Reactions of tetrakis(trimethylsilylmethyl)hafnium with trimethylaluminum

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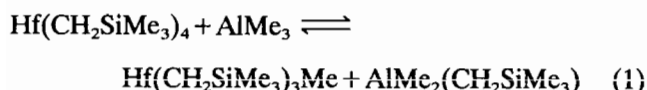[b] *Advanced Technology Materials, 7 Commerce Drive, Danbury, CT 06810, USA*

Abstract

Reactions between TiMe$_4$, Cp$_2$ZrMe$_2$ or Hf(CH$_2$SiMe$_3$)$_4$ and AlMe$_3$ were investigated using conductivity measurements and ^{1}H NMR spectroscopy. Little change was observed in the conductivity of Hf(CH$_2$SiMe$_3$)$_4$/AlMe$_3$ or AlMe$_3$/Cp$_2$ZrMe$_2$ mixtures in dichloromethane relative to the molar conductivity of the reactants. In the presence of PEt$_3$, a small increase in conductivity was observed for the latter solution. A 50-fold increase in the conductivity was observed in mixtures of TiMe$_4$ and AlMe$_3$. Spectroscopic studies on mixtures of Hf(CH$_2$SiMe$_3$)$_4$ and AlMe$_3$ were consistent with formation of a thermally unstable, alkyl bridged heterobimetallic complex, **2**, present in a 5:1 ratio to the starting materials.

Keywords: Hafnium complexes; Alkylsilyl complexes; Aluminum complexes; Alkyl complexes

1. Introduction

Reactions between aluminum alkyls and early transition metal alkyl compounds have been of great interest in Ziegler–Natta catalysis of olefin polymerization [1]. The authors of the earliest reports on the degenerate exchange of methyl groups between TiMe$_4$ and AlMe$_3$ suggested an ionic intermediate of the type [Me$_3$Ti(solvent)$^+$][AlMe$_4$$^-$] based solely on spectroscopic evidence [2]. Others have proposed neutral heterobimetallic products in the reaction of Zr(CH$_2$Ph)$_4$ with Al(CH$_2$Ph)$_3$ [3]. More recently, an ionic intermediate was proposed for the alkyl exchange reactions between AlMe$_3$ or AlEt$_3$ and bis(cyclopentadienyl)-(dimethyl)zirconium and hafnium compounds [4]. By comparison, reaction of AlMe$_3$ with Cp$_2$TiMe$_2$, yielded Cp$_2$Ti(μ-CH$_3$)(μ-CH$_2$)AlMe$_2$ [5]. Our interest in the reaction of alkyl hafnium compounds with aluminum alkyls for the chemical vapor deposition of hafnium aluminide, prompted the present investigation of the reaction of tetrakis(trimethylsilylmethyl)hafnium with trimethylaluminum (reaction (1)).

$$Hf(CH_2SiMe_3)_4 + AlMe_3 \rightleftharpoons$$
$$Hf(CH_2SiMe_3)_3Me + AlMe_2(CH_2SiMe_3) \quad (1)$$

2. Experimental

All compounds described in this work were handled using Schlenk techniques, an M.I. Braun glovebox under a purified argon atmosphere or on a vacuum line equipped with oil diffusion and mechanical pumps (10^{-2} Torr) [6]. Trimethyl aluminum, triethylphosphine, TiCl$_4$, HfCl$_4$ and Cp$_2$ZrCl$_2$ were purchased from Strem Chemical Co. and used as received. 1.0 M LiCD$_3$ in hexanes and 1.0 M LiMe$_3$SiCH$_2$ in hexanes were purchased from Aldrich Chemical Co. Solvents were purified by refluxing over Na/benzophenone (benzene, hexane, toluene, tetrahydrofuran, dioxane, diethyl ether) or P$_2$O$_5$ (dichloromethane) and distilled prior to use. Deuterated solvents were purchased from Cambridge Isotope Laboratories and dried as described above. [Fe(dmpe)$_2$acac][AlMe$_4$], [Co(bipy)$_2$Me$_2$][AlMe$_4$], TiMe$_4$, Cp$_2$ZrMe$_2$ and Hf(CH$_2$SiMe$_3$)$_4$ were prepared by literature methods [7–11].

