

## Gas-phase chemistry of the dimethylaluminum oxide anion, $[(\text{CH}_3)_2\text{AlO}]^-$

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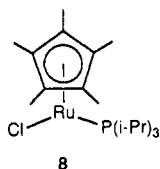
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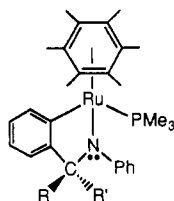
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diastereomer interconversion rates are half the phosphine exchange rates and must be multiplied by 2 to correspond to an elementary reaction step.

In principle, the intermediate may be planar (I), or it may be pyramidal (II)<sup>6</sup> with a low inversion barrier. Several observations bear upon this point. First, Brunner has studied the racemization (25–40 °C) of the optically active manganese complexes  $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{NO})(\text{PAR}_3)\text{-}(\text{X})$ ,<sup>11,12</sup> He finds  $\text{PAR}_3$  dissociation to be rate determining with  $\text{X} = \text{COOCH}_3$  but a preequilibrium step with  $\text{X} = \text{COC}_6\text{H}_5$ . The latter requires an intermediate that retains configuration, such as a pyramidal species of the type II. However, we have yet to acquire evidence for the intermediacy of the  $d^6$  16-valence-electron fragment  $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)]^+$  in substitution or isomerization reactions of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{L})]^+$  complexes.<sup>13</sup> Also, Tilley finds the  $d^6$  complex  $(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}(\text{Cl})(\text{P}(i\text{-Pr})_3)$  (8) to be nearly planar at ruthenium, with a short Ru–Cl



8



9

bond suggestive of chlorine-to-metal  $\pi$  bonding.<sup>14</sup> Indeed, the LUMO of a planar  $d^6$   $(\eta^5\text{-C}_5\text{R}_5)\text{M}(\text{L})(\text{L}')$  fragment is of appropriate symmetry for such overlap.<sup>6</sup> Finally, Brynzda and Bercaw have invoked the participation of amide ligand lone pairs to account for enhanced rates of phosphine dissociation in  $(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}(\text{PMe}_3)_2(\text{NRR}')$ .<sup>15</sup> They find a  $\Delta S^\ddagger$  range (9–12 eu) similar to ours. These  $\Delta S^\ddagger$  values are much lower than usual for phosphine dissociation<sup>15</sup> and suggest some type of bond making in the transition state. Hence, we propose that  $\text{PPh}_3$  dissociation from **2f** occurs with anchimeric assistance of the amide ligand lone pairs, leading directly to the planar, 18-valence-electron species I.

Boncella has recently reported the diastereospecific synthesis of ruthenium amide complexes **9** by addition of carbon nucleophiles to chelated imine complexes.<sup>16</sup> These compounds also epimerize by a phosphine dissociation mechanism. Finally, studies similar to those in Scheme I have established carbon epimerization in closely related compounds. These results, and attendant applications in catalysis, will be reported in the near future.<sup>2b</sup>

**Acknowledgment.** We thank the DOE for support of this research.

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## Gas-Phase Chemistry of the Dimethylaluminum Oxide Anion, $[(\text{CH}_3)_2\text{AlO}]^-$

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**Summary:** Flowing afterglow-selected ion flow tube technology (FA-SIFT) has been used to generate and select  $[(\text{CH}_3)_2\text{AlO}]^-$  (1), whose ion-molecule chemistry has been extensively studied. This ion reacts with several fluoroaromatics to give  $[(\text{CH}_3)_2\text{Al}(\text{F})\text{OH}]^-$ , which is formally an HF adduct of 1. Similarly,  $\text{H}_2\text{O}$ ,  $\text{HCl}$ ,  $\text{H}_2\text{S}$ , and  $\text{CH}_3\text{SH}$  formally add to 1 in reactions with carboxylic acids, chloro aromatics, thioacetic acid, and methyl disulfide, respectively. Finally, several smaller neutral molecules react to give products that are formulated as adducts.

