in both the dependent and independent variables.²¹

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Supplementary Material Available: Figures giving variable-temperature ¹H{³¹P} NMR spectra of 1a and their computer simulations and variable-temperature ¹³C¹H NMR spectra of an equilibrium mixture of the isomers 1b and 1c (2 pages). Ordering information is given on any current masthead page.

Solvolysis of Dimethylzirconocene by Trialkylaluminum Compounds

A. R. Siedle,* R. A. Newmark, J. N. Schroepfer, and P. A. Lyon

3M Corporate Research Laboratories, St. Paul, Minnesota 55144

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Liquid metal alkyls are strong Lewis acids and bases and useful solvents in which to conduct organometallic reactions. Cp₂ZrMe₂ undergoes rapid methyl exchange with pure Me₃Al but reacts with EtAlMe₂ in Me₃Al to form $Cp_2Zr(\mu-CH_3)(\mu-CH_2CH_2)AlMe_2$. Neat R₃Al reagents in which R has a hydrogen atom produce solvated Cp_2ZrH_2 derivatives. The gas-phase reaction of $Cp_2ZrCH_3^+$ with Me₃Al, studied by ion cyclotron resonance spectrometry, produces an ion formulated as $Cp_2Zr(\mu-CH_2)_2Al^+$.

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_3 -F·SbF₅, commonly known as magic acid.¹ In an analogous context, liquid metal alkyls such as Me₆Al₂, Me₃Ga, and Me₂Zn 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 ($Cp = \eta^5 \cdot C_5H_5$) with some trialkylaluminum compounds, R₃Al, 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

¹³C NMR spectroscopy shows that, in 0.3 M toluene solution, there occurs a facile ($\Delta G^* = 16.7 \text{ kcal mol}^{-1}$) statistical scrambling of ¹³CH₃ groups in Cp₂Zr(¹³CH₃)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 Me₃Al were used as both solvent and reactant. In fact, a new reaction has been detected but it is due to EtAlMe₂ present as an impurity at a 2.2 mol % level in commercial Me₃Al that is recognizable by its ¹H signals

at 1.00 (t, CH_3) and -0.01 (q, CH_2) ppm.⁴

In neat Me₃Al, EtAlMe₂ slowly reacts with Cp₂ZrMe₂ to form $Cp_2Zr(\mu-CH_3)(\mu-CH_2CH_2)AlMe_2$ (1) and methane (identified by mass spectrometry). In hydrocarbon sol-



vents, 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 ¹³C NMR spectrum of 1 exhibits a single Cp resonance at 107.2 ppm ($J_{CH} = 173 \text{ Hz}; \delta(^{1}\text{H}) 5.30 \text{ ppm}$). The Zr-C-H₃-Al bridging methyl group is associated with a peak at -21.5 ppm ($J_{\rm CH} = 115$ Hz; $\delta(^{1}{\rm H}) - 0.79$ ppm). The highfield chemical shift is in accord with those observed in crystallographically characterized compounds known to contain a Zr-CH₃-Al bridge.⁵ The Zr-CH₂ portion of the Zr-CH₂-CH₂-Al ethylene bridge gives rise to a ¹³C resonance at 33.7 ppm ($J_{\rm CH}$ = 144 Hz; cf. Cp₂ZrMe₂, δ (¹³C) 30.7, $J_{\rm CH}$ = 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). ¹³C NMR measurements yield second-order rate constants for formation of 1 of 0.98 and

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Table L ¹³ C NMR	Data
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compd	$\delta(^{13}\mathrm{C})~(J_{\mathrm{CH}}, \mathrm{assignt})^a$
$\overline{\mathrm{Cp}_{2}\mathrm{Zr}(\mu-\mathrm{CH}_{2})(\mu-\mathrm{C}_{2}\mathrm{H}_{4})}$	107.2 (173, Cp), 33.7 (144, Zr-CH ₂),
$AlMe_2(1)$	1.39 (127, $-CH_2Al$, $T_1 = 1.9$ s), -4.6
	$CH_{3}Al$), -21.52 (115, $Zr-CH_{3}-Al$, T_{1}
	= 4.5 s)
$Cp_2Zr(\mu-CH_3)(\mu-C_2H_4)$ -	106.7 (Cp), 33.0 (Zr-CH ₂), 10.23 (123,
Al(Me)Et (3a)	CH ₂ CH ₃), 5.5 (AlCH ₂ CH ₃), -0.82
	$(126, CH_2CH_2Al), -6.5 (AlCH_3),$
	-23.69 (Zr $-CH_3$ -Al, $T_1 = 5.6$ s)
$\mathrm{Cp}_{2}\mathrm{Zr}(\mu\text{-}\mathrm{CH}_{3})(\mu\text{-}\mathrm{C}_{2}\mathrm{H}_{4})\text{-}$	106.7 (Cp), 33.0 ($Zr-CH_2$), 10.05 (124,
$AlEt_2$ (3b)	$AlCH_2CH_3$), 4.2 ($AlCH_2CH_3$), -2.71
	$(126, CH_2CH_2Al), -25.37 (114,$
	$Zr-CH_3-Al, T_1 = 5.1 s)$
$Me_2Si(C_5H_4)_2Zr(\mu-CH_3)$ -	121.6, 116.8, 109.2, 100.5 (Cp), 98.2 (Cp
$(\mu$ -C ₂ H ₄)AlMe ₂ (4)	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 ₂ HfMe 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 ¹³C NMR spectra of aged, deactivated catalysts high-field resonances that are characteristic of the Zr-CH₃-Al bridge moiety in 1.