2.1. Conductivity measurements

Conductivity measurements were performed on 0.035 M solutions in CH$_2$Cl$_2$ using a Beckman Instruments model RC 16B2 conductivity bridge. A solution of TiMe$_4$ was prepared in an Et$_2$O/hexane mixture but was not isolated [11]. The cold solution was transferred to the conductivity cell by cannula at −30 °C. After measuring

the resistivity of the solution, approximately one equivalent of $AlMe_3$ (based on 50% yield of $TiMe_4$ from the literature) was added at $-30\ °C$ and the resistivity measured again.

2.2. NMR studies

^1H and $^{27}Al\{^1H\}$ spectra were recorded on a Varian 300XL spectrometer in 5 mm tubes equipped with a Teflon valve (J. Youngs). Proton chemical shifts are listed relative to residual protons in the solvent ($CDHCl_2$ at $\delta\ 5.23$ ppm). Aluminum chemical shifts are referenced to $AlMe_3$ at 156 ppm (relative to aqueous Al^{3+}) in C_6D_6 [12].

2.3. Reactions of $Hf(CH_2SiMe_3)_4$ with $AlMe_3$

Solutions were prepared in the glove box by mixing weighed quantities of $Hf(CH_2SiMe_3)_4$, $AlMe_3$ and Lewis bases in small vials. Dichloromethane-d_2 was added to the vials and the solutions combined in the NMR tubes. In a typical experiment, a solution of 0.100 g $Hf(CH_2SiMe_3)_4$ (0.19 mmol) in 0.75 ml of CD_2Cl_2 was placed in the NMR tube. A solution of 0.015 g $AlMe_3$ (0.20 mmol) in 0.75 ml of CD_2Cl_2 was added. The tube was sealed by closing the Teflon valve. ^1H (CD_2Cl_2): δ -0.96, -0.82, -0.77, -0.081, 0.47, 0.012, 0.30. ^{13}C (C_6D_6): -7.0, 3.05, 86.46. ^{27}Al (C_6D_6): 149 ppm.

In reactions involving triethylphosphine, a solution of 0.100 g $Hf(CH_2SiMe_3)_4$ (0.19 mmol) and 0.025 g PEt_3 (0.21 mmol) in 0.75 ml of CD_2Cl_2 was placed in the NMR tube. A solution of 0.015 g $AlMe_3$ (0.20 mmol) in 0.75 ml of CD_2Cl_2 was added. ^1H (CD_2Cl_2): δ -1.05, -0.86, -0.84, -0.035, -0.025, 0.10, 0.38, 0.44, 1.12 d of t, 1.65 q of d. ^{27}Al (C_6D_6): 156 ppm.

For low temperature studies, samples were prepared as described above but the $AlMe_3$ solution was prevented from mixing with the transition metal compound. After removing the apparatus from the glove box, the hafnium solution was cooled and the reagents allowed to mix. The tube was frozen to $-196\ °C$ and flame sealed under vacuum. Alternatively, some samples were prepared by vacuum transfer of $AlMe_3$ to a frozen solution of $Hf(CH_2SiMe_3)_4$ (and PEt_3) cooled to $-196\ °C$.

