

Mechanism of equilibration of diastereomeric rhenium amide complexes of the formula $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{NHCHR}'):$ rhenium versus carbon epimerization

Michael A. Dewey, and J. A. Gladysz

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Reactions of (+)-(SS)- and (+)-(SR)-**1f** with $(\text{CH}_3\text{CH}_2)_4\text{N}^+\text{CN}^-$ as above gave the optically active cyanide complex (+)-(S)-**5**, with $[\alpha]_{589}^{25} = 183 \pm 3^\circ$.¹⁵ The absolute configuration, corresponding to retention at rhenium, was assigned as above. Importantly, (+)-Eu(hfc)₃ analysis showed the (+)-(S)-**5** to be of >98% ee, thus bounding the optical purities of (+)-(SS)- and (+)-(SR)-**1f**.

We have previously shown that secondary phosphine complexes $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{PHRR}')]\text{X}^-$ can be deprotonated to the corresponding phosphido complexes $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{PRR}')$.¹⁶ Accordingly, amine complexes **1a,c**, (+)-(SS)-**1f**, and (+)-(SR)-**1f** were treated with *n*-BuLi (1.0 equiv) in THF at -80°C (Scheme II). Amide complexes $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{NRR}')$ (**2a,c**, (SS)-**2f**, (SR)-**2f**) formed in quantitative yields, as assayed by ³¹P NMR spectroscopy. Solvent evaporation gave spectroscopically pure powders that contained the by-product LiOTf. Further purification attempts gave decomposition. Amine complex deprotonation could also be effected with freshly sublimed $\text{K}^+(t\text{-BuO}^-)$.

Complexes **2a,c,f** were characterized by IR and NMR spectroscopy.¹¹ The nitrogen substituents in symmetrically substituted **2a,c** generally gave a single set of NMR resonances. However, **2c** exhibited two methyl ¹H NMR resonances in $\text{CD}_2\text{Cl}_2/\text{THF}-d_8$ at -115°C . These coalesced at -105°C ($\Delta G^\ddagger_{\text{TC}} = 7.8$ kcal/mol). For a pyramidal -NR_2 moiety, both nitrogen inversion and Re-N bond rotation are required to render the substituents equivalent.^{16,17} Hence, 7.8 kcal/mol is an upper limit on any nitrogen inversion barrier. Thus, nitrogen-derived diastereomers of the unsymmetrically substituted complexes **2b,e,f** should not be observable under normal NMR conditions.

Chemical properties of the amide complexes **2** were briefly probed. First, **2a,c** and (SR)-**2f** reacted with 1.0 equiv of $(\text{CH}_3\text{CH}_2)_3\text{NH}^+\text{TfO}^-$ within 5 min in THF at -80°C . Amine complexes **1a,c** and (+)-(SR)-**1f** formed quantitatively, as assayed by ³¹P NMR spectroscopy (Scheme II). Hence, the $\text{-NRR}'$ nitrogens in **2** are considerably more basic than those in organic amines. Second, **2a** and $(\text{CH}_3)_3\text{SiCH}_2\text{OTf}$ (1.2 equiv) rapidly reacted in THF at -60°C to give the amine complex $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{NH}_2\text{CH}_2\text{Si}(\text{CH}_3)_3)]^+\text{TfO}^-$ (**1g**; 62% after workup; Scheme II). Thus, the $\text{-NRR}'$ nitrogens in **2** are also highly nucleophilic.

In summary, this study has established that (1) the title compounds are readily available in both racemic and optically active forms and (2) the chemical properties of both classes of compounds are influenced by the high basicity and nucleophilicity of the amide nitrogen in **2**. Many useful applications of these compounds are readily envisioned (e.g., precursors to imine complexes, chiral LiNRR' bases, mechanism probes) and will be reported in due course.

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Supplementary Material Available: Tables of spectroscopic data for **1a-g** and **2a,c,f** and analytical data for **1a-g** (7 pages). Ordering information is given on any current masthead page.

(16) Buhro, W. E.; Zwick, B. D.; Georgiou, S.; Hutchinson, J. P.; Gladysz, J. A. *J. Am. Chem. Soc.* **1988**, *110*, 2427.

(17) Amide ligand nitrogens are generally planar: Lappert, M. F.; Power, P. P.; Sanger, A. R.; Srivastava, R. C. *Metal and Metalloid Amides*; Wiley: New York, 1980. However, structurally characterized complexes that would be good models for **2** (e.g., $d^6(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{L})(\text{L}')(\text{NR}_2)$) are lacking.

