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Reaction of Trimethylaluminum with Crown Ethers. The Synthesis and Structure of (Dibenzo-18-crown-6)bis(trimethylaluminum) and of (15-Crown-5)tetrakis(trimethylaluminum)

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$[\mathrm{AlMe_3}]_2$[dibenzo-18-crown-6] (I) and $[\mathrm{AlMe_3}]_4$[15-crown-5] (II) have been prepared from the reactions of stoichiometric quantities of trimethylaluminum with dibenzo-18-crown-6 and 15-crown-5 in toluene. I crystallizes in the monoclinic space group $P2_1/c$ with lattice dimensions a = 11.500 (4) Å, b = 17.816 (6) Å, c = 7.545 (3) Å, β = 105.39 (4)°, and D_{calcd} = 1.19 g cm^{-3} for Z = 2. II belongs to the monoclinic space group C2/c with lattice parameters a = 22.134 (8) Å, b = 11.815 (5) Å, c = 18.347 (7) Å, β = 135.07 (4)°, and D_{calcd} = 1.00 g cm^{-3} for Z = 4. Least-squares refinement gave a final R value of 0.037 for I (1059 observed reflections) and 0.072 for II (939 observed reflections). In I the six oxygen atoms of the crown adopt a chair configuration which allows a strong Al–O interaction (the bond length is 1.967 (3) Å). The benzo rings impart sufficient rigidity to prevent Al–O bond formation to the neighboring oxygen atoms. II, on the other hand, has considerable flexibility and can bind four $\mathrm{AlMe_3}$ units. The Al–O average bond distance is 2.005 (6) Å. The fifth oxygen atom of the crown is oriented toward the inside of the ring and is not accessible for additional bond formation. I resides on a crystallographic center of inversion and II, on a twofold axis. Both I and II react with a wide variety of ionic compounds of formulation MX (M = alkali-metal or similar ion; X = halide, pseudohalide, or related ion).

Introduction

The reaction of $\mathrm{AlR_3}$ with MX has been under investigation for many years.[1,2] The initial restriction of M to include only alkali-metal or tetraalkylammonium ions, and X to halide or pseudohalide ions has given way to ever-widening definitions. Thus, M may be such diverse ions as $(\mathrm{CH_3})_2\mathrm{Tl}^+$,[3] $(\mathrm{C_6H_6})_2\mathrm{Cr}^+$,[4] or $(\mathrm{C_5H_5})_2\mathrm{Co}^+$.[4] The range of X is even more extensive: $\mathrm{NO_3}^-$,[5] $\mathrm{NO_2}^-$,[6] $\mathrm{CH_3COO}^-$,[7] OH^-,[8] $\mathrm{O_2}^-$,[9] $\mathrm{CO_3}^{2-}$,[10] or O^{2-}.[11] Reactions leading to the formation of 1:1 (eq 1) or 1:2 (eq 2) compounds were previously

$$\mathrm{MX} + \mathrm{AlR_3} \rightarrow \mathrm{M[AlR_3X]} \qquad (1)$$

$$\mathrm{MX} + 2\mathrm{AlR_3} \rightarrow \mathrm{M[Al_2R_6X]} \qquad (2)$$

carried out either neat or in aromatic solvents. The only limitation in the choice of MX is that the lattice energy of MX must be overcome by a temperature at which both the aluminum alkyl and the resulting compound are stable. This meant that many of the important $\mathrm{M[Al_2R_6X]}$ could not be prepared (M = Na^+ or Ba^{2+}, for example). We have found that the use of crown ethers together with aluminum alkyls to increase the solubility of MX in aromatic solvents affords a vast extension of the area. The aluminum alkyl forms a stable complex with the crown ether, but the substance readily dissociates to yield the desired compound according to the general reaction (3). We now wish to

$$n\mathrm{AlR_3} + \mathrm{CE}^{12} \xrightarrow[\text{solvent}]{\text{aromatic}} [\mathrm{AlR_3}]_n\mathrm{CE} \xrightarrow{\mathrm{MX}} [\mathrm{M{\cdot}CE}][\mathrm{Al_2R_6X}] \qquad (3)$$

discuss the ramifications of (3) and the structures of $[\mathrm{AlMe_3}]_2$[dibenzo-18-crown-6] and $[\mathrm{AlMe_3}]_4$[15-crown-5].

