Reductive Cleavage of Aryl–Palladium Bonds

BY D. A. WHITE AND G. W. PARSHALL*

Methanol has been found to be a very effective reagent for *reductive* cleavage of C–Pd bonds in phenylpalladium complexes and in ortho-bonded chelate compounds derived from benzyldimethylamine and N-phenylpyrazole. When the reduction is carried out in the presence of triphenylphosphine, $((C_6H_5)_3P)_4Pd$ and the free aromatic ligand are formed in high yield together with formaldehyde produced by oxidation of the methanol. With CD_3OD as the reducing agent, the aromatic ligand is deuterated on the carbon originally bonded to palladium. Similarly reduction by D_2 gas results in monodeuteration of the arylamine ligand.

Alcohols have been used extensively in the protolytic cleavage of organometallic compounds but the reaction is often accompanied by complex side reactions.[1] For example, ethanolysis of $(CH_3)_2Pd(P(C_2H_5)_3)_2$ led to the formation of ethane, ethylene, and acetaldehyde, in addition to the methane that was anticipated.[2] Ethanol containing sodium ethoxide has been reported to cleave alkyl–palladium σ bonds by reduction rather than by protolysis.[3]

We have now observed that methanol cleaves aryl–palladium bonds in a reaction that closely resembles the hydrogenation of the C–Pd bond.

Experimental Section

Palladium Complexes.—Bis(2,2,6,6-tetramethylheptanedionato)palladium was obtained from the reaction of the β-diketone with $Na_2Pd_2Cl_6$ in methanol in the presence of sodium carbonate. The ortho-bonded arylpalladium β-diketonate complexes were prepared from the corresponding arylpalladium chloride dimer as illustrated for the benzyldimethylamine derivative. The phenylpalladium β-diketonate was prepared similarly from chlorophenylbis(triphenylphosphine)palladium.

2,2,6,6-Tetramethylheptane-3,5-dionato[2-(dimethylaminomethyl)phenyl]palladium.—A mixture of the dimer di-μ-chlorobis[2-(dimethylaminomethyl)phenyl]dipalladium[4] (13.8 g; 50.0 mmol), 2,2,6,6-tetramethylheptane-3,5-dionatothallium (19.4 g; 50.0 mmol), and methylene chloride (300 ml) was stirred at 0° for 2 hr. The mixture was filtered and the filtrate was evaporated to dryness to yield a yellow oil, which crystallized on standing. This solid, the title compound, was recrystallized from methanol to give long lemon yellow needles (16.75 g, 89%). *Anal.* Calcd for $C_{20}H_{31}NO_2Pd$: C, 56.7; H, 7.4; N, 3.3; O, 7.6; Pd, 25.1. Found: C, 56.6, 56.4; H, 7.6, 7.6; N, 3.3, 3.3; O, 7.7; Pd, 24.1.

Methanol Reactions. 1. Phenylpalladium Complex.—A mixture of 2,2,6,6-tetramethylheptane-3,5-dionato(phenyl)triphenylphosphinepalladium (3.14 g; 5.0 mmol), triphenylphosphine (3.93 g; 15.0 mmol), and methanol (15 ml) was heated in a sealed tube at 100° for 2 hr. The tube was cooled and opened and the mixture was filtered under nitrogen. The solvent was distilled from the solution on a steam bath and was examined by gas chromatography, which showed a peak at the same retention time as that of benzene. A 5-ml sample of the distillate gave a deep violet color with chromotropic acid in concentrated

sulfuric acid solution.[5] A 5-ml sample of methanol from the same bottle as that used in the reaction gave only a very weak coloration, when similarly tested. The residue from the distillation was transferred to a microstill and distilled under water aspirator vacuum, using a bath temperature of 160°. A water white liquid was obtained, which was identified by its infrared and nmr spectra as 2,2,6,6-tetramethylheptane-3,5-dione (462 mg; 51%).

The yellow residue from the filtration was washed with large amounts of ether and dried in a stream of nitrogen overnight to give tetrakis (triphenylphosphine)palladium (4.84 g; 84%).

2. Benzyldimethylamine Complex.—A mixture of 2,2,6,6-tetramethylheptane-3,5-dionato[2-(dimethylaminomethyl)phenyl]palladium (1.06 g; 2.5 mmol), triphenylphosphine (2.60 g; 10.0 mmol), and 34 ml of methanol-d_1 was boiled under reflux under nitrogen for 1 hr. Filtration under nitrogen gave yellow crystals of tetrakis(triphenylphosphine)palladium (2.18 g; 76%). A portion of the complex was oxidized with H_2O_2 to give triphenylphosphine oxide (mp 157–159°) which was analyzed by its ^{1}H nmr spectrum in C_6D_6 to establish that no deuteration of the ligand had occurred.[6]

Evaporation of the filtrate yielded a large quantity of a yellow semisolid, which was transferred to a microstill and distilled at *ca.* 10 mm to give a water white liquid. The nmr spectrum of this liquid showed it to be a mixture of dimethylbenzylamine and tetramethylheptanedione-d_2 in the molar ratio of approximately 1:2. Treatment of the mixture with CH_3I gave white crystals of benzyltrimethylammonium iodide. The ^{1}H nmr spectrum in water showed aryl, methylene, and methyl signals in a ratio 5:2:9, consistent with no deuteration of the amine ligand.