Mechanism of Equilibration of Diastereomeric Rhenium Amide Complexes of the Formula $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{NHCHRR}')$: Rhenium vs Carbon Epimerization

Michael A. Dewey and J. A. Gladysz*

Department of Chemistry, University of Utah
Salt Lake City, Utah 84112

Received January 16, 1990

Summary: Amide complexes (SR)- and (SS)- $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{NHCH}(\text{CH}_3)\text{C}_6\text{H}_5)$ epimerize at rhenium ($32\text{--}60^\circ\text{C}$) by a mechanism involving initial and rate-determining PPh_3 dissociation. Anchimeric assistance of the amide ligand lone pair and an intermediate with a planar, trigonal rhenium are proposed.

In studying the addition of nucleophiles to chiral imine complexes $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\eta^1\text{-RN}=\text{CHR}')]\text{X}^-$, we found that the products, amide complexes $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{NRCH}(\text{R}')\text{Nu})$, sometimes underwent epimerization slightly above room temperature.¹ Similar behavior has been noted in the related alkoxide complexes $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{OCHR}')^2$. In theory, these epimerizations could occur at rhenium or carbon. Either event would be of considerable interest. For example, while a carbon-based epimerization would complicate the application of these reactions in asymmetric organic synthesis, it would represent an unusual and potentially exploitable type of C-H bond activation. Thus, we sought to probe the mechanisms of these configurational processes.

Accordingly, the diastereomeric optically active amine complexes (+)-(SR)- and (+)-(SS)- $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{NH}_2\text{CH}(\text{CH}_3)\text{C}_6\text{H}_5)]^+\text{TfO}^-$ ((+)-(SR)- and (+)-(SS)-**1f**, $\text{TfO}^- = \text{triflate}$)³ were converted to the corresponding amide complexes (SR)- and (SS)- $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{NHCH}(\text{CH}_3)\text{C}_6\text{H}_5)$ ((SR)- and (SS)-**2f**), as described in the preceding paper (Scheme I).⁴ The solvents were replaced by $\text{THF}-d_8$, and ¹H NMR analyses (C_5H_5 resonances) showed that each amide complex was of >98% de.⁵

Next, a $\text{THF}-d_8$ solution of (SR)-**2f** was kept at 60°C . Epimerization occurred over the course of 2.5 h to give a $(30 \pm 2):(70 \pm 2)$ mixture of diastereomers, with the *new* diastereomer predominating (see Scheme I). An identical reaction was conducted with (SS)-**2f**. Epimerization occurred to give a $(70 \pm 2):(30 \pm 2)$ mixture of diastereomers, with the *original* diastereomer predominating. These experiments establish that (SS)-**2f** is slightly more stable than (SR)-**2f** ($K_{\text{eq}} = 2.3$) and that the pyramidal rhenium fragment⁶ $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)]^+$ exhibits a moderate degree of chiral recognition in binding enantiomers of the $\text{-NHCH}(\text{CH}_3)\text{C}_6\text{H}_5$ fragment.

(1) Dewey, M. A. Unpublished results, University of Utah.

(2) (a) Dalton, D. M.; Gladysz, J. A. *J. Organomet. Chem.* **1989**, *370*, C17. (b) Saura-Llamas, I.; Garner, C. M.; Gladysz, J. A. Manuscript in preparation.