Table I. Bond Lengths (Å) and Angles (Deg) for $[\mathrm{AlMe_3}]_2$[dibenzo-18-crown-6]

	Bond Lengths		
Al-O(2)	1.967 (3)	Al-C(11)	1.957 (4)
Al-C(12)	1.982 (4)	Al-C(13)	1.941 (5)
O(1)-C(1)	1.430 (5)	O(1)-C(10)	1.392 (5)
O(2)-C(2)	1.469 (4)	O(2)-C(3)	1.485 (4)
O(3)-C(4)	1.408 (5)	O(3)-C(5)	1.354 (5)
C(1)-C(2)	1.509 (5)	C(3)-C(4)	1.500 (6)
C(5)-C(6)	1.396 (5)	C(5)-C(10)	1.393 (6)
C(6)-C(7)	1.368 (6)	C(7)-C(8)	1.367 (7)
C(8)-C(9)	1.406 (6)	C(9)-C(10)	1.379 (6)
	Bond Angles		
O(2)-Al-C(11)	102.4 (2)	O(2)-Al-C(12)	102.2 (2)
C(11)-Al-C(12)	114.8 (2)	O(2)-Al-C(13)	102.6 (2)
C(11)-Al-C(13)	117.1 (3)	C(12)-Al-C(13)	114.7 (2)
C(1)-Al-C(10)	119.5 (3)	Al-O(2)-C(2)	117.2 (2)
Al-O(2)-C(3)	123.2 (2)		

Results and Discussion

The strength of the Al–O bond is known to be the thermodynamic driving force for the extreme water and oxygen sensitivity of aluminum alkyls. By the same token, the Lewis basicity of ethers such as diethyl ether, tetrahydrofuran, or dioxane is sufficient to overcome dimer formation in trimethyl- or triethylaluminum and to lead

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[12] CE = 18-crown-6, dibenzo-18-crown-6, or 15-crown-5.

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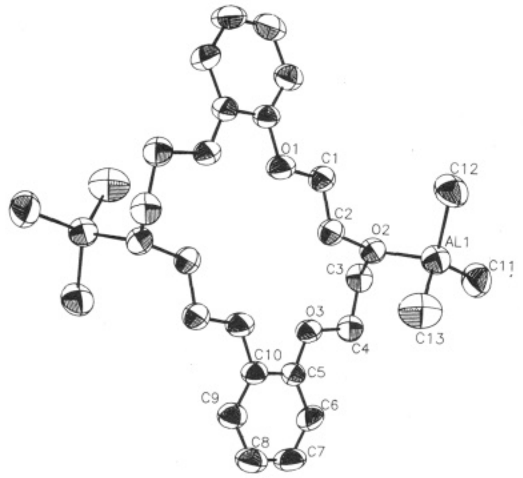

Figure 1. Molecular structure and atom numbering scheme for $[AlMe_3]_2$[dibenzo-18-crown-6], I. The molecule resides on a crystallographic center of inversion.

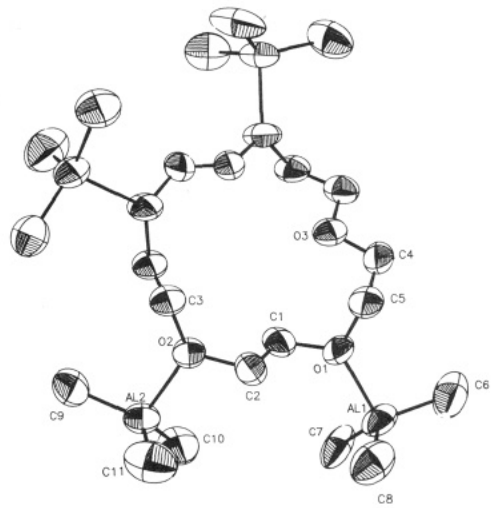

Figure 2. Molecular structure and atom numbering scheme for $[AlMe_3]_4$[15-crown-5], II. The molecule contains a crystallographic twofold axis.