The yield of 1 is limited by the amount of adventitious EtAlMe₂ present in the neat Me₃Al solvent. However, if additional Et₃Al 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 ²⁷Al 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–CH₃–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-CH₂-CH angle.⁶



Reaction of Cp₂ZrMe₂ with 0.33 mol of Et₃Al in toluene (i.e. Zr:Et = 1:1 with Me₃Al being omitted) gives rise to a statistical mixture containing 1 and the two other possible $Cp_2Zr(\mu-CH_3)(\mu-CH_2CH_2)AlRR'$ species (R = Me, R'





= Et, 3a; R,R' = Et, 3b; cf. Table I). Significantly, the ¹H undecoupled high-field ¹³C resonances of these compounds are all quartets; i.e., no $Zr-CH_2(CH_3)-Al$ compounds are detected. Use of more concentrated Et₃Al solutions leads to different chemistry that is described below.

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 Me₂Si- $(C_5H_4)_2$ ZrMe₂ with EtAlMe₂ produces an analogue of 1, $Me_2Si(C_5H_4)_2Zr(\mu-CH_3)(\mu-CH_2CH_2)AlMe_2$ (4). In the ¹³C NMR spectrum of this, the nonequivalent SiCH₃ 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 SiMe₂ bridge; cf. Table I. The shifts of the Zr-CH₃-Al, Zr-CH₂-CH₂-Al, and Zr-CH₂- 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 Cp₂ZrMe₂ and Me₃Al react to give Cp_2ZrMe^+ and $AlMe_4^-$; the reverse of this reaction leads to the observed scrambling of Zr-CH₃ 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-CH₃-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, (Me₅Cp)₂Zr(Me)- (CF_3SO_3) , which arguably contains an incipient cationic zirconium species, is simply methylated by Me₃Al to form (Me₅Cp)₂ZrMe₂.⁸ In the case of EtAlMe₂, additional chemistry involving the Zr-H-CH₂-CH₂-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 Me₃Al (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-CH₃-Al position. Thus, Me₃Al acts as a Lewis acid $(CH_3^- \text{ acceptor})$ and a base $(H^+ \text{ acceptor})$. A similar dual functionality of R_3Al has been observed by Grubbs et al. in a study of the reaction of Cp₂TiCl₂ with Me₃Al.¹⁰ With respect to both structure and means of formation, 1 deserves comment in relation to titanium chemistry.

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Tebbe observed that Cp_2TiMe_2 and $AlMe_3$ form the μ methylene compound $Cp_2Ti(\mu-CH_2)(\mu-CH_3)AlMe_2$.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 [Cp₂TaMe₂][AlMe₄] is reported to eliminate methane to form Cp₂Ta(Me)[CH₂AlMe₃].¹³ Our data indicate that, in the Cp₂ZrMe₂-Me₂AlR 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, Me₃Al is both a solvent and a reactant. The products obtained from Cp₂ZrMe₂ and neat R₃Al 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 Cp₂ZrR₂ compounds formed by alkyl exchange may then undergo β -elimination to form zirconium hydride species that may react further.¹⁶ A solution of Cp₂ZrMe₂ in neat Et₃Al 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 $[Cp_2Zr(\mu-H)H-AlEt_3]_2$ (5), which is analogous to the com-



plex of Cp₂ZrH₂ with Me₃Al reported earlier.¹⁷ In mixtures of trialkylaluminums, as the Et₃Al:Me₃Al ratio decreases, less 5 and more 1 is produced.

