonding between the *p*-cyanophenoxide and the *p*-cyanophenol. The molecular structure of 2 has been determined by X-ray crystallography. Crystal data: monoclinic, space group $P2_1/a$, $a = 29.332$ (5) Å, $b = 13.741$ (8) Å, $c = 13.568$ (3) Å, $\beta = 102.37$ (2)°, $V = 5341.9$ Å^3, $Z = 8$, $R = 0.061$, $R_w = 0.070$ for 6011 reflections with $|F_o| > 3\sigma(F_o)$. ^1H and ^{31}P NMR spectra of the reaction mixture of $RuH_2(PMe_3)_4$ with phenol at low temperature indicate formation of an ionic complex formulated as $[RuH_3(PMe_3)_4]OPh$ (4), which is gradually converted into 1 at room temperature. Reaction mixtures of $RuH_2(PMe_3)_4$ with other Brønsted acids such as HBF_4 and 1,1,1,3,3,3-hexafluoro-2-propanol show similar ^1H and $^{31}P\{^1H\}$ NMR signals at low temperature, indicating the formation of complexes such as $[RuH_3(PMe_3)_4]BF_4$ and $[RuH_3(PMe_3)_4]OCH(CF_3)_2$. The ^1H NMR signal of hydrogen bonded to ruthenium in $[RuH_3(PMe_3)_4]OCH(CF_3)_2$ shows a value of 70 ms for T_1 at −40 °C and 500 MHz.

Introduction

Recent studies on late-transition-metal phenoxides with tertiary phosphine ligands have revealed their interesting properties such as C–O bond formation through coupling of the phenoxide and acyl ligands,[1,2] association of the phenoxide ligand with phenol through O–H···O hydrogen bonding,[3-5] and CO insertion into the metal–phenoxide bond.[6] The phenoxide complexes of Pd, Pt, Rh, and Ir were prepared easily by reactions of hydride or alkyl complexes of these metals with phenol. However, similar $\eta^1(O)$-bonded phenoxide complexes with tertiary phosphine ligands have not been separated for ruthenium. Previously the reaction of $RuH_2(PPh_3)_4$ with phenol was reported to liberate two PPh_3 ligands and give a complex formulated as $RuH(\eta^5\text{-}C_6H_5{=}O)(PPh_3)_2$, having an η^5-coordinated phenoxide ligand.[7]

We have investigated the preparation of ruthenium complexes having $\eta^1(O)$-bonded aryloxide ligands by the reaction of $RuH_2(PMe_3)_4$, having nonlabile PMe_3 ligands, with phenols and studied their structures and chemical properties. Several ruthenium aryloxide complexes of the type *cis*-$RuH(OAr)(PMe_3)_4$ and *cis*-$RuH(OAr)(PMe_3)_4(HOAr)$ were isolated and characterized by means of IR and NMR spectroscopy and X-ray crystallography. NMR studies of the reaction mixture of $RuH_2(PMe_3)_4$ with phenol at low temperature revealed the initial formation of the ionic complex $[RuH_3(PMe_3)_4]OPh$, which released dihydrogen to give *cis*-$RuH(OPh)(PMe_3)_4$ at room temperature.

Here we report the preparation, structures, and mechanism of formation of these ruthenium aryloxide complexes.

Results and Discussion

Preparation and Characterization of *cis*-RuH(OC$_6$H$_5$)(PMe$_3$)$_4$ (1) and *cis*-RuH(OC$_6$H$_4$-*p*-Me)(PMe$_3$)$_4$ (2). Reactions of $RuH_2(PMe_3)_4$ with a slight excess of phenol and *p*-methylphenol at room temperature

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