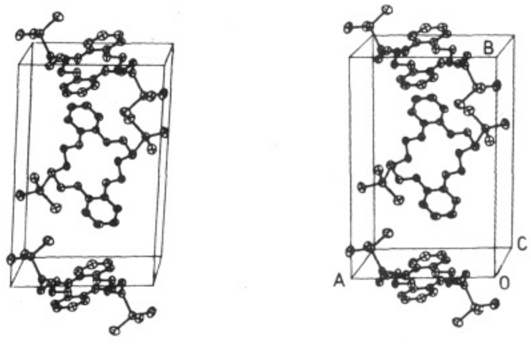

Figure 3. Stereoscopic view of the unit cell packing of I.

to a relatively strong donor–acceptor interaction.[13] The latter is, in fact, so substantial as to preclude the use of donor solvents for the bulk of our studies of the reaction of MX with AlR_3. Crown ethers, however, act to effect the transport of AlR_3 to the X^- moiety.[14] With this in mind it is surprising to observe the structure of $[AlMe_3]_2$[dibenzo-18-crown-6], I, given in Figure 1. One might suppose that steric problems associated with the crown would lead to a weak Al–O linkage. Contrary to this view, dibenzo-18-crown-6 has sufficient flexibility to make two of the oxygen atoms readily available as donor sites for the $AlMe_3$ units.[15–19] The strength of the bond is revealed by the Al–O length of 1.967 (3) Å (Tables I and II). This is marginally shorter than the 2.02 (2) Å value found in $[AlMe_3]_2[C_4H_8O_2]$.[20]

The distortion of the plane of the oxygen atoms in dibenzo-18-crown-6 is considerable. O(2) resides 0.97 Å out of the plane of O(1), O(1)′, O(3), and O(3)′. The overall geometry is shown clearly in Figure 3 if one notes that the plane of C(2), O(2), and C(3) makes an angle of 120° with that of O(1), O(1)′, O(3), and O(3)′.

The benzo rings in I impart sufficient rigidity to prevent Al–O bond formation to the neighboring oxygen atoms. Only two $AlMe_3$ molecules may be added to the dibenzo-18-crown-6 molecule,[21] but the 15-crown-5 moiety possesses greater flexibility. The structure of $[AlMe_3]_4$[15-crown-5], Figure 2, shows that the crown has, to a large extent, been turned "inside out". In so doing four strong Al–O bonds have been formed.[22] The independent bond lengths, both 2.005 (6) Å (Table III), are at the long end of the range of Al–O interactions shown in Table II but should be regarded as normal for neutral donor ligand complexes in which the aluminum atom is four-coordinate.

O(3) (Figure 2) remains uncoordinated; this appears to arise as a result of constraints placed on the 15-membered ring. Indeed, O(3) is forced toward the interior of the system and is sterically unavailable for bond formation to another Lewis acid molecule. The position of O(3) and the overall distortion of the oxygen atoms from planarity[23] may be observed in Figure 4.

The title compounds show that crown ethers will readily deviate from their usual configuration in the presence of aluminum alkyls. However, I and II react in a facile fashion with MX species as in 3 to transfer the AlR_3 to an X^- and to return the crown ether to its typical bonding mode. In subsequent contributions the synthesis of several new 1:1 and 1:2 complexes ($M[AlR_3X]$ and $M[Al_2R_6X]$) and the structure of [K·dibenzo-18-crown-6]$[Al_2Me_6O_2]$,[9] [K·dibenzo-18-crown-6]$[Al_2Me_6Cl]$,[24] [K·dibenzo-18-crown-6]$[AlMe_3NO_3]$,[25] [K·dibenzo-18-crown-6]-$[GaMe_3NCS]$,[26] and [K·18-crown-6]$[GaMe_3NCS]$[26] will be described. In general reactions 1 and 2 can be effected at much lower temperature with the aid of the crown ether.

