$$[Co_2(CO)NO]^{+*} \xrightarrow{CA} \begin{cases} Co_2NO^+ + CO & (5) \\ Co_2N^+ + CO_2 & (6) \end{cases}$$

carbonyls as the only fragmentation processes.[16] Formation of Co_2N^+, process 6, may also proceed by successive elimination of CO and O. The direct elimination of CO_2 from activated $Co_2(CO)NO^+$ was confirmed by directly observing the dissocation of Co_2NO^+, formed in process 5, where facile elimination of nitrosyl was the only process observed, reaction 7. The formation

$$[Co_2NO]^{+*} \xrightarrow{CA} Co_2^+ + NO \qquad (7)$$

of transition-metal cluster nitrides from transition-metal cluster-nitrosyl-carbonyl complexes is found to be facile for large saturated or nearly saturated species.[2a] Collisional activation of $Co_2(CO)_2NO^+$ yields initial loss of a carbonyl followed by either elimination of CO or CO_2, vide supra.

Co_2NO^+ reacts with CO yielding Co_2N^+ exclusively, process 8, with linear first-order kinetics giving a rate constant of 3.3 ±

$$Co_2NO^+ + CO \rightarrow Co_2N^+ + CO_2 \qquad (8)$$

0.7×10^{-11} cm^3 molecule^{-1} s^{-1}. Comparison with the corresponding collision rate of 6.9×10^{-10} cm^3 molecule^{-1} s^{-1} indicates that decarboxylation occurs on only one of every 21 collisions.[17] In addition $Co_2(CO)NO^+$ is unreactive with CO in accord with the collisional activation results for $Co_2(CO)_2NO^+$. This slow rate of decarboxylation, process 8, is surprising since it is competitive with direct CO elimination for collisional activation of $Co_2(CO)NO^+$ at low collision energy, Figure 1. These results suggest a kinetic barrier for oxygen transfer to CO from Co_2NO^+ which may result from spin restrictions in the intermediate complex.[18] Such a kinetic barrier has previously been inferred for the absence of oxygen abstraction from N_2O by both atomic[19] and small bare transition-metal cluster ions,[20] and this barrier was attributed to spin multiplicity differences. It appears that $Co_2(CO)NO^+$ has achieved an electronic configuration favorable for oxygen transfer to CO prior to collisional activation. Finally, observation of reaction 8 implies $D°(Co_2N^+–O) < 127.2$ cal/mol.[21] For comparison $D°(N–O) = 151$ kcal/mol[21] and $D°(Co_2^+–O) > 119$ kcal/mol.[20] In contrast to the above results collisional activation of $Co_3(CO)NO^+$ yields exclusively loss of CO as its primary fragmentation with *no* Co_3N^+ formation observed. In addition Co_3NO^+ is unreactive with carbon monoxide. The inert behavior of $Co_2(CO)NO^+$ and Co_3NO^+ with CO clearly shows that both the degree of saturation as well as cluster size are critical for NO activation.

The mechanism of the above oxygen transfer is unclear at this time. Since only the highly unsaturated dimeric species participates suggests that dissociation of NO forming an oxide-nitrido species may precede oxygen transfer to CO. This is supported by the observation that nitric oxide generally dissociates on clean metal surfaces at low coverages while at higher coverages molecular absorption becomes more favorable.[22] In addition stable oxide-nitrido clusters have recently been characterized.[8,23] We are currently attempting to determine if dissociation of NO precedes oxide transfer for $Co_2(CO)NO^+$.

The above results demonstrate that unsaturated metal cluster nitrosyls exhibit a rich and varied chemistry compared with their corresponding binary carbonyl systems. Clearly additional work in this area should yield equally exciting results.