3. Results

3.1. Conductivity studies

By comparison to solutions of $[Co(2,2'-bipy)_2Me_2^+][AlMe_4^-]$ ($\Lambda_M = 31.7$ S cm^2 mol^{-1}) and $[Fe(acac)(dmpe)_2^+][AlMe_4^-]$ ($\Lambda_M = 21.4$ S cm^2 mol^{-1}), the observed molar conductivities of dichloromethane solutions (Table 1) for $AlMe_3$, PEt_3 and $Hf(CH_2SiMe_3)_4$ were between 150 and 350 times lower ($\Lambda_M \leqslant 0.15$ S

cm^2 mol^{-1}). The value in Table 1 for the molar conductivity of $[Fe(acac)(dmpe)_2^+][AlMe_4^-]$ compared well with the reported value of 33 S cm^2 mol^{-1} in THF solution [8] and was in the range reported for 1:1 electrolytes in CH_2Cl_2 solution [13]. Mixtures of $AlMe_3$ and $Hf(CH_2SiMe_3)_4$, $AlMe_3$ and PEt_3, or $Hf(CH_2SiMe_3)_4$ and PEt_3 showed very slight increases in molar conductivity. Even the three component mixture, $AlMe_3$, PEt_3 and $Hf(CH_2SiMe_3)_4$, had a molar conductivity of 0.30 S cm^2 mol^{-1}.

Investigation of the reaction between Cp_2ZrMe_2 and $AlMe_3$ using conductivity measurements revealed a similar pattern for the molar conductivities. Molar conductivities of dichloromethane solutions of Cp_2ZrMe_2 and mixtures of Cp_2ZrMe_2 with $AlMe_3$ were in the same range as those for reactions involving $Hf(CH_2SiMe_3)_4$ (~ 0.05–0.15 S cm^2 mol^{-1}). Addition of triethylphosphine to the mixture of Cp_2ZrMe_2 with $AlMe_3$ did lead to an approximately ten-fold increase in the molar conductivity ($\Lambda_M = 2.06$ S cm^2 mol^{-1}). In contrast, the conductivities of $TiMe_4$ solutions prepared in diethyl ether/hexane at $-30\ °C$ (conditions under which alkyl exchange occurs) [2] were observed to increase 50-fold after addition of one equivalent of $AlMe_3$. The conductivity of a hexane solution of $AlMe_3$ solution was unchanged upon addition of ether.

3.2. Spectroscopic studies of the reaction of $Hf(CH_2SiMe_3)_4$ with $AlMe_3$

The results of spectroscopic investigations on the reactions between $Hf(CH_2SiMe_3)_4$ and $AlMe_3$ are summarized in Fig. 1 and Table 2. For reactions containing a slight excess of $Hf(CH_2SiMe_3)_4$ in dichloromethane-d_2 at $-78\ °C$, new resonances were observed at -0.081, -0.77 and -0.96 ppm in a 9:9:2 ratio. By comparison with the reported ^1H spectrum of $[K^+][Al-(CH_2SiMe_3)_3H^-]$ (0.41 ppm Me_3SiCH_2 and -0.98 ppm Me_3SiCH_2 in C_6D_6) [14], these resonances are assigned to $AlCH_2SiMe_3$, $AlMe$ and $AlCH_2SiMe_3$ protons, respectively. The resonance at -0.77 ppm is the superposition of more than one resonance indicative of more complex behavior. Another new resonance at 0.47 ppm is assigned to the $(Me_3SiCH_2)_3Hf$ protons with the resonance for the $(Me_3SiCH_2)_3Hf$ protons overlapped with the $(Me_3SiCH_2)_4Hf$ protons of the starting materials as demonstrated by integration of the 0.012 ppm resonance of the methyl groups to the 0.47 and 0.30 ppm resonances of both methylene groups (9:2 ratio). Integration of the 0.47 ppm resonance (($Me_3SiCH_2)_3$-$Hf(\mu$-$CH_2SiMe_3)AlMe_3$) to the -0.96 ppm resonance (3:1 ratio) supports the assignment of these resonances to two different kinds of Me_3SiCH_2 groups. The ambiguities posed by the complex nature of the resonance at -0.77 ppm and the overlapped resonances for Me_3SiCH_2 resonances at 0.012 ppm are resolved in

Table 1
Conductivity and molar conductivity data for reactions of AlMe$_3$ with Hf(CH$_2$SiMe$_3$)$_4$ and Cp$_2$ZrMe$_2$