Stereoscopic views of the unit cell packing of I and II are shown in Figures 3 and 4, respectively. No unusual

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(15) The oxygen atoms of 18-crown-6 in the free molecule,[16] the hydrogen-bonded molecule,[17] and the alkali-metal bonding ligand[18] are normally planar. However, flexibility of the crown has been noted in the hydrated NaSCN complex of 18-crown-6.[19]

(16) Dunitz, J. D.; Seiler, P. *Acta Crystallogr., Sect. B* **1974**, *B30*, 2739.

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(21) The title substances fall into the classification of "neutral molecule complexes": see, for example: Newkome, G. R.; Taylor, H. C. R.; Fronczek, F. R.; Delord, T. J.; Kohli, D. K.; Vogtle, F., submitted for publication in *J. Am. Chem. Soc.*

(22) The molecule contains a crystallographic two-fold axis which passes through O(3) and bisects the C(3)–C(3)′ bond. Therefore only two independent Al–O lengths were determined.

(23) The five oxygen atoms are only planar to 0.25 Å.

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(25) Rogers, R. D.; Crissinger, K. D.; Atwood, J. L., unpublished results.

(26) Zaworotko, M. J.; Atwood, J. L., unpublished results.

Table II. Comparison of Al–O Bond Distances in Organoaluminum Compounds

compd	coordinatn no. Al	coordinatn no. O	dist, Å	ref
$[Me_2AlOC(Ph)N(Ph)]\cdot ONMe_3$	4	2	1.771 (7)	*a*
			1.815 (8)	
$K[AlMe_2(OPh)_2]$	4	2	1.79 (2)	*b*
$[Me_2AlOC(Ph)N(Ph)]_2$	4	2	1.805 (6)	*c*
$[(C_5H_5)W(CO)_3(AlMe_2)]_2$	4	2	1.81 (2)	*d*
$[NMe_4][AlMe_3(MeCOO)]$	4	2	1.83 (1)	7
$[NMe_4][Al_2Me_6(MeCOO)]$	4	2	1.871 (4)	7
$AlMe_2(ONNMeO)AlMe_3$	4	2	1.881 (6)	*e*
	4	3	1.909 (6)	
			2.004 (6)	
$K_2[Al_4Me_{12}SO_4]$	4	2	1.90 (2)	*f*
$K_2[Al_4Me_{12}SO_4]\cdot 0.5p\text{-}C_6H_4Me_2$	4	2	1.91 (3)	*f*
$[K\cdot DB\text{-}18\text{-}C\text{-}6][AlMe_3NO_3]\cdot 0.5C_6H_6$	4	2	1.92 (1)	25
$K[AlMe_3NO_3]\cdot C_6H_6$	4	2	1.930 (6)	5
$K[Al_2Me_6NO_3]$	4	2	1.98 (3)	5
$Fe_2(C_5H_5)_2(CO)_2(CO\cdot AlEt_3)_2$	4	2	2.00 (2)	*g*
$[AsMe_4][AlMe_2OAlMe_3]_2$	4	3	1.78 (2)	*h*
			1.80 (2)	
$Cs[Al_7O_6C_{16}H_{48}]\cdot 3C_6H_5Me$	4	3	1.81 (2)	*i*
			1.84 (1)	
$K[Al_7O_6C_{16}H_{48}]\cdot C_6H_6$	4	3	1.81 (1)	*i*
			1.84 (1)	
$Mg[Al(OMe)_2Me_2]_2\cdot C_4H_8O_2$	4	3	1.83 (4)	*j*
$[Me_2AlOMe]_3$	4	3	1.851 (3)	*k*
$[K\cdot DB\text{-}18\text{-}C\text{-}6][Al_2Me_6O_2]\cdot 1.5C_6H_6$	4	3	1.86 (1)	9
$[AlMe_3]_2[DB\text{-}18\text{-}C\text{-}6]$	4	3	1.967 (3)	this study
$[AlMe_3]_4[15\text{-}C\text{-}5]$	4	3	2.000 (9)	this study
$[AlMe_3]_2[C_4H_8O_2]$	4	3	2.02 (2)	20
$[Me_2AlOC(Ph)N(Ph)\cdot MeCHO]_2$	5	3	1.868 (6)	1
			1.966 (6)	
		2	2.047 (7)	