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Organometallic Coordination Chemistry of Aluminum. Synthesis and Molecular Structure of $[Al(CH_3)]_2[C_8H_{20}N_6][Al(CH_3)_2]_2$: A Novel Example of a Neutral Organoaluminum Complex Containing Two Five-Coordinate Aluminum Atoms in Square Pyramidal Environments

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The reaction of aluminum alkyls with amines is perhaps one of the most celebrated reactions in organoaluminum chemistry. Investigations may be traced to 1930 when Krause and Dittmar[1] reported the synthesis of $(H_3N)Al(p\text{-tolyl})_3$ and $(H_3N)Al(Ph)_3$. In terms of contemporary organoaluminum chemistry, the most definitive work in the area has concerned poly(*N*-alkyliminoalanes)[2-16] and aluminum–nitrogen oligomers.[17-25] The coordination

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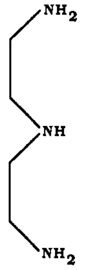

Figure 1. Diethylenetriamine.

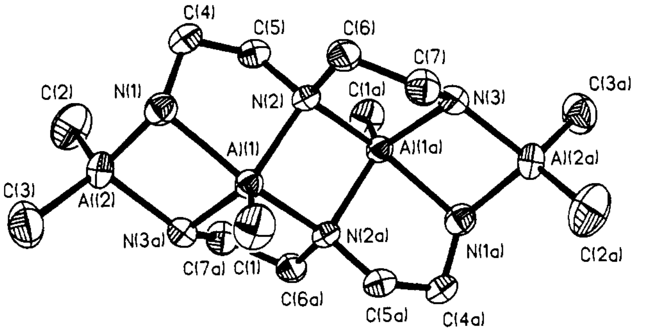

Figure 2. A view of the $[Al(CH_3)]_2[C_8H_{20}N_6][Al(CH_3)_2]_2$ molecule showing the atom labeling scheme. Thermal ellipsoids show 50% probability levels; hydrogen atoms have been omitted.

of the aluminum atoms in all of the aforementioned organoaluminum complexes may be described as four-coordinate tetrahedral. Indeed, such is the predominant coordination geometry of aluminum throughout organometallic chemistry. Herein, we report the synthesis[26] and structure of $[Al(CH_3)]_2[C_8H_{20}N_6][Al(CH_3)_2]_2$ isolated from the reaction of an excess of trimethylaluminum with diethylenetriamine (Figure 1). Surprisingly, two of the four aluminum atoms in the title compound are five-coordinate. Furthermore, the environment of these two aluminum atoms is square pyramidal. This represents the first report of an organometallic complex containing aluminum atoms in such an environment. The X-ray crystal structure of $[Al(CH_3)]_2[C_8H_{20}N_6][Al(CH_3)_2]_2$ is shown in Figure 2.

X-ray intensity data were collected on a Nicolet R3m/V diffractometer by using an ω-scan technique with Mo Kα radiation (λ = 0.71073 Å) at 26 °C. The title compound crystallizes in the monoclinic space group $C2/c$ with unit cell parameters a = 21.110 (1) Å, b = 8.499 (4) Å, c = 13.635 (8) Å, β = 115.19 (4)°, V = 2213.83 Å^3 and D_{calcd} = 1.20 g cm^{-3} for $Z = 4$. Least-squares refinement based on 1229 observed reflections with intensities $I > 3\sigma(I)$ in the range $2.0° \leq 2\theta \leq 45.0°$ converged at $R = 0.041$ ($R_w = 0.045$). Anisotropic thermal parameters were used for all non-hydrogen atoms. Hydrogen atoms, located from difference Fourier maps, were placed in idealized positions with fixed isotropic temperature factors.