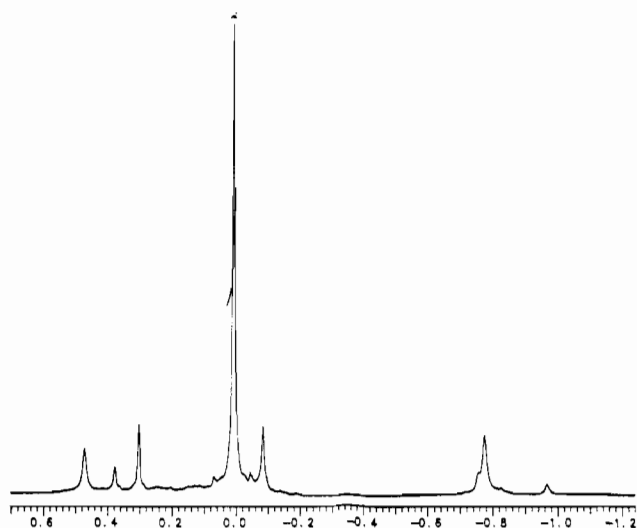| Mixture or compound	Conductivity ($\mu\Omega^{-1}$)	Molar conductivity, Λ (S cm^2 mol^{-1})
AlMe$_3$	2.45	0.15
PEt$_3$	2.45	0.15
Hf(CH$_2$SiMe$_3$)$_4$	1.28	0.08
Cp$_2$ZrMe$_2$	0.86	0.05
[Fe(dmpe)$_2$acac][AlMe$_4$]	345.0	21.4
[Co(bipy)$_2$Me$_2$][AlMe$_4$]	510.0	31.7
[^{n}Bu$_4$][Br]	862.0	53.5
AlMe$_3$ + PEt$_3$	4.80	0.30
AlMe$_3$ + Hf(CH$_2$SiMe$_3$)$_4$	4.80	0.30
Hf(CH$_2$SiMe$_3$)$_4$ + PEt$_3$	5.22	0.32
AlMe$_3$ + Hf(CH$_2$SiMe$_3$)$_4$ + PEt$_3$	4.80	0.30
Cp$_2$ZrMe$_2$ + AlMe$_3$	2.45	0.15
Cp$_2$ZrMe$_2$ + AlMe$_3$ + PEt$_3$	33.2	2.06

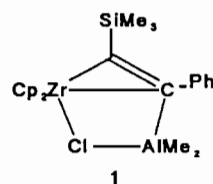Fig. 1. ^{1}H NMR spectra of Hf(CH$_2$SiMe$_3$)$_4$ and AlMe$_3$ in CD$_2$Cl$_2$ at −78 °C.

the spectra obtained in the presence of PEt$_3$ (vide infra).

Integration of the resonances for AlMe$_3$(CH$_2$SiMe$_3$) to AlMe$_3$ indicated a 5:1 ratio of the new complex to residual AlMe$_3$. By comparison with the spectrum of Cp$_2$HfMe$_2$, the absence of resonances at −0.30 ppm (of intensity three protons) argued against alkyl exchanges at hafnium [7]. With the exception of the resonances assigned to Hf(Me$_3$SiCH$_2$)$_4$, all of the remaining resonances were exchange broadened at −58 °C. Coalescence was observed at −28 °C. At 0 °C, broad resonances were observed at 0.19, −0.17 and −0.72 ppm. Upon standing at room temperature, the solution changed color from a colorless mixture to yellow and subsequently to brown and black over 30 min.