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Table III. Bond Lengths (Å) and Angles (Deg) for $[AlMe_3]_4$[15-crown-5]

	Bond Lengths		
Al(1)–O(1)	2.005 (6)	Al(1)–C(6)	1.90 (1)
Al(1)–C(7)	1.99 (1)	Al(1)–C(8)	1.91 (1)
Al(2)–O(2)	2.005 (6)	Al(2)–C(9)	1.94 (1)
Al(2)–C(10)	1.99 (1)	Al(2)–C(11)	1.93 (1)
	Bond Angles		
O(1)–Al(1)–C(6)	102.2 (4)	O(1)–Al(1)–C(7)	101.2 (4)
C(6)–Al(1)–C(7)	114.9 (5)	O(1)–Al(1)–C(8)	102.0 (4)
C(6)–Al(1)–C(8)	117.1 (5)	C(7)–Al(1)–C(8)	115.8 (5)
O(2)–Al(2)–C(9)	103.6 (4)	O(2)–Al(2)–C(10)	99.7 (4)
C(9)–Al(2)–C(10)	116.8 (5)	O(2)–Al(2)–C(11)	100.8 (4)
C(9)–Al(2)–C(11)	114.8 (6)	C(10)–Al(2)–C(11)	117.1 (5)
Al(1)–O(1)–C(1)	123.2 (6)	Al(1)–O(1)–C(5)	120.8 (5)
Al(2)–O(2)–C(3)	122.0 (5)	Al(1)–O(1)–C(1)′	110 (1)
Al(2)–O(2)–C(2)′	129 (1)	Al(2)–O(2)–C(2)	112.3 (6)

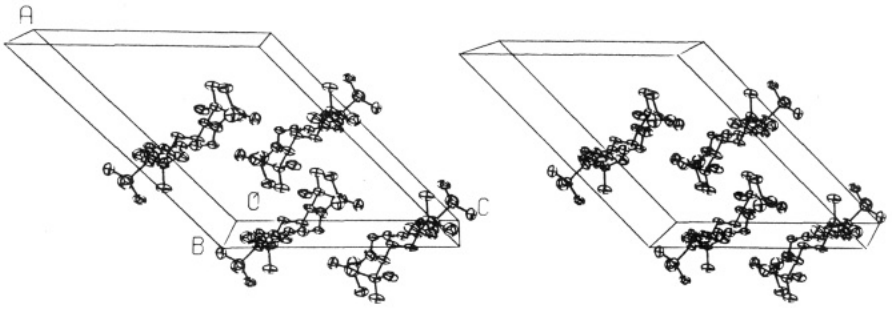

Figure 4. Stereoscopic view of the unit cell packing of II.

Table IV. Crystal Data and Summary of Intensity Data Collection and Structure Refinement

	$[AlMe_3]_2$[dibenzo-18-crown-6]	$[AlMe_3]_4$[15-crown-5]
mol wt	504.6	508.6
space group	$P2_1/c$	$C2/c$
cell constants		
a, Å	11.500 (4)	22.134 (8)
b, Å	17.816 (6)	11.815 (5)
c, Å	7.545 (3)	18.347 (7)
β, deg	105.39 (4)	135.07 (4)
cell vol, Å^3	1409.4	3388.5
molecules/ unit cell	2	4
D_{calcd}, g cm^{-3}	1.19	1.00
μ (calcd), cm^{-1}	1.45	1.67
radiation, Å	Mo Kα (0.71069)	Mo Kα (0.71069)
max crystal dimens, mm	0.30 × 0.45 × 0.60	0.20 × 0.35 × 0.65
std reflctns	(040), (400), (002)	(040), (004)
variation of stds	±2%	±2%
reflctns measd	2018	1150
2*θ* range, deg	≤42	≤36
reflctns obsd ($I > 3\sigma(I)$)	1059	939
no. of parameters varied	163	141
goodness of fit (GOF)	0.85	3.34
R	0.037	0.070
R_w	0.038	0.068

intermolecular contacts are noted.

