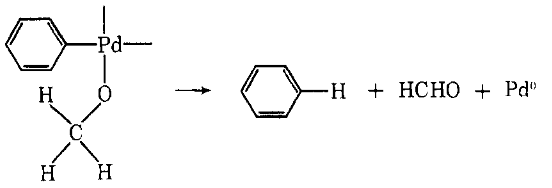
In contrast, the reductive cleavages encountered in the present work correspond to hydrogenolysis of the C–Pd bond. The experiments with deuterated methanol suggest that a key step in the mechanism is transfer of hydrogen (or deuterium) from a coordinated methoxide group



The intermediate methoxide complex is probably formed by methanolysis of the β-diketonate ligand, a selective cleavage of the O–Pd bond in preference to C–Pd like that observed with π-allylpalladium β-diketonate complexes.[13] The reduction of the C–Pd bond occurs by transfer of H from the methyl group to the aryl ligand. Thus, as observed, only C-deuterated methanol leads to aryl–D products. The zerovalent palladium species finally precipitates from solution as palladium metal or as $[(C_6H_5)_3P]_4Pd$ if triphenylphosphine is present.

[13] B. F. G. Johnson, J. Lewis, and D. A. White, *J. Amer. Chem. Soc.* **91**, 5186 (1969).

Notes

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Dihydrotrimethylsiloxyaluminum

BY CHARLES B. ROBERTS AND DARELL D. TONER

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Dichloro- and dibromotrimethylsiloxyaluminum, analogous to dihydrotrimethylsiloxyaluminum, have been reported[1] and their structures have been determined by X-ray.[2] These compounds were used to prepare polyorganoaluminosiloxanes by treating them with dialkylcyclosiloxanes.[3]

This paper reports a method for synthesizing dihydrotrimethylsiloxyaluminum[4] which is more reactive than either of the dichloro or dibromo compounds mentioned above. Consequently, it is of interest as a starting material for the synthesis of polyorganoaluminosiloxanes.

Experimental Section

Materials.—An ether solution of 0.25 *M* aluminum hydride was prepared according to the method of Finholt, Bond, and Schlesinger[5]

$$3LiAlH_4 + AlCl_3 \xrightarrow{(C_2H_5)_2O} 4AlH_3\cdot(C_2H_5)_2O + LiCl\downarrow$$

In a typical procedure, the ethereal aluminum hydride solution was prepared in a nitrogen-filled drybox. An ether solution of lithium aluminum hydride (75 ml, 1.0 *M*) was added to 300 ml of diethyl ether, followed by the addition of 25 ml of an ether solution of 1.0 *M* aluminum chloride. After stirring for a few minutes, the solution, which contained 100 mmol of AlH_3, was filtered through a medium-porosity glass frit to remove the lithium chloride, placed in a 1-l. flask, capped, and removed from the drybox.

Trimethylsilanol (99% purity) was obtained by hydrolyzing trimethylsilazane in an ammonium acetate buffer. Purification of the silanol was accomplished by washing the reaction mixture until it was neutral, diluting it with dry mineral oil, and carrying out an azeotropic distillation at 40 mm. The first fraction of distillate contained higher amounts of hexamethyldisiloxane, $[(CH_3)_3Si]_2O$, and water. As distillation proceeded almost all of the $[(CH_3)_3Si]_2O$ was removed, and the water content dropped to 0.6–0.7% where it remained constant. The purified silanol was stored at $-15°$ to prevent condensation of the silanol to hexamethyldisiloxane and water.

Preparation of $H_2AlOSi(CH_3)_3$.—A diethyl ether solution (150 ml) containing 9.1 g (100 mmol) of trimethylsilanol was added dropwise from a dropping funnel to the ether solution of aluminum hydride. The addition rate was approximately 2 ml/min, with the temperature of the reaction mixture maintained between 0 and 5° during the addition. Air was excluded by a continuous nitrogen purge. The reaction resulted in a clear solution of $H_2AlOSi(CH_3)_3$, formed according to $AlH_3 + (CH_3)_3SiOH \rightarrow H_2AlOSi(CH_3)_3 + H_2$.