^{27}Al NMR spectra were recorded for the reaction between Hf(CH$_2$SiMe$_3$)$_4$ and AlMe$_3$ as well as two tetramethylaluminate salts of transition metal complexes (168 ppm for both [Fe(dmpe)$_2$acac][AlMe$_4$] and [Co(bipy)$_2$Me$_2$][AlMe$_4$]). The chemical shifts for mixtures of Hf(CH$_2$SiMe$_3$)$_4$ and AlMe$_3$ were in the range observed for neutral three- and four-coordinate aluminum complexes (AlMe$_3$ and AlMe$_3 \cdot$ PEt$_3$, respectively) [12]. Given the broad linewidths of the ^{27}Al resonances for anionic AlMe$_4^-$ salts of [Co(2,2'-bipy)$_2$Me$_2^+$] and [Fe(acac)(dmpe)$_2^+$], the latter were also observed in the same range.

^{13}C chemical shifts are, in principle, diagnostic of bridging hydrocarbyl groups in transition metal complexes, however, carbon atoms bonded to quadrupolar Al nuclei lead to broadening of the signal. Clearly discernable carbon resonances for the μ-CH$_2$SiMe$_3$ and μ-CH$_2$SiMe$_3$ groups were not observed in the ambient or low temperature ^{13}C NMR spectra of Hf(CH$_2$SiMe$_3$)$_4$/AlMe$_3$ mixtures. The failure to observe carbon atoms bridging between aluminum and transition metals has been previously reported for the alkynyl bridged Zr–Al heterobimetallic compound 1 [15].
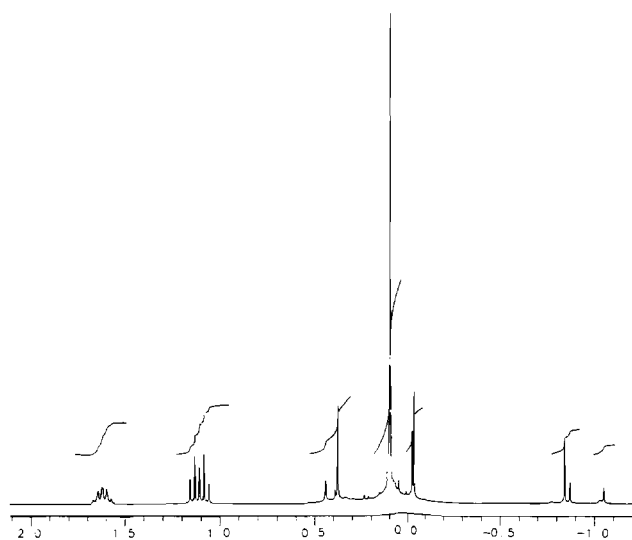

Low temperature ^{1}H NMR spectra of mixtures of AlMe$_3$, Hf(CH$_2$SiMe$_3$)$_4$ and PEt$_3$ in CD$_2$Cl$_2$ over the temperature range −78 to 0 °C were consistent with the presence of Hf(CH$_2$SiMe$_3$)$_4$ and AlMe$_3 \cdot$ PEt$_3$. The latter was confirmed by addition of one equivalent of PEt$_3$ to a solution of AlMe$_3$. After reaction at ambient temperature for 1 h, new resonances were observed at −0.035, −0.84, −1.05 ppm (9:9:2 ratio) and at −0.025 and 0.45 ppm (9:2 ratio), shifted upfield from those observed in the absence of phosphine and clearly dif-

Table 2
¹H NMR resonances for reactions of AlMe₃ with Hf(CH₂SiMe₃)₄

Compound	Chemical shift (δ) ᵃ					
	CH₂Si*Me₃*	C*H₂*SiMe₃	μ-CH₂Si*Me₃*	μ-C*H₂*SiMe₃	μ-Me	Me
AlMe₃						−0.32
Hf(CH₂SiMe₃)₄	0.11	0.39				
HfR₄ + AlMe₃	0.012	0.47	−0.081	−0.96		−0.77
HfR₄ + AlMe₃ + PEt₃	−0.025	0.44	−0.035	−1.05		−0.84
[Fe(dmpe)₂acac][AlMe₄] [9]						−1.07
[Co(bipy)₂Me₂][AlMe₄] [10]						−1.22
Cp₂Sc(μ-Me₂)AlMe₂ [23]					−0.29	−0.84
Cp₂Y(μ-Me₂)AlMe₂ [21]					−0.32	−0.98
Cp₂Ti(μ-Me)(μ-CH₂)AlMe₂ ᵇ					−0.40	−1.58

ᵃ Referenced to residual protons in CD₂Cl₂ at ambient temperature.