Study of the chemistry of unusual ions derived from complex reaction mixtures has been made considerably easier by the introduction of tandem flowing afterglow-selected ion flow tube (FA-SIFT) technology.<sup>1</sup> We have recently used FA-SIFT to study a variety of important anions of silicon that are related to unsaturated carbon analogues. In particular, the chemistry of  $[\text{HCSi}]^-$ , related to silaacetylene,<sup>2</sup> of  $[\text{HSiO}]^-$ , related to silaformaldehyde,<sup>3</sup> and of  $[\text{RSiO}]^-$ , related to silaacetaldehyde and methyl silaformate<sup>4</sup> (with  $\text{R} = \text{CH}_3$  and  $\text{CH}_3\text{O}$ , respectively), has been studied. We now turn our attention to the gas-phase chemistry of organoaluminum compounds, whose importance as industrial catalysts is manifest and whose gas-phase ion-molecule chemistry is practically unexplored.<sup>5</sup> In this communication, we report our initial findings on  $[(\text{CH}_3)_2\text{AlO}]^-$  (1).

The reaction of  $\text{HO}^-$  with the trimethylaluminum dimer is carried out in the first flow tube and gives a mixture of anions consisting of 1 (80%),  $(\text{CH}_3)_2\text{AlCH}_2^-$  (15%), and  $[(\text{CH}_3)_3\text{AlOH}]^-$  (5%).<sup>6</sup> At the end of the flow tube, the neutral reactant and the helium carrier gas are removed and the ion of interest, in this case 1, is mass-selected by

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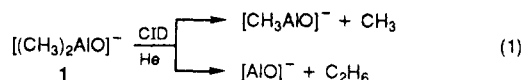
(3) Gronert, S.; O'Hair, R. A.; Prodnuk, S.; Sülzle, D.; Damrauer, R.; DePuy, C. H. *J. Am. Chem. Soc.* 1990, 112, 997.

(4) Damrauer, R.; Krempp, M. *Organometallics*, in press.

(5) (a) We are aware of only one published study of the ion-molecule chemistry of organoaluminum compounds, and that is a positive ion study: Kappes, M. M.; Uppal, J. S.; Staley, R. H. *Organometallics* 1982, 1, 1303. (b) In a recently published study, the negative ion-molecule chemistry of aluminum clusters has been reported: Hettich, R. L. *J. Am. Chem. Soc.* 1989, 111, 8582. (c) There have, of course, been a number of gas-phase structural studies of organoaluminum species. For example see: Almendinger, A.; Halvorsen, S.; Haaland, A. *Acta Chem. Scand.* 1971, 25 1937.

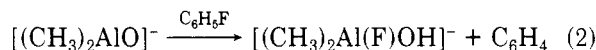
(6) Although the chemistry of ion 1 is consistent with an  $[(\text{CH}_3)_2\text{AlO}]^-$  rather than the isomeric  $[\text{CH}_3\text{Al}(\text{OH})\text{CH}_2]^-$  formulation, a reviewer has suggested that this structural assignment be considered in more detail. We have done so by preparing 1 from trimethylaluminum dimer and  $\text{DO}^-$  and find that there is no incorporation of deuterium, giving additional credence to our assignment. Strictly speaking, the yields given for the reaction of hydroxide and trimethylaluminum dimer result by injecting hydroxide into the second flow tube and determining the branching ratios as discussed in ref 10. When hydroxide and trimethylaluminum dimer are reacted in the first flow tube, several products, in addition to those given, result in the plasma.

a quadrupole mass filter and injected into a second flow tube, where its chemistry with a variety of neutral compounds is studied. Some ions, when injected with sufficient kinetic energy, undergo collisionally induced decomposition (CID).<sup>3</sup> For the case at hand,  $[(CH_3)_2AlO]^-$  can be cleanly injected at low kinetic energies but undergoes CID at higher energies (eq 1). The proton affinity of 1 and  $[AlO]^-$

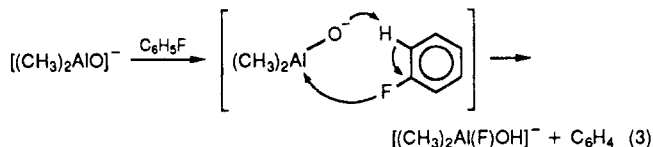


have been determined to be  $\Delta G^\circ_{acid} = 352.0$  and  $353.6$  kcal/mol, respectively; these represent the acidities of compounds  $(CH_3)_2AlOH$  and  $AlOH$ .<sup>7</sup>