Smith and co-workers[17] reported that reaction temperature played a pivotal role in determining the nature of the reaction products when aluminum alkyls react with amines. It was further noted that primary and secondary amines react with aluminum alkyls at low temperatures forming 1:1 addition compounds ($(H_3N)AlR_3$). However, at significantly higher temperatures alkane was released due to cleavage of N–H and Al–R bonds, resulting in reaction products possessing Al_2N_2 fragments. Such reactions were characteristically referred to as intermolecular condensations. A plethora of interesting organoaluminum compounds were subsequently reported consisting of networks of Al_2N_2 four-membered rings.[17-25] We have recently reported similar results from the reaction of trimethylaluminum with macrocyclic tetradentate amines such as [14]aneN$_4$[27] and $(CH_3)_4$[14]aneN$_4$.[28]

A total of six methyl groups were eliminated from four trimethylaluminum units (one from Al(2) and Al(2a) and two from Al(1) and Al(1a)) while six aza-hydrogen atoms were eliminated from the two diethylenetriamine units (one from each of the six nitrogen atoms). Thus, although not overtly isolated, it is not unreasonable to postulate the formation of CH_4 (eq 1) during the

$$2(H_2NCH_2CH_2)_2NH + 4Al(CH_3)_3 \rightarrow [Al(CH_3)]_2[C_8H_{20}N_6][Al(CH_3)_2]_2 + 6CH_4 \quad (1)$$

course of the reaction. The molecule resides upon a crystallographic center of symmetry. Furthermore, the molecule consists of a series of three four-membered Al_2N_2 rings. The central Al_2N_2 ring is planar and slightly asymmetric with distances of 1.976 (2) Å and 2.04 Å for Al(1)–N(2) and Al(1)–N(2a), respectively.

Of paramount significance is the coordination of the aluminum atoms in $[Al(CH_3)]_2[C_8H_{20}N_6][Al(CH_3)_2]_2$. Two aluminum atoms, Al(2) and Al(2a), have the usual four-coordinate tetrahedral organoaluminum coordination. However, the situation for the remaining aluminum atoms is quite different. An examination of Al(1) reveals it to be five-coordinate being bonded to an axially positioned methyl carbon atom, C(1), in addition to four amine nitrogen atoms. The coordination may, thus, be described as square pyramidal. The mean Al–N distance in the square pyramid is 2.02 (3) Å. The Al(1)–C(1) distance of 1.962 (4) Å is only slightly longer than that of 1.947 (4) and 1.956 (4) Å for the dimethylaluminum fragment (Al(2)–C(2) and Al(2)–C(3), respectively). The Al···Al contacts of 2.907 (1) and 3.20 Å, for Al(2)–Al(1) and Al(1)–Al(1a), respectively, is not indicative of significant metal–metal interaction. Since the molecule resides on a crystallographic center of symmetry, Al(1a) has a similar coordination. Thus, the title compound $[Al(CH_3)]_2[C_8H_{20}N_6][Al(CH_3)_2]_2$ contains two aluminum atoms both in square pyramidal environments. Such is, heretofore, completely unprecedented. The literature reveals only five other structural reports of neutral five-coordinate organoaluminum complexes.[29-33] Notably, of these complexes only the organoaluminum–macrocyclic ligand complex, $[Al(C_{22}H_{22}N_4)]$,[31] has square pyramidal coordination as the other four complexes have trigonal bipyramidal coordination.

The novel coordination of the aluminum atoms in the title compound represents an inherently important contribution to organometallic chemistry. Studies are currently underway concerning factors which determine coordination geometries (i.e., square pyramidal or trigonal bipyramidal) in five-coordinate organoaluminum complexes.

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Supplementary Material Available: Tables of crystal data, bond distances and angles, final fractional coordinates, and thermal parameters (4 pages); a listing of observed and calculated structure factors (5 pages). Ordering information is given on any current masthead page.

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[26] Reaction of diethylenetriamine (4.6 mmol) with an excess of trimethylaluminum (13.9 mmol) in methylene chloride (25 mL), under an atmosphere of nitrogen, affords the title compound after considerable heating and subsequent cooling. A quantitative amount of product formed. A substantial portion of amorphous material in addition to a multitude of colorless, platelike, extremely air-sensitive, X-ray quality crystals were isolated: ^1H NMR (C_6H_6) δ −0.765 (s, 3 H, $AlCH_3$), −0.512 (s, 6 H, $Al(CH_3)_2$), 0.04–2.88 (m, 8 H, NCH_2CH_2N).

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