ᵇ Chemical shifts in Ref. [5] were reported relative to C₆D₅H at 7.37 ppm. These values in this text have been corrected to reflect our benzene spectra referenced to 7.15 ppm.

Fig. 2. ¹H NMR spectra of Hf(CH₂SiMe₃)₄, PEt₃ and AlMe₃ in CD₂Cl₂ at 20 °C.

ferent from the ¹H and ³¹P NMR spectra of mixtures containing Hf(CH₂SiMe₃)₄/PEt₃ and AlMe₃/PEt₃ (Fig. 2). The ratio of Al*Me₃*(CH₂SiMe₃) to Al*Me₃* in Hf(CH₂SiMe₃)₄/AlMe₃/PEt₃ mixtures was also found to be ~5:1 based on integration of the −0.84 and −0.86 ppm resonances. When the sample was cooled to −78 °C, there was no change in the spectrum with only a single Al*Me* resonance being observed. The solution changed color from yellow to brown over a period of 2 h at ambient temperature and was black after 24 h. The lack of thermal stability of the reaction products has thwarted our efforts at isolating and characterizing the products in reaction (1).
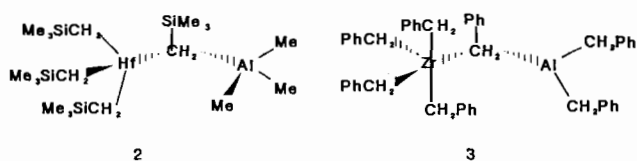
4. Discussion

While the existence and utility of cationic Group IVB metal complexes in olefin polymerization has been

firmly established, in our view, the role of ionic intermediates/products in the exchange reactions between aluminum and transition metal alkyl compounds remains ambiguous [16]. Examples of isolated cationic transition metal complexes containing AlMe₄⁻ anions include [Fe(dmpe)₂acac][AlMe₄], [Co(bipy)₂Me₂][AlMe₄] and [Cp₂TaMe₂][AlMe₄] [9,10,17], however, the list does not include examples of Group IVB transition metal cations with organoaluminum counterions [16]. The failure to observe any significant increase in conductivity in reaction (1) was consistent with the qualitative results reported for mixtures of Zr(CH₂Ph)₄ and Al(CH₂Ph)₃ [3]. Aluminum alkyls themselves have very low specific conductivities, in the order of 10^{-3} $\mu\Omega^{-1}$, consistent with a very small degree of auto-ionization [18]. Molar conductivities of [Fe(dmpe)₂acac][AlMe₄] and [Co(bipy)₂Me₂][AlMe₄] were found to be significantly larger and consistent with reported molar conductivities for [(Ph₂PCH₂PPh₂)Rh(CO)₂⁺][Cl⁻] in CH₂Cl₂ ($\Lambda_M =$ 27 S cm² mol⁻¹) at 25 °C [9]. To our knowledge, molar conductivities of hafnium alkyls have not been reported.

Formation of *significant* concentrations of ionic products should be accompanied by an increase in conductivity for solutions containing the transition metal organometallics and AlMe₃ over solutions of the individual reactants. The data in Table 1 do not support the presence of 1:1 electrolytes in reaction (1). Nevertheless, the presence of low concentrations of highly reactive ionic intermediates as proposed in NMR studies of Cp₂ZrMe₂/AlMe₃ mixtures, would have a minimal effect on the observed molar conductivity. The spectroscopic studies, however, indicate that significant concentrations of new metastable compounds *exist* in solution (~80% of the observed products). If these compounds were indeed ionic in nature, a significant increase in conductivity would be expected for solutions

containing $AlMe_3$ and $Hf(CH_2SiMe_3)_4$. Taken together, the data argues against the role of ionic products from the reactions between Group IVB transition metal alkyls and aluminum alkyls in reaction (1) in dichloromethane.