Reaction of Cp_2ZrMe_2 with neat $(i-Bu)_3Al$ yields isobutene and 6. The ¹³C NMR spectrum of 6 comprises a singlet at 104.3 ppm, the various alkyl resonances being obscured by $(i-\hat{Bu})_3Al$. The ¹H NMR spectrum demonstrates peaks at δ 5.71 (s, Cp), -2.23 (br s, 1 H, H₁ or H₃), -1.75 (br s, 1 H, H₃ or H₁), and -1.22 (t, 1 H, $J_{H2-H1,3} = 6$ Hz, H₂). Splitting of H₂ by coupling to H_{1,3} is presumably obscured by the large line width associated with neighboring quadrupolar nuclei (²⁷Al, $I = \frac{3}{2}$; ⁹¹Zr, $I = \frac{5}{2}$) but the expected coupling was verified by a ¹H COSY experiment. Broadening of the $H_{1,3}$ (but not H_2) signals occurs

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Figure 1. FT MS spectrum of ions produced from Cp₂ZrCH₃⁺ and Al(CH₃)₃.

at 50 °C. The NMR parameters of 6 bear a close resemblance to those of a zirconium hydride-triisobutvlaluminum complex reported by Schwartz,¹⁸ and this is the basis for the structure proposed.

Exchange Reactions in Related Systems

Although (Me₅Cp)₂ZrMe₂ undergoes degenerate exchange of Zr-methyl groups with Me₃Al, no exchange (or any other reaction) with Et₃Al is detectable at 25 °C in toluene solution. Likewise, no alkyl exchange (or other reaction) is observed between Cp₂ZrMe₂ and the less acidic organometallics Et₃B and Me₃Ga. Dialkylzincs comprise a special case.

Cp₂ZrMe₂ and Me₂Zn undergo rapid methyl exchange in toluene solution, and no new compounds are detectable by NMR spectroscopy. In contrast, Cp₂ZrMe₂ catalyzes the decomposition of Et₂Zn 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.

Cp₂HfMe₂ reacts with 1 equiv of Et₃Al 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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generated in the gas phase by action of an 11-eV electron beam upon Cp_2ZrMe_2 .²² The interaction of Cp_2ZrMe^+ with Me₃Al 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 $Cp_2Zr(\mu-CH_2)_2Al^+$ (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 $Cp_2Zr(\mu-CH_3)_2AlMe_2^+$. Such reactions in fluid solution are wellknown 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 $Cp_2Zr(\mu$ - $^{12}CH_2(\mu - ^{13}CH_2)Al^+$ and $Cp_2Zr(\mu - ^{12}CH_2)_2Al^+$ 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 Me₃Al pressure is changed from 1.5×10^{-6} to 4.5×10^{-6} mm. The ¹³C-labeling experiment demonstrates that, at minimum, the product formed initially from Cp₂ZrMe⁺ and Me₃Al is unlikely to have a single Zr-CH₃-Al bridge, for then all the ¹³C 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 ¹³C in the final ion product.

This gas-phase chemistry, too, is more complex than anticipated. The reaction of $Cp_2Zr(CD_3)^+$ with Me₃Al produces $Cp_2^{99}Zr(^{12}C_2D_nH_{4-n})Al^+$, which contains 36% D₀, $0 \pm 1\%$ D₁, 13% D₂, 51% D₃, and no D₄. This isotopomer distribution is unchanged over the same Me₃Al pressure regime. A minimalist, but not necessarily unique, interpretation of the *striking absence of a D*₁ species and of the ¹³C-labeling experiment is that $Cp_2ZrCH_3^+$ reacts to form $Cp_2Zr(\mu-CH_3)_2AlMe_2^+$, in which the two bridging $Zr-CH_3$ -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 : $(\mu^{-12}CH_2)(\mu^{-13}CH_3)Rh(COD)$ to $Cp_2Ti(\mu^{-13}CH_2)(\mu^{-12}CH_3)$ -Rh(COD).²⁴

The gas-phase reactivity of $Cp_2ZrCH_3^+$ toward Me₃Ga parallels that of Me₃Al. According to Scheme II, the methane lost derives from a CH₃ group on Al (or Ga) and a hydrogen atom from the μ -CH₃ groups. We expect that loss of only one molecule of methane from $Cp_2Zr(\mu$ -CH₃)₂ZnMe⁺ should occur. Accordingly, $Cp_2ZrCH_3^+$ and Me₂Zn produce an ion cluster whose masses correspond to isotopomers of $Cp_2Zr(\mu$ -CH₂)(μ -CH₃)Zn⁺. Among these is m/z 312.9928 (calcd for ${}^{12}C_{12}{}^{11}H_{15}{}^{64}Zn^{90}Zr$ 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⁺ – CH₂Zn, CpZr⁺, and CH₃Zn⁺.