3. Phenylpyrazole Complex.—A mixture of 2,2,6,6-tetramethylheptane-3,5-dionato[2-(1-pyrazolyl)phenyl]palladium[7] (4.32 g; 10.0 mmol), triphenylphosphine (10.50 g; 40.0 mmol), and methanol (400 ml) was refluxed under nitrogen for 1 hr. Filtration under nitrogen gave tetrakis(triphenylphosphine)palladium (10.44 g; 90%). The combined filtrate and washings were evaporated to dryness to give a yellow oil. Addition of ether to this oil followed by filtration gave a further small amount of tetrakis(triphenylphosphine)palladium (0.26 g, total yield 93%). The ether was removed from the filtrate and the residue was distilled at a pressure of 0.1 mm to give a low-boiling fraction (0.52 g) and a high-boiling fraction (1.22 g). The former fraction was identified by nmr as primarily the β-diketone and the latter as 1-phenylpyrazole. At the pressure used in the distillation some of the low-boiling β-diketone was lost from the apparatus.

In a subsequent series of experiments to determine the effect of deuterated methanols, a 5.0-mmol sample of the phenyl-

* To whom correspondence should be addressed.

(1) G. W. Parshall and J. J. Mrowca, *Advan. Organometal. Chem.*, **7**, 180 (1968).

(2) G. Calvin and G. E. Coates, *J. Chem. Soc.*, 2008 (1960).

(3) H. Takahashi and J. Tsuji, *J. Amer. Chem. Soc.*, **90**, 2387 (1968).

(4) A. C. Cope and E. C. Friedrich, *ibid.*, **90**, 909 (1968).

(5) M. J. Boyd and M. A. Logan, *J. Biol. Chem.*, **146**, 279 (1962); J. F. Walker, "Formaldehyde," Reinhold, New York, N. Y., 1964, p 469.

(6) G. W. Parshall, *J. Amer. Chem. Soc.*, **90**, 1669 (1968).

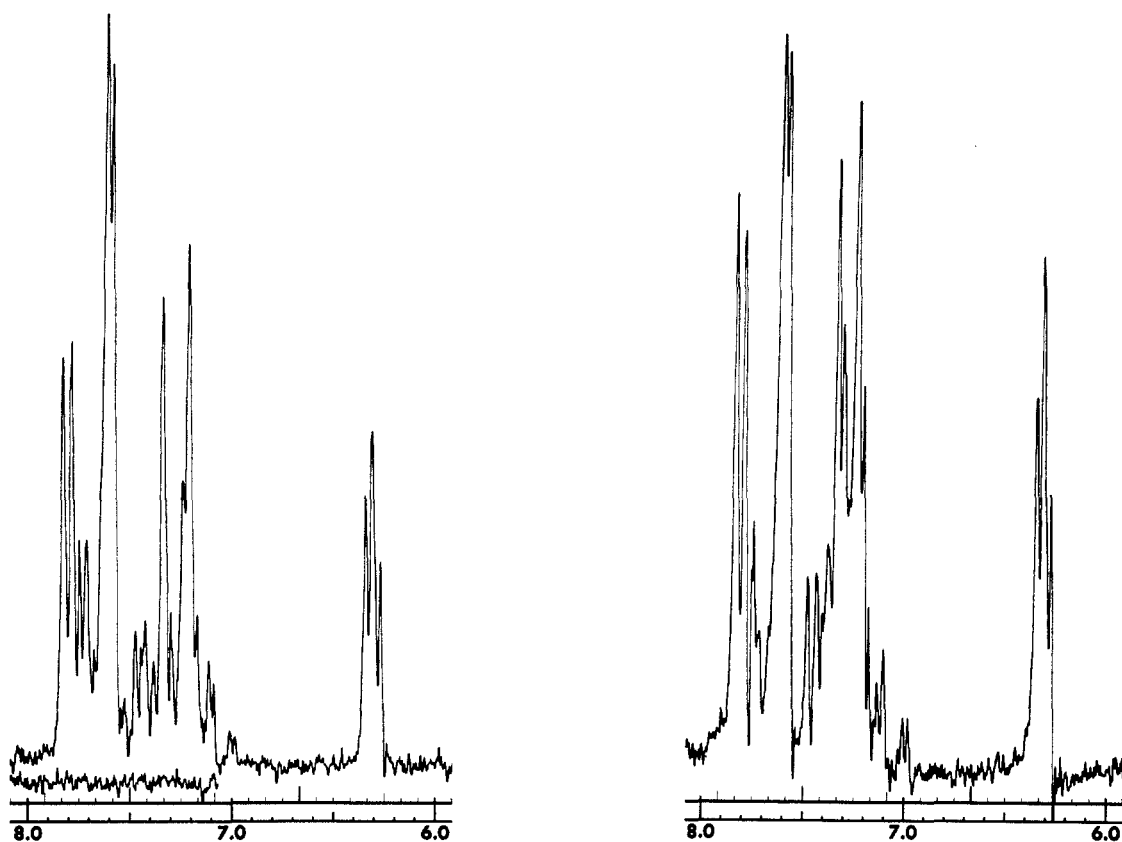(7) S. Trofimenko, to be submitted for publication.