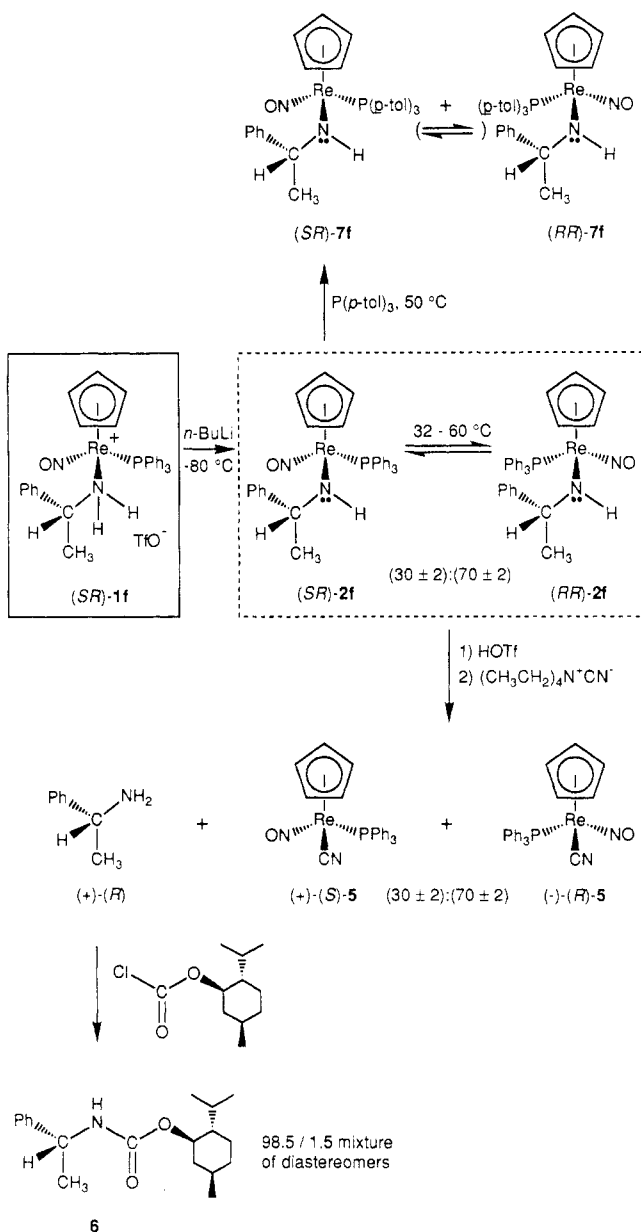
(3) In all diastereomeric compounds, the rhenium configuration is specified first, by *R/S* conventions described previously: Fernández, J. M.; Gladysz, J. A. *Organometallics* **1989**, *8*, 207.

(4) Dewey, M. A.; Bakke, J. M.; Gladysz, J. A. *Organometallics*, preceding paper in this issue.

(5) Distinguishing NMR features of (SR)- and (SS)-**2f** ($\text{THF}-d_8$):⁴ ¹H (δ), 5.16/5.06 (s, C_5H_5), 3.97/4.10 (dq, CH), 1.04/1.14 (d, NH); ³¹P (ppm), 27.37/28.08 (s).

(6) Theory predicts pyramidal ground states for $d^6(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{L})(\text{L}')$ fragments: Hoffmann, P. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 536.

Scheme I. Epimerization and Substitution Reactions of Amide Complex
(*SR*)-(η⁵-C₅H₅)Re(NO)(PPh₃)(NHCH(CH₃)C₆H₅) ((*SR*)-2f)

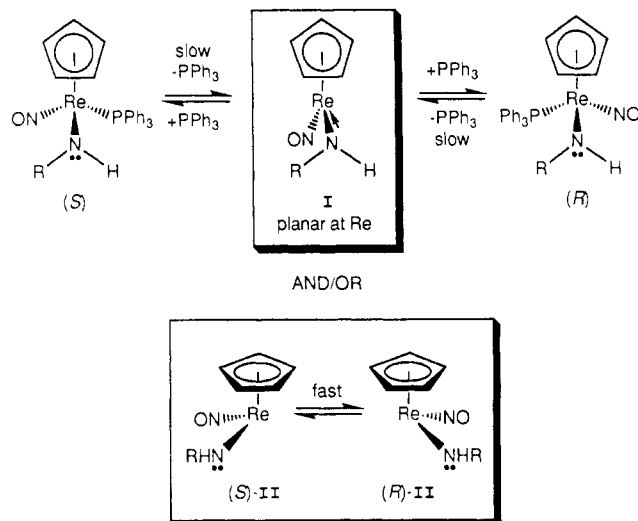


The site of epimerization was assayed. First, the mixture derived from (*SR*)-2f was treated with TfOH (-80 °C) to give the amine complex 1f (Scheme I). Subsequent addition of (CH₃CH₂)₄N⁺CN⁻ gave the cyanide complex (η⁵-C₅H₅)Re(NO)(PPh₃)(CN) (5; 65%, [α]₅₈₉²⁵ = -67 ± 1°), a reaction that occurs with retention of configuration at rhenium.⁴ Polarimetric and (+)-Eu(hfc)₃ analysis showed 5 to be a (30 ± 2):(70 ± 2) mixture of (+)-(*S*)/(-)-(*R*) enantiomers. Thus, epimerization of (*SR*)-2f occurs via inversion of configuration at rhenium to give (*RR*)-2f. An identical analysis of the epimerization of (*SS*)-2f gave analogous results.

As a check, carbon configurations were also assayed. Hence, the α-methylbenzylamine formed in the cyanide displacement was isolated (53%) and derivatized with excess (-)-menthyl chloroformate. Capillary GC analysis of the resulting urethane 6 (Scheme I)⁷ showed a 98.5:1.5

(7) Westley, J. W.; Halpern, B. *J. Org. Chem.* 1968, 33, 3978.