The solvent was removed under reduced pressure, yielding a white solid, which was purified by a double sublimation in a 50-g Nessler-Faust sublimer at 1 mm and 50°. An overall yield of approximately 50% was obtained.

Characterization of $H_2AlOSi(CH_3)_3$.—The elemental analysis agreed closely with the theoretical value of $H_2AlOSi(CH_3)_3$. *Anal.* Calcd for $C_3H_{11}AlOSi$: C, 30.5; H, 9.4; Al, 22.8; Si, 23.5. Found: C, 30.4; H, 9.1; Al, 22.6; Si, 22.2.

A split mull was used to obtain the infrared spectrum. This confirmed the presence of AlH_2 bonding, with a possibility of hydrogen bonding indicated by a broad peak at 1600 cm^{-1}. Other absorbance peaks corresponded to those expected from the structure.

A Raman spectrum for crystalline $H_2AlOSi(CH_3)_3$ showed four bands. The strongest band appeared at 1871 cm^{-1} and was assigned to Al–H stretching. A weak band attributed to skeletal stretch was observed at 640 cm^{-1} and two additional bands resulting from the CH_3 group appeared at 2901 and 2952 cm^{-1}.

The proton nmr spectrum was obtained with a Varian Model A-60 spectrometer at 60 MHz. The sublimed material in a 10% benzene solution showed single sharp absorptions at chemical shifts of +6.98 and +2.775 ppm shielding relative to benzene; the chemical shift of a 1% solution of the common standard, tetramethylsilane, in benzene, is +7.16 ppm. The areas corresponded to the theoretical 9:2 ratio expected for three methyl groups and two equivalent hydrogens bonded to aluminum. Impurities, except for small amounts of diethyl ether, were absent.

The molecular weight, determined by the ebulliometric method, was 214; this agrees reasonably well with the molecular weight of a dimer (236).

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[1] N. F. Orlov, *Dokl. Akad. Nauk SSSR*, **114**, 1033 (1957).

[2] M. Bonamico and G. Dessy, *J. Chem. Soc. A*, 1786 (1967).

[3] C. Ercolani, A. Camilli, and L. DeLuca, *ibid.*, 5278 (1964).

[4] U. S. Patent 3,444,227 (1969) covers composition and method of preparation.

[5] A. E. Finholt, A. C. Bond, and H. I. Schlesinger, *J. Amer. Chem. Soc.*, **69**, 1199 (1947).

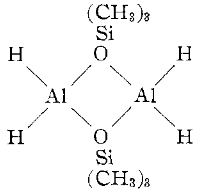
The X-ray diffraction data of $H_2AlOSi(CH_3)_3$ are shown in Table I.

TABLE I
X-RAY POWDER DIFFRACTION DATA OF DIHYDROTRIMETHYLSILOXYALUMINUM

d, Å	*I*/*I*₁	*d*, Å	*I*/*I*₁	*d*, Å	*I*/*I*₁
9.5	30	3.42	8	2.25	10
7.3	100	3.16	5	2.21	3
5.65	50	3.08	15	2.17	4
4.95	6	3.02	15	2.13	12
4.70	75	2.90	6	2.09	4
4.20	20	2.81	6	2.04	4
4.00	5	2.60	5	2.00	4
3.90	5	2.53	5	1.98	4
3.77	20	2.42	8	1.94	5
3.51	8	2.35	10	1.90	8

Discussion

A new nonsolvated aluminum dihydride, $H_2AlOSi(CH_3)_3$, has been synthesized by the reaction between etherated aluminum hydride and trimethylsilanol. Nmr and molecular weight data indicate that it is a dimer of the structure



This structure is similar to those of the analagous dihalogen compounds characterized by Ercolani, *et al.*, and $(CH_3)_2AlOC(C_6H_5)_2CH_3$ prepared by Ashby, Laemmle, and Parris.[6] It is a white crystalline compound, soluble in diethyl ether and benzene. Upon standing at room temperature, a benzene solution of $H_2AlOSi(CH_3)_3$ forms a gel, accompanied by the release of a gas identified as trimethylsilane by gas–liquid chromatography and nmr. The formation of the gel may be due to the formation of Al–O–Al bonds, which occurs simultaneously with the release of $(CH_3)_3SiH$.