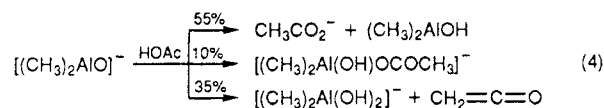
The aluminum oxide anion 1 undergoes several unusual gas-phase reactions, which presumably occur because of the ability of 1 to abstract a proton and of the neutral species to donate a lone-pair atom during reaction. Ion 1 reacts with fluorobenzene, pentafluorobenzene, and 2-fluoropyridine to give the aluminate  $[(CH_3)_2Al(F)OH]^-$ . This is the formal equivalent of the addition of HF to 1 with the concomitant loss of neutral benzyne, tetrafluorobenzene, and pyridyne, respectively (eq 2). Ion 1



is not sufficiently basic to abstract a proton from fluorobenzene ( $\Delta G^\circ_{acid} = 379.4$  kcal/mol), thus eliminating proton abstraction to initiate reaction 2. Rather, we suggest that a six-centered, concerted process occurs as shown in eq 3. Although little is known about bond



strengths in organoaluminum compounds, the very strong Al-F bond strength in  $AlF$  suggests that Al-F bond formation is sufficient to drive this reaction.<sup>8</sup> In an analogous example of a reaction driven in this case by the strong Al-O bond,<sup>8</sup> 1 reacts with acetic acid to give  $[(CH_3)_2Al(OH)_2]^-$  and ketene (eq 4) (among other products). Several

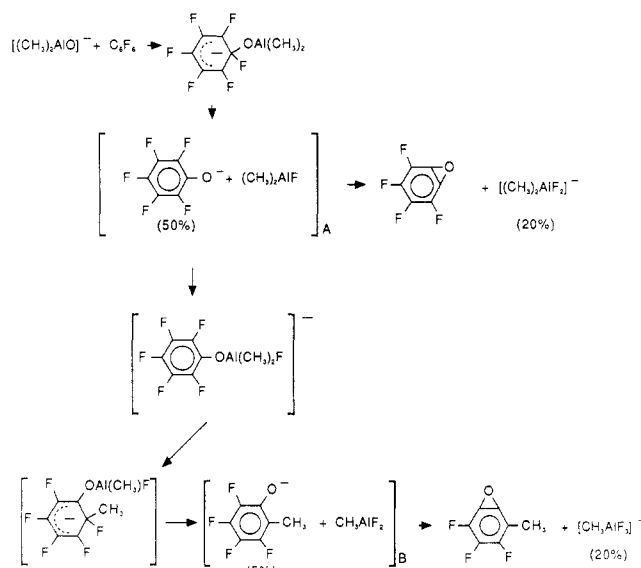


other reactions also lead to Al-O bond formation. In one other example,  $CH_3CO_2Si(CH_3)_3$  reacts, giving  $[(CH_3)_2Al(OH)OSi(CH_3)_3]^-$  and ketene. Each of these reactions can be viewed as a six-centered process like that shown in eq 3. Since the strengths of the Al-Cl and Al-O bonds are probably about the same,<sup>8</sup> chlorine analogues of these reactions might be expected to occur. This has been shown with chlorobenzene and 1,3-dichlorobenzene, which give

(7) (a) Gas-phase acidity is defined as the standard free energy change for  $HA \rightarrow H^+ + A^-$ , a weak acid corresponding to a large  $\Delta G_{acid}$  value. Bases are reacted with a series of reference acids, and the acidity corresponding to their conjugate acid is, thus, determined by the so-called bracketing technique. The anions under discussion here have been bracketed as follows: 1 between pyrrole (+) and hexamethyldisilazane (-) and  $[AlO]^-$  between hexamethyldisilazane (+) and trifluoroethanol (-). The plus sign (+) corresponds to the formation of the M - 1 ion and the minus sign to no M - 1 formation. (b) All reference acidities are taken from: Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data, Suppl.* **1988**, *17*(1).

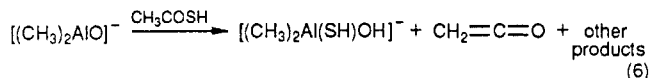
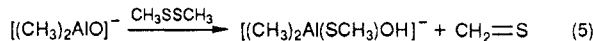
(8) Estimates of the relative bond strengths of Al-X bonds are based on reported data on the corresponding diatomic species  $Al-F \approx 160$  kcal/mol,  $Al-O \approx 120$  kcal/mol,  $Al-Cl \approx 120$  kcal/mol, and  $Al-S \approx 87$  kcal/mol from: Chase, M. W., Jr.; Davies, C. A.; Downey, J. R., Jr.; Frurip, D. J.; McDonald, R. A.; Syverud, A. N. *J. Phys. Chem. Ref. Data, Suppl.* **1985**, *14*(1).