Scheme II. Proposed Mechanism for Amide Complex Epimerization



mixture of diastereomers, indicative of little or no epimerization at carbon. An identical analysis of the α-methylbenzylamine derived from epimerized (*SS*)-2f gave analogous results.

The epimerizations were repeated at 49.4 °C, and rates were measured by ¹H NMR spectroscopy. Standard data workup⁸ gave $k_1 = (2.34 \pm 0.12) \times 10^{-4} \text{ s}^{-1}$ and $k_{-1} = (0.90 \pm 0.09) \times 10^{-4} \text{ s}^{-1}$ for conversion of (*SR*)-2f to (*RR*)-2f and $k_1 = (0.90 \pm 0.19) \times 10^{-4} \text{ s}^{-1}$ and $k_{-1} = (2.30 \pm 0.49) \times 10^{-4} \text{ s}^{-1}$ for conversion of (*SS*)-2f to (*RS*)-2f. As expected, the k_1 value of each reaction matched the k_{-1} value of the other. Analogous rate experiments were conducted with (*SR*)-2f at 32.3, 40.4, and 59.1 °C.⁹

Other aspects of these reactions were probed. First, (*SR*)-2f was treated with excess P(*p*-tol)₃ (tol = tolyl) in THF-*d*₈ at 49.4 °C (Scheme I). The amide complex no longer epimerized but was instead converted to a (50 ± 2):(50 ± 2) mixture (at <1 *t*_{1/2}) of diastereomers of (η⁵-C₅H₅)Re(NO)(P(*p*-tol)₃)(NHCH(CH₃)C₆H₅) (7f). With time, 7f independently epimerized. An authentic sample of 7f (racemic mixture of diastereomers) was prepared by a reaction sequence analogous to that used to obtain 2f.⁴ The k_{obs} value for the conversion of (*SR*)-2f to 7f, $(4.6 \pm 0.6) \times 10^{-4} \text{ s}^{-1}$, was twice that of k_1 for the conversion of (*SR*)-2f to (*RR*)-2f. Finally, the k_1 and k_{-1} values⁹ for the latter reaction were multiplied by 2. Eyring plots gave $\Delta H^\ddagger = 26 \pm 1 \text{ kcal/mol}$ and $\Delta S^\ddagger = 6 \pm 3 \text{ eu}$ for the forward direction and $\Delta H^\ddagger = 28 \pm 1 \text{ kcal/mol}$ and $\Delta S^\ddagger = 11 \pm 3 \text{ eu}$ for the reverse.

The preceding data are best modeled by a mechanism involving initial and rate-determining PPh₃ dissociation from the amide complexes 2f (Scheme II). In the presence of excess P(*p*-tol)₃, the resulting intermediate is efficiently scavenged to give 7f. In the absence of a trap, the intermediate partitions equally¹⁰ between returning to the original diastereomer and forming a new diastereomer. Thus,

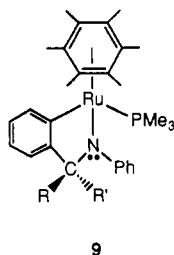
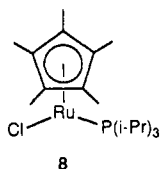
(8) Capellos, C.; Bielski, B. H. *Kinetic Systems*; Wiley: New York, 1972; Chapter 8.

(9) Rate data: 32.3 °C $k_1 = (0.23 \pm 0.02) \times 10^{-4} \text{ s}^{-1}$, $k_{-1} = (0.82 \pm 0.08) \times 10^{-5} \text{ s}^{-1}$; 40.4 °C: $k_1 = (0.77 \pm 0.04) \times 10^{-4} \text{ s}^{-1}$, $k_{-1} = (2.7 \pm 0.3) \times 10^{-5} \text{ s}^{-1}$; 59.1 °C $k_1 = (7.9 \pm 0.4) \times 10^{-4} \text{ s}^{-1}$, $k_{-1} = (39 \pm 0.4) \times 10^{-5} \text{ s}^{-1}$. In all cases, (30 ± 2):(70 ± 2) diastereomer ratios were obtained. Thus, K_{eq} is not strongly dependent upon temperature.

(10) The transition states leading from I or II to diastereomers of 2f in theory differ in energy. However, the initial formation of 50:50 mixtures of diastereomers of 7f indicates that the energies are comparable.