We believe that the reactions of $Hf(CH_2SiMe_3)_4$ with $AlMe_3$ are best understood in terms of a primarily covalently bonded, heterobimetallic product, possibly $(Me_3SiCH_2)_3Hf(\mu\text{-}CH_2SiMe_3)AlMe_3$ (2), similar to that proposed in reactions between $Zr(CH_2Ph)_4$ and $Al(CH_2Ph)_3$ (3), [3] or a contact ion pair. Solutions of 3 were non-conductive and showed no exchange of benzyl groups between aluminum and zirconium. Comparison of the spectroscopic data for 2 with ^1H NMR data (Table 2) for a series of heterobimetallic aluminum complexes suggests that the observation of a single aluminum methyl resonance and only two types of Me_3SiCH_2 groups in the proper ratio is consistent with structure 2 in which there is a single bridging trimethylsilylmethyl ligand, although a bridging or agostic methyl group cannot be ruled out. Singly bridging μ-CH_2SiMe_3 ligands have been crystallographically characterized for $[Cu(CH_2SiMe_3)]_4$ [19].

A range of products including contact ion pairs, solvent separated ion pairs and solvated cation–anion pairs were recently identified in the $Cp_2TiCl_2/AlCl_3$ and $Cp_2Ti(CH_2SiMe_3)Cl/AlCl_3$ systems [20]. The nature of the product was found to be dependent on temperature, concentration, the ratio of the reactants and the reaction solvent. Of greatest relevance to the present work is the observation of an downfield shifted ^1H resonance of the CH_2SiMe_3 ligands in $Cp_2Ti(CH_2SiMe_3)Cl/AlCl_3$ mixtures relative to $Cp_2Ti(CH_2SiMe_3)Cl$ (3.04 versus 2.26 ppm in $ClCH_2CH_2Cl$). The latter observation was interpreted as consistent with the deshielding of the CH_2 protons resulting from the development of increased positive charge at the titanium and formation of either a contact ion pair, 4, or a solvent separated ion pair, 5, as shown in reaction (2). These observations are consistent with the downfield shift of the CH_2SiMe_3 protons in 2 relative to $Hf(CH_2SiMe_3)_4$. Curiously, the ratio of the signals at 3.04 and 2.26 ppm in the $Cp_2Ti(CH_2SiMe_3)Cl/AlCl_3$ system was found to be 5:1, similar to that observed in $Hf(CH_2SiMe_3)_4/AlMe_3$ mixtures (compound 2: $AlMe_3$). The equilibrium in reaction (2) was proposed as a step in the conversion of 4 and 5 to solvated cation–anion pairs and eventual formation of Cp_2TiCl_2 and $Al(CH_2SiMe_3)Cl_2$ by exchange of halide for alkyl ligands. It is possible that reaction of $Hf(CH_2SiMe_3)_4$ with $AlMe_3$ initially produces a contact

ion pair. Subsequent solvation to solvent separated ion pairs and solvated cation–anion pairs leads to the observed decomposition. The formulation of 2 as a contact ion pair is consistent with the conductivity measurements. The latter are expected to show small molar conductivities while solvated cation–anion pairs are expected to have higher molar conductivities [21].

$$\text{(2)}$$
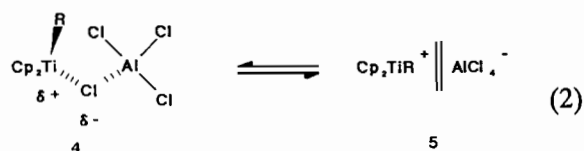
In light of the data presented for the reactions between $Hf(CH_2SiMe_3)_4$ and $AlMe_3$, it is useful to re-examine the other reported cases for ionic products (solvated cation–anion pairs) in alkyl exchange reactions between Group IVB alkyls and aluminum alkyls. The absence of solvated cation–anion pair products in reactions of $Zr(CH_2Ph)_4$ and $Al(CH_2Ph)_3$ seems to be well established by conductivity studies. The formation of a new compound is equally plausible based on the isolation of a red precipitate from the colorless reaction mixture. The absence of major changes in the NMR spectra (relative to the starting materials) of the product, however, precludes the definitive assignment of a structure for compound 3.