Scheme I. Mechanism of the Reaction of 1 and Hexafluorobenzene



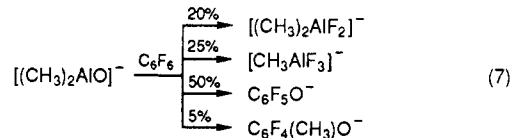
$[(CH_3)_2Al(Cl)OH]^-$  and the corresponding benzyne, and by acetyl chloride and vinyl chloride, which give  $[(C-H_3)_2Al(Cl)OH]^-$  and ketene and acetylene, respectively.<sup>9</sup>

Several other reactions are similar in that they involve the formal abstraction of a proton and the addition of a nucleophile to 1 along with the extrusion of a small, neutral molecule. For example, 1 reacts with methyl disulfide to give  $[(CH_3)_2Al(SCH_3)OH]^-$  and thioformaldehyde<sup>9</sup> and with thioacetic acid to give  $[(CH_3)_2Al(SH)OH]^-$  and the M - 1 ion of thioacetic acid (eqs 5 and 6). The Al-S



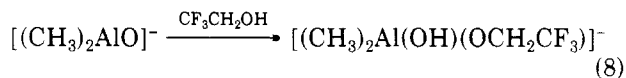
single-bond driving force is not expected to be nearly as strong as that for fluorine, oxygen, or chlorine.<sup>8</sup> A cyclic extrusion mechanism like that in eq 3 explains the two aluminate products shown in eqs 5 and 6.

When 1 reacts with hexafluorobenzene, which cannot lose HF, several interesting products result (eq 7). These



products are formed in a complex series of reactions that are initiated by ipso attack of 1 on hexafluorobenzene (Scheme I).<sup>10</sup>

Ion 1 also reveals a rich chemistry with a wide variety of other neutral species. Among these are  $H_2O$ ,  $NH_3$ ,  $CH_3OD$ ,  $CF_3CH_2OH$ , and  $t-BuSH$ . Each gives a 1:1 product that can be formulated as either a cluster ion or an aluminate adduct (illustrated for  $CF_3CH_2OH$  in eq 8).



(9) The possibility that the reaction with acetyl chloride as well as that with methyl disulfide (eq 5) might have been caused by HCl and  $CH_3SH$  impurities, respectively, is unlikely since these neutral starting materials have been distilled and degassed before their reactivity with 1 was studied.

(10) Branching ratios were determined as a function of reaction distance and are reported as extrapolations to zero reaction distance to eliminate any effects of secondary reactions.

In view of the chemistry just presented in eqs 2-7, these aluminate adducts could form by proton abstraction and nucleophilic attack through a four-centered transition state. It is, of course, also possible that these processes occur by stepwise, noncyclic pathways. Finally, both OCS and CS<sub>2</sub> react with 1 to give [(CH<sub>3</sub>)<sub>2</sub>AlS]<sup>-</sup>. The reactions with OCS and CS<sub>2</sub> are similar to those between these neutral species and [(CH<sub>3</sub>)<sub>3</sub>SiO]<sup>-</sup>.<sup>11,12</sup>

Additional studies of 1 and related ions are in progress.

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(12) The reaction rates of 1 and [(CH<sub>3</sub>)<sub>3</sub>SiO]<sup>-</sup> with CS<sub>2</sub> are 5.8 × 10<sup>-10</sup> and 1.4 × 10<sup>-10</sup> cm<sup>3</sup> (molecule)<sup>-1</sup> s<sup>-1</sup>, respectively; with OCS the rates are 9.6 × 10<sup>-10</sup> and 6.5 × 10<sup>-10</sup> cm<sup>3</sup> (molecule)<sup>-1</sup> s<sup>-1</sup>, respectively. The corresponding reaction efficiencies are 0.53, 0.13, 0.88, and 0.62.

### Lithium-Tellurium Exchange Reaction. A Convenient Method for Generation of Heteroatom-Substituted Methylolithiums

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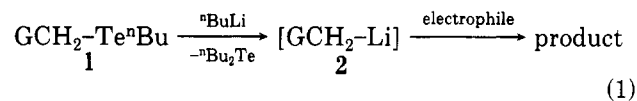
**Summary:** A variety of heteroatom-substituted methylolithiums (GCH<sub>2</sub>Li; G = MeOCH<sub>2</sub>CH<sub>2</sub>O-, PhCH<sub>2</sub>O-, Me<sub>2</sub>N-, Me<sub>3</sub>Si-, Me<sub>3</sub>Ge-, <sup>n</sup>Bu<sub>3</sub>Sn-, <sup>n</sup>BuTe-) were generated by the lithium-tellurium exchange reaction of corresponding tellurides with butyllithium and were trapped with electrophiles. The potent utility of bis(butyltelluro)methane as a methylene dianion synthon was demonstrated, where both of the butyltelluro groups were displaced stepwise by different electrophiles with use of this metalation/trapping sequence repeated twice.