Figure 1.—Proton nmr spectra of phenylpyrazole (left) and (phenyl-2-d)pyrazole (right). Measured in carbon tetrachloride solution with internal tetramethylsilane reference, at 60 Mc/s. Numeration indicates chemical shift in ppm from reference signal.

pyrazole complex was heated for 2 hr at 100° in a sealed tube with 20 mmol of triphenylphosphine and 10 ml of CH_3OH, CH_3OD, or CD_3OD. The isotopic composition of the volatile products is shown in Table I. The composition of the distilled

TABLE I

REACTIONS WITH DEUTERATED METHANOL

| | | Deuterium content, % | | |
| | | Phenylpyrazole | | |
Reagent	β-Diketone	d_0	d_1	d_2
CH_3OH	d_0	100	...	
CH_3OD	d_2	93.2^a	6.7	<0.1
CD_3OD	d_2	1.7	89.6	8.6

a Ca. 100% by nmr.

β-diketone was determined by nmr and that of the phenylpyrazole (purified by gas chromatography) by mass spectrometry.

The deuterium content of the 1-phenylpyrazole was also estimated from its ^1H nmr and infrared spectra. In the nmr spectra (Figure 1) the high-field triplet is due to the central proton of the pyrazole ring and serves as a convenient reference for counting the other protons. Inspection shows that the proton which is replaced by a deuteron has a resonance located under the intense doublet near 7.62 ppm. The infrared spectra (Figure 2) of the phenylpyrazole specimens recovered from CH_3OH and CH_3OD treatment were virtually identical. In contrast, that from CD_3OD treatment showed splitting of an intense aromatic vibration (normally at 753 cm^{-1}) into two bands at *ca.* 739 and 762 cm^{-1}.

In each experiment, the recovered methanol was shown to contain formaldehyde by the chromotropic acid test. The yield of $((C_6H_5)_3P)_4Pd$ was constant at 81–86%. In each sample, the triphenylphosphine ligand contained little or no deuterium by the analysis described in the preceding experiment.

4. Bis-β-Diketonate Complex.—Bis(2,2,6,6-tetramethylheptanedionato)palladium (4.72 g) and triphenylphosphine (10.48

L_____I_____I_____I_____I_____I_____I_____I
4000 3000   2000   1500   1200   1000 900   800   700
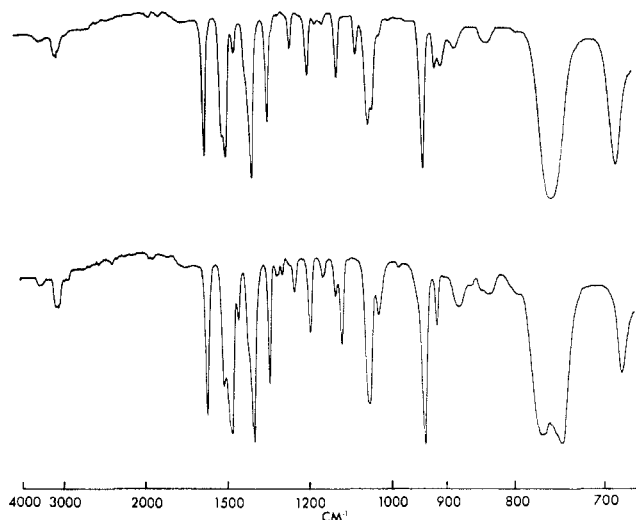   CM⁻¹

Figure 2.—Infrared spectra of phenylpyrazole (upper) and (phenyl-2-d)pyrazole (lower). Measured as thin films between sodium chloride plates.

g) in 200 ml of methanol were boiled under reflux overnight. Filtration gave 3.46 g (60%) yellow crystals of tetrakis(triphenylphosphine)palladium(0). Distillation of the filtrate gave tetramethylheptanedione, identified by its infrared spectrum.

Hydrogen and Deuterium Reactions.—In qualitative experiments, benzene solutions of the benzyldimethylamine and phenylpyrazole complexes reacted with hydrogen at 25° and 600 mm to deposit palladium metal. The hydrogenation appeared to be autocatalytic since metal deposition was rapid and quantitative once begun, but an induction period of 3–24 hr was noted before any metal appeared. The reaction was promoted by addition of a 5% palladium-on-carbon catalyst and was retarded by addition of triphenylphosphine.

1. *o*-Dimethylaminomethylphenyl(ethyl 3-ketobutyrato)palladium.[7]—A solution of 1.11 g (3.0 mmol) of the title compound in 30 ml of benzene was stirred at room temperature for 17 hr with 13 mmol of D_2. Hydrogenation appeared to be complete since the solution became colorless and 0.30 g (94%) of bright palladium metal was deposited. The solution was distilled from the metallic residue. The distillate was treated with 1