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)⁶ 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 ($\eta^5\text{-C}_5\text{H}_5$)Mn(NO)(PAr₃)(X),^{11,12} He finds PAr₃ dissociation to be rate determining with X = COOCH₃ but a preequilibrium step with X = COC₆H₅. 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 d⁶ 16-valence-electron fragment [$\eta^5\text{-C}_5\text{H}_5$]Re(NO)(PPh₃)⁺ in substitution or isomerization reactions of [$\eta^5\text{-C}_5\text{H}_5$]Re(NO)(PPh₃)(L)⁺ complexes.¹³ Also, Tilley finds the d⁶ complex ($\eta^5\text{-C}_5\text{Me}_5$)Ru(Cl)(P(*i*-Pr)₃) (8) to be nearly planar at ruthenium, with a short Ru–Cl



bond suggestive of chlorine-to-metal π bonding.¹⁴ Indeed, the LUMO of a planar d⁶ ($\eta^5\text{-C}_5\text{R}_5$)M(L)(L') fragment is of appropriate symmetry for such overlap.⁶ Finally, Brynzda and Bercaw have invoked the participation of amide ligand lone pairs to account for enhanced rates of phosphine dissociation in ($\eta^5\text{-C}_5\text{Me}_5$)Ru(PMe₃)₂(NRR').¹⁵ They find a ΔS^\ddagger range (9–12 eu) similar to ours. These ΔS^\ddagger values are much lower than usual for phosphine dissociation¹⁵ and suggest some type of bond making in the transition state. Hence, we propose that PPh₃ 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.¹⁶ 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.^{2b}

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

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(12) (a) Brunner, H.; Aclasis, J.; Langer, M.; Steger, W. *Angew. Chem., Int. Ed. Engl.* 1974, 13, 810. (b) Brunner, H.; Schindler, H.-D. *Z. Naturforsch.* 1971, 26B, 1220. (c) Brunner, H.; Langer, M. *J. Organomet. Chem.* 1975, 87, 223. (d) Brunner, H.; Aclasis, J. A. *Ibid.* 1976, 104, 347. (e) Brunner, H.; Steger, W. *Ibid.* 1976, 120, 239. (f) Brunner, H.; Fisch, K.; Jones, P. G.; Salbeck, J. *Angew. Chem., Int. Ed. Engl.* 1989, 28, 1521.

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(16) Martin, G. C.; Boncella, J. M. *Organometallics* 1989, 8, 2968.

Gas-Phase Chemistry of the Dimethylaluminum Oxide Anion, [(CH₃)₂AlO]⁻

R. Damrauer* and M. Krempp

Department of Chemistry
University of Colorado at Denver
Denver, Colorado 80204

Received January 12, 1990

Summary: Flowing afterglow-selected ion flow tube technology (FA-SIFT) has been used to generate and select [(CH₃)₂AlO]⁻ (1), whose ion-molecule chemistry has been extensively studied. This ion reacts with several fluoroaromatics to give [(CH₃)₂Al(F)OH]⁻, which is formally an HF adduct of 1. Similarly, H₂O, HCl, H₂S, and CH₃SH formally add to 1 in reactions with carboxylic acids, chloro aromatics, thiolacetic 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.¹ 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 [HCSi]⁻, related to silaacetylene,² of [HSiO]⁻, related to silaformaldehyde,³ and of [RSiO]⁻, related to silaacetaldehyde and methyl silaformate⁴ (with R = CH₃ and CH₃O, 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.⁵ In this communication, we report our initial findings on [(CH₃)₂AlO]⁻ (1).

The reaction of HO⁻ with the trimethylaluminum dimer is carried out in the first flow tube and gives a mixture of anions consisting of 1 (80%), (CH₃)₂AlCH₂⁻ (15%), and [(CH₃)₃AlOH]⁻ (5%).⁶ 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

(1) (a) Van Doren, J. M.; Barlow, S. E.; DePuy, C. H.; Bierbaum, V. M. *Int. J. Mass Spectrom. Ion Processes* 1987, 81, 85. (b) For initial observations of collisional activation in a SIFT instrument, see: Henchman, M.; Viggiano, A. A.; Paulson, J. F.; Freedman, A.; Worhouth, J. J. *Am. Chem. Soc.* 1985, 107, 1453.

(2) Damrauer, R.; DePuy, C. H.; Barlow, S. E.; Gronert, S. *J. Am. Chem. Soc.* 1988, 110, 2005.

(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 [(CH₃)₂AlO]⁻ rather than the isomeric [CH₃Al(OH)CH₂]⁻ 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 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.