The presence of an intermediate in the degenerate exchange between $TiMe_4$ and $AlMe_3$ was based on the observation of new ^1H NMR resonances at 4.4 ppm (assigned to Me_3Ti^+) and -0.8 ppm ($AlMe_4^-$) with significant intensity ($>50\%$ of products) in hexane/diethyl ether solutions. The ^1H chemical shift of the $AlMe_4^-$ groups in both $[Fe(acac)(dmpe)_2^+][AlMe_4^-]$ and $[Co(2,2'\text{-bipy})_2Me_2^+][AlMe_4^-]$ were observed to be ~ 0.7–1.0 ppm upfield of $AlMe_3$ in CD_2Cl_2 (Table 2). ^1H NMR chemical shifts for alkali metal salts of $AlMe_4^-$ (e.g. $LiAlMe_4$) have been reported at ~ -0.8 ppm [2]. Comparison of the reported chemical shifts for $AlMe_4^-$ anions with the data in Table 2 for the compounds formed in reaction (1) (e.g. 2, -0.77 ppm and its triethylphosphine adduct), however, indicate that observation of an upfield shift in $AlMe_3$ resonances does not represent *conclusive* evidence for the presence of $AlMe_3R^-$ anions. Nevertheless, our results on the conductivity showed a significant (50-fold) increase in conductivity for $TiMe_4/AlMe_3$ mixtures in hexane/diethyl ether relative to solutions of either reactant, consistent with an 'ionic' or solvated cation–anion pair intermediate [1]. The evidence for solvated cation–anion pair intermediates in $Cp_2ZrMe_2/AlMe_3$ mixtures is more difficult to evaluate. The conductivity data in Table 1

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[1] Given that $TiMe_4$ is present in only 50% in the conductivity experiment, it is possible that the observed increase in conductivity is the result of reactions between $AlMe_3$ and other compounds present in solution.

are consistent with either a low concentration of such intermediates, the presence of contact ion pairs or the presence of solvent separated ion pair intermediates. While the reported spectroscopic evidence for the reaction of Cp_2ZrMe_2 with $AlMe_3$ does not allow for distinguishing between these possibilities, substitution of $B(C_6F_5)_3$ for $AlMe_3$ leads to the isolation of cationic $[Cp_2ZrMe^+][B(C_6F_5)_3Me^-]$. Clearly the ability of the Group III Lewis acid (e.g. $B(C_6F_5)_3$ or $AlCl_3$) to polarize the transition metal–alkyl bond plays a critical role in determining the nature of the intermediate in the reaction [22].

5. Conclusions

In conclusion, the observations presented in this paper on alkyl exchange reactions of aluminum alkyls with Group IVB alkyls suggest that the nature of the intermediates and/or products is highly dependent on the nature of the alkyl ligands on both the aluminum and the transition metal. In cases where alkyl exchange is observed and spectroscopically detected intermediates are also found to have increased conductivity (e.g. $TiMe_4/AlMe_3$), the formation of ionic intermediates appears most consistent with the data. In cases where significant concentrations of intermediates are observed yet neither alkyl exchange nor increased conductivity is observed (e.g. $Hf(CH_2SiMe_3)_4/AlMe_3$), the conclusions are less clear. In the absence of structural data beyond spectroscopic detection of thermally sensitive compounds, arguments for covalently bonded, heterobimetallic intermediates and contact ion pair formation must be considered.

Acknowledgements

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