Experimental Section

All reactions were carried out under a nitrogen atmosphere by using Schlenk techniques or an inert atmosphere box. Solvents were dried and degassed in the normal manner. The crown ethers were purchased from Aldrich Chemical Co., and the trimethylaluminum was purchased from Alfa Products. Both were used as obtained.

Preparation of $[AlMe_3]_2$[dibenzo-18-crown-6], I. A mixture of 1.00 mL of $AlMe_3$ (0.01 mol) was added to a slurry of 1.80 g of dibenzo-18-crown-6 (0.005 mol) in ca. 20 mL of toluene. Reaction was immediate, but the mixture was heated to 50 °C for 1 h, filtered, concentrated to ca. 10 mL, and cooled to room temperature. Colorless, extremely air-sensitive crystals resulted. The reaction is essentially quantitative. The same procedure with a fivefold excess of $AlMe_3$ produced only $[AlMe_3]_2$[dibenzo-18-crown-6], I. Reaction of I with acetone produces decomposition products and a quantitative recovery of dibenzo-18-crown-6.

Preparation of $[AlMe_3]_4$[15-crown-5], II. The colorless, extremely air-sensitive crystalline material was produced by using the above-mentioned procedure. In all mole ratios ($AlMe_3$:15-crown-5) from 1:1 to 8:1, the only crystalline product obtained was II.

X-ray Data Collection, Structure Determination, and Refinement for $[AlMe_3]_2$[dibenzo-18-crown-6], I. Single crystals of the compound were sealed under N_2 in thin-walled glass capillaries. Final lattice parameters as determined from a least-squares refinement of $(\sin\theta/\lambda)^2$ values for 15 reflections ($\theta > 20°$) accurately centered on the diffractometer are given in Table IV. The space group was uniquely defined by systematic absences to be $P2_1/c$.

Data were collected on an Enraf-Nonius CAD-4 diffractometer by the $\theta/2\theta$ scan technique. The method has been previously described.[27] A summary of data collection parameters is given in Table IV. The intensities were corrected for Lorentz and polarization effects, but not for absorption.

Table V. Final Fractional Coordinates for $[AlMe_3]_2$[dibenzo-18-crown-6]

atom	*x/a*	*y/b*	*z/c*
Al	0.1286 (1)	−0.13073 (8)	−0.0625 (2)
O(1)	0.3831 (3)	0.0597 (2)	−0.2325 (4)
O(2)	0.2187 (2)	−0.0398 (2)	0.0395 (3)
O(3)	0.4285 (3)	−0.0613 (2)	0.3416 (4)
C(1)	0.2789 (4)	0.0501 (2)	−0.1656 (6)
C(2)	0.3168 (4)	−0.0163 (3)	−0.0393 (6)
C(3)	0.2324 (4)	−0.0138 (3)	0.2310 (5)
C(4)	0.3117 (4)	−0.0661 (3)	0.3664 (5)
C(5)	0.5171 (4)	−0.1068 (2)	0.4384 (5)
C(6)	0.5118 (5)	−0.1514 (3)	0.5882 (6)
C(7)	0.6101 (5)	−0.1932 (3)	0.6758 (6)
C(8)	0.7148 (5)	−0.1923 (3)	0.6225 (6)
C(9)	0.7226 (4)	−0.1482 (2)	0.4716 (6)
C(10)	0.6231 (4)	−0.1066 (2)	0.3824 (5)
C(11)	0.0058 (4)	−0.1364 (3)	0.0735 (7)
C(12)	0.0663 (5)	−0.1044 (3)	−0.3260 (6)
C(13)	0.2531 (6)	−0.2074 (3)	−0.0113 (7)