The neat crystalline material slowly decomposes at room temperature. When a tightly sealed bottle containing the compound was kept in a drybox for 10 days, a clear viscous liquid appeared. Upon opening the bottle the sample foamed up, leaving a dry, white solid which was soluble in ether. It is presumed that the same process was occurring as in benzene, except that in this case the $(CH_3)_3SiH$, unable to escape, remained as a liquid. On releasing the pressure it quickly volatilized, leaving a partially polymerized solid.

Dihydrotrimethylsiloxyaluminum is readily oxidized and reacts violently with water. It can be polymerized by the controlled addition of either oxygen or water, forming a clear compound with a molecular weight between 1600 and 3000. This material is film forming but hydrolyzes slowly when exposed to air.

Acknowledgment—The authors wish to express their appreciation to Dow Corning Corporation for supplying the trimethyltriazane and method of preparation for trimethylsilanol.

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[6] E. C. Ashby, J. Laemmle, and G. E. Parris, *J. Organometal. Chem.*, **19**, 24 (1969).

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Substitution Reactions of Metallic Complexes of β,β′,β′′-Triaminotriethylamine. IV. Kinetics of Aquation of *cis*-Bromoaquo(triaminotriethylamine)-cobalt(III) Ion

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A considerable amount of kinetic data has been reported for the acid hydrolyses of complex ions of the type $MA_4X_2^+$ where M is either Co(III) or Cr(III), A represents a nonreplaceable monodentate or polydentate amine, and X represents either Cl or Br. In all of the complexes of this type which have been studied, the aquation was found to occur in two separate steps

$$MA_4X_2^+ + H_2O \xrightarrow{k_1} MA_4H_2OX^{2+} + X^- \tag{1}$$

$$MA_4H_2OX^{2+} + H_2O \xrightarrow{k_2} MA_4(H_2O)_2^{3+} + X^- \tag{2}$$

In the case of Cr(III) both aquation steps have been studied for several *cis* and *trans* complexes.[3,4] However, in the case of cobalt, while the primary aquation step for many *cis*- and *trans*-dihaloaminecobalt(III) complexes has been studied extensively, very little is known about the secondary aquation step of the corresponding haloaquo species. In fact, the only data available in the literature for the aquation of complexes of this type are the aquation constants for *cis*- and *trans*-$Co(en)_2H_2OCl^{2+}$ at 25° in the pH range 2–3 reported by Chan.[5]

The lack of kinetic studies on such complexes may be due in part to the difficulty in obtaining accurate data because of the complicating isomerization reactions of the haloaquo species.

Since octahedral Co^{III}–tren complexes (tren = β,β′,β′′-triaminotriethylamine) have been previously shown to form only the *cis* isomer,[6,7] the haloaquotriaminotriethylaminecobalt(III) complexes should be ideal systems for studying the aquation reactions of species of this type.

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[1] NDEA Predoctoral Fellow, 1969–1970.

[2] Author to whom inquiries should be addressed.

[3] T. J. Williams and C. S. Garner, *Inorg. Chem.*, **9**, 52 (1970), and references therein.

[4] L. P. Quin and C. S. Garner, *J. Chem. Soc.*, 1348 (1964).

[5] S. C. Chan, *ibid.*, 5137 (1963).

[6] (a) S. K. Madan and J. Peone, Jr., *Inorg. Chem.*, **6**, 463 (1967); (b) S. K. Madan and J. Peone, Jr., *ibid.*, **7**, 824 (1968).

[7] S. K. Madan, W. M. Reiff, and J. C. Bailar, Jr., *ibid.*, **4**, 1366 (1965).