Thus, the gas-phase ICR experiments are consistent with and provide indirect support for the chemistry that occurs in liquid Me₃Al sketched in Scheme I. A critical feature in the steps that lead to Cp₂Zr(μ -CH₃)(μ -CH₂CH₂)AlMe₂ is an interaction between zirconium and the CH₃CH₂ hydrogen atoms in EtAlMe₂ 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 -CH₃ group.

Experimental Section

Toluene and hexane were purified by distillation under nitrogen from Na-Ph₂CO-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 R₃Al 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-d₈ solutions with a Varian XL-400 instrument whose ¹H operating frequency is 400 MHz. ¹H, ¹³C, and ²⁷Al chemical shifts are expressed relative to internal $(CH_3)_4Si$ and external 1 M Al(ClO_4)₃ in D₂O. 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.

 $Cp_2Zr(\mu-CH_3)(\mu-CH_2CH_2)AlMe_2$. To 0.5 g (2 mmol) of Cp₂ZrMe₂ dissolved in 10 mL of 2 M Me₃Al in toluene was added 0.175 mL of a 1.9 M solution of Et₃Al 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 AlMe₃. 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 C₁₅H₂₃AlZr: 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 $500 \pm 5 \text{ cm}^{-1}$ (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 Me₃Al shows Me₂Al⁺ as the base peak; no dinuclear ions are apparent. Consequently, we discuss the gas-phase chemistry in terms of monomeric Me₃Al.

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Kinetic experiments were carried out with 0.6 M Cp₂ZrMe₂ and 0.23 M EtAlMe2 in neat Me3Al. Product formation was followed by ¹³C NMR spectroscopy. The method of Levin and Eberhart²⁵ was used to calculate second-order rate constants. Integration of the rate equation gave excellent correlation coefficients with

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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)(PMe₃)₄ (Ar = C₆H₅, C₆H₄-p-Me) and cis-RuH(OC₆H₄-p-CN)(PMe₃)₄(HOC₆H₄-p-CN)

Kohtaro Osakada,* Kimitaka Ohshiro, and Akio Yamamoto*,†

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 227, Japan

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Reactions of $\operatorname{RuH}_2(\operatorname{PMe}_3)_4$ with phenol, p-methylphenol, and p-cyanophenol give the hydrido-aryloxido complexes cis-RuH(OPh)(PMe₃)₄ (1), cis-RuH(OC₆H₄-p-Me)(PMe₃)₄ (2), and cis-RuH(OC₆H₄-p-CN)-(PMe₃)₄(HOC₆H₄-p-CN) (3-HOC₆H₄-p-CN), respectively. NMR spectra (¹H, ¹³C, and ³¹P) of these complexes are consistent with the cis structures. The ¹H NMR spectrum of complex 3-HOC₆H₄-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 Å³, Z = 8, R = 0.061, $R_w = 0.070$ for 6011 reflections with $|F_0| > 3\sigma(F_0)$. ¹H and ³¹P 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 $\operatorname{RuH}_2(\operatorname{PMe}_3)_4$ with other Brønsted acids such as HBF_4 and 1,1,1,3,3,3-hexafluoro-2-propanol show similar ¹H and ³¹P{¹H} NMR signals at low temperature, indicating the formation of complexes such as $[\operatorname{RuH}_3(\operatorname{PMe}_3)_4]\operatorname{BF}_4$ and $[\operatorname{RuH}_3(\operatorname{PMe}_3)_4]\operatorname{OCH}(\operatorname{CF}_3)_2$. The ¹H NMR signal of hydrogen bonded to ruthenium in $[\operatorname{RuH}_3(\operatorname{PMe}_3)_4]\operatorname{OCH}(\operatorname{CF}_3)_2$ 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 PPh₃ ligands and give a complex formulated as $\operatorname{RuH}(\eta^5 - \operatorname{C}_6H_5 = O)(\operatorname{PPh}_3)_2$, 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 RuH₂(PMe₃)₄, having nonlabile PMe₃ ligands, with phenols and studied their structures and chemical properties. Several ruthenium aryloxide complexes of the type cis-RuH(OAr)(PMe₃)₄ and cis-RuH(OAr)(PMe₃)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)(PMe₃)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- $(OC_6H_5)(PMe_3)_4$ (1) and cis-RuH $(OC_6H_4$ -p-Me)- $(\mathbf{PMe}_3)_4$ (2). Reactions of $\mathrm{RuH}_2(\mathrm{PMe}_3)_4$ with a slight excess of phenol and *p*-methylphenol at room temperature

[†]Present address: Department of Applied Chemistry, School of Science and Engineering, Waseda University, Ohkubo, Shinjyukuku, Tokyo 169, Japan.

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