Table VI. Final Fractional Coordinates for $[AlMe_3]_4$[15-crown-5]

atom	*x/a*	*y/b*	*z/c*
Al(1)	0.1707 (2)	0.3832 (3)	0.6118 (2)
Al(2)	0.1469 (2)	−0.0806 (3)	0.4875 (2)
O(1)	0.0868 (4)	0.3406 (6)	0.4621 (4)
O(2)	0.0735 (4)	0.0482 (5)	0.3908 (4)
O(3)	0.0000	0.4081 (8)	0.2500
C(1)[a]	0.0989 (8)	0.239 (1)	0.4223 (9)
C(2)	0.0749 (8)	0.151 (1)	0.447 (1)
C(1)′	0.063 (2)	0.212 (3)	0.449 (2)
C(2)′	0.097 (2)	0.170 (2)	0.399 (2)
C(3)	−0.0077 (6)	0.0294 (8)	0.2838 (7)
C(4)	0.0073 (6)	0.4759 (8)	0.3197 (7)
C(5)	0.0055 (5)	0.4031 (9)	0.3843 (7)
C(6)	0.1650 (7)	0.544 (1)	0.6058 (9)
C(7)	0.2786 (6)	0.318 (1)	0.6639 (8)
C(8)	0.1247 (7)	0.308 (1)	0.6559 (8)
C(9)	0.1209 (7)	−0.2009 (9)	0.3969 (8)
C(10)	0.2614 (6)	−0.009 (1)	0.5767 (8)
C(11)	0.1026 (7)	−0.103 (1)	0.5469 (9)

[a] Atoms C(1) and C(2) have occupancy factors of 0.75 (1); atoms C(1)′ and C(2)′ have occupancy factors of 0.25 (1).

Calculations were carried out with the SHELX system of computer programs.[28] Neutral atom scattering factors for Al, O, and C were taken from Cromer and Waber.[29] Scattering factors for H were from ref 30.

The structure was solved by the straightforward application of the direct methods program MULTAN.[31] Least-squares refinement with isotropic thermal parameters led to $R = \sum||F_o - F_c||/\sum|F_o| = 0.090$. Hydrogen atoms were located with the aid of a difference Fourier map, but their parameters were not refined. Refinement of the nonhydrogen atoms with anisotropic temperature factors and inclusion of the hydrogen atom contributions gave final values of $R = 0.037$ and $R_w = \{\sum w(F_o - F_c)^2/\sum w(F_o)^2\}^{1/2} = 0.038$. A final difference Fourier map showed no feature greater than 0.3 e/Å^3. Unit weights were used at all stages of refinement. The positional parameters are given in Table V, and the temperature factors are available elsewhere.[32]

X-ray Data Collection, Structure Determination, and Refinement for $[AlMe_3]_4$[15-crown-5], II. The compound was manipulated and data collected in the same manner as for I. In

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[32] See paragraph at the end of paper regarding supplementary material.

the course of the refinement of the data, disorder was noted with regard to atoms C(1) and C(2). On the basis of relative peak heights, initial occupancies of 0.75 were assigned to C(1) and C(2) and 0.25 to C(1)′ and C(2)′. These factors were refined for three cycles in the following manner: refinement of C(1) and C(2) (x, y, z) and U's only, refinement of C(1)′ and C(2)′ only, and refinement of the occupancy factors only (the total was constrained to equal 1.0). This produced values of 0.75 (1) and 0.25 (1). C(1)′ and C(2)′ could not be refined with anisotropic thermal parameters. Final positional parameters are given in Table VI, and temperature factors are available elsewhere.[32]

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Supplementary Material Available: Tables of thermal parameters, hydrogen atom coordinates, complete bond lengths and angles, and structure factors for I and II (19 pages). Ordering information is given on any current masthead page.

Monosubstituted Triazenido Complexes as Intermediates in the Formation of Amido Complexes from Hafnium Hydrides and Aryl Azides[†]

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$(\eta^5\text{-}C_5Me_5)_2HfH_2$, **1**, has been shown to react smoothly with RN_3 (R = Ph, *p*-tolyl) to afford moderately stable triazenido complexes of hafnium, $(\eta^5\text{-}C_5Me_5)_2HfH(NHNNR)$, **2**. Upon thermolysis at 80 °C, **2** loses dinitrogen to form hafnium arylamido complexes $(\eta^5\text{-}C_5Me_5)_2HfH(NHR)$, **4**, which can alternatively be prepared from **1** and RNH_2. Treatment of **1**, **2**, or **4** with excess RN_3 results in rapid formation of $(\eta^5\text{-}C_5Me_5)_2Hf(NHR)_2$, which can also be prepared from **4** and RNH_2 at 80 °C.