Heteroatom-substituted organolithium compounds<sup>1</sup> are very useful reagents for construction of carbon skeletons with coincidental introduction of functional groups. As for the generation of these organolithiums, a lithium-tin exchange reaction has been frequently employed when a conventional hydrogen abstraction or lithium-halogen exchange reaction cannot be applied. Recently, we have demonstrated that diorganyl tellurides undergo rapid transmetalation by the reaction with alkylolithiums to give thermodynamically more stable organolithium compounds.<sup>2</sup> These successful results led us to attempt the

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formation of heteroatom-substituted methylolithiums 2 such as (alkoxymethyl)-,<sup>3</sup> (aminomethyl)-,<sup>4</sup> (silylmethyl)-,<sup>5</sup> (germylmethyl)-,<sup>6</sup> (stannylmethyl)-,<sup>7</sup> and (telluro-methyl)lithiums<sup>8</sup> via lithium-tellurium exchange reactions.



a, G = OCH<sub>2</sub>CH<sub>2</sub>OMe; b, G = OCH<sub>2</sub>Ph; c, G = NMe<sub>2</sub>; d, G = SiMe<sub>3</sub>; e, G = Te<sup>n</sup>Bu; f, G = Sn<sup>n</sup>Bu<sub>3</sub>

When butyllithium was added to the THF solution of butyl (2-methoxyethoxy)methyl telluride (1a)<sup>9</sup> at -78 °C, lithium-tellurium exchange proceeded efficiently to give the corresponding (alkoxymethyl)lithium 2a. Addition of benzaldehyde to the resulting mixture followed by the usual workup gave the  $\beta$ -alkoxy alcohol 3 in 70% yield together with 76% of dibutyl telluride (run 1 in Table I). In Table I are summarized the results of the generation of several heteroatom-substituted methylolithiums that were trapped with various electrophiles.<sup>10</sup> It should be noted that this lithium-tellurium exchange reaction proceeded satisfactorily in a variety of solvents, such as Et<sub>2</sub>O, toluene, and hexane (runs 2-4). This is in marked contrast to the lithium-tin exchange reaction, which is sluggish in solvents of low polarity.<sup>11</sup> In the formation of

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(8) Seebach, D.; Beck, A. K. *Chem. Ber.* 1975, 108, 314.

(9) Tellurides were prepared as follows: 1a-e from lithium butane-telluroate and (2-methoxyethoxy)methyl chloride, benzyl chloromethyl ether, dimethylmethyleammonium chloride, (trimethylsilyl)methyl iodide, and dichloromethane, respectively, in THF; 1f, according to the procedure depicted in eq 2 (run 15 in Table I).

(10) A typical reaction is as follows (run 1 in Table I): Into a solution of 1a (1.0 mmol, 274 mg) in THF (5 mL) was added a 1.6 M hexane solution of butyllithium (1.0 mmol, 0.63 mL) at -78 °C. After 15 min, benzaldehyde (1.1 mmol, 117 mg) was added in one portion. The reaction mixture was warmed to 25 °C over a period of 1 h and then poured into a saturated aqueous NH<sub>4</sub>Cl (30 mL) solution. The product was extracted with Et<sub>2</sub>O (30 mL × 3) and dried over MgSO<sub>4</sub>. Analysis of the mixture with GLC showed the formation of 3 in 86% yield. Subsequent radial layer chromatography on silica gel provided 137 mg (0.70 mmol, 70%) of 3 together with 183 mg (0.76 mmol, 76%) of dibutyl telluride. Runs 2-14 in Table I were carried out under identical conditions unless otherwise stated. The Li-Te exchange reaction proceeds very quickly and is complete within 15 min at -78 °C in THF and in ether. Only small amounts of the starting telluride (1a) remained unreacted in toluene (5%, run 3) and in hexane (12%, run 4). The yield of adduct 3 was not improved even when the exchange reaction was conducted for 1 h in hexane (see run 4).

(11) Seyferth, D.; Weiner, M. A. *J. Am. Chem. Soc.* 1962, 84, 361.