Introduction

The reactions of organic azides, RN_3, with transition-metal complexes are varied, but usually result in the loss of molecular nitrogen and addition of the "RN" fragment to the metal's coordination sphere.[1] The "RN" moiety can be incorporated either as a coordinated nitrene (imido) ligand or as the product of a coupling or insertion reaction between "RN" and another coordinated ligand. Since organic azides are known to be excellent sources of free nitrenes ($R{-}\ddot{N}{:}$) in photoassisted and thermal reactions,[2] it is not surprising that early workers often attributed organometallic nitrene-like products to the interactions of free nitrenes with metal complexes.

$$\mathrm{R{-}\ddot{N}{=}\overset{+}{N}{=}\overset{-}{\ddot{N}}\,:} \leftrightarrow \mathrm{R{-}\overset{-}{\ddot{N}}{-}\overset{+}{N}{\equiv}N:} \xrightarrow[\Delta]{h\nu\ \text{or}} \mathrm{R{-}\ddot{N}: + :N{\equiv}N:}$$

Most nitrenes have triplet ground states and are extremely reactive.[2] It would be surprising if such species were particularly selective in their reactions with organometallic complexes. Indeed, evidence is compelling that rarely, if ever, are free nitrenes involved in reactions of metal complexes with organic azides. Instead, most of these reactions probably proceed via metal azide intermediates which subsequently lose dinitrogen.

Transition-metal hydrido complexes are often quite reactive toward these azides. In some instances unexpected products are obtained. For example, $RhH(dppe)_2$ is reported to react with tosyl azide to afford a dimeric diimide-bridged complex $[Rh(dppe)_2]_2(\mu\text{-TosNNTos})$,[3] while the same azide reacts with $OsH_4(PEtPh_2)_3$ to give the monomeric dinitrogen species $OsH_2(N_2)(PEtPh_2)_3$ and tosyl amine.[4] The most common products from the reactions of transition-metal hydrides with organic azides, however, are metal amido complexes, formally resulting from the insertion of the "RN" fragment of the azide into a metal–hydride bond. Typical examples include *trans*-$Pt(NHPh)Cl(PPh_3)_2$ from PhN_3 and $PtHCl(PPh_3)_2$,[5] $Re(NHC(O)Ph)(CO)_2(PPh_3)_2$ from benzoyl azide and $ReH(CO)_2(PPh_3)_3$,[1] $(\eta^5\text{-}C_5H_5)W(CO)_3(NHTos)$ from $(\eta^5\text{-}C_5H_5)WH(CO)_3$ and tosyl azide,[6] and $Os_3H(\mu\text{-NHTos})(CO)_{10}$ from tosyl azide and $Os_3H_2(CO)_{10}$.[7] Although several authors have speculated on the mechanisms by which these amido complexes form, no convincing evidence has been advanced to support any of the proposed mechanisms. The isolation of the monosubstituted triazenido complexes $W(NO)(NHNNTol)(CO)(PPh_3)_2$ and $Re(NHNNTol)(CO)_2(PPh_3)_2$ from the reactions of *p*-tolyl azide with $WH(NO)(CO)_2(PPh_3)_2$ and $ReH(CO)_2(PPh_3)_3$, respectively, suggested triazenido complexes might be reactive intermediates in the formation of amides from azides and metal hydrides.[8] It is known that free phenyltriazene, $PhN{=}N{-}NH_2$, decomposes above −20 °C to give aniline and dinitrogen quantitatively, an observation compatible with the suggestion that triazenido complexes might be unstable with respect to dinitrogen loss and

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[†] Contribution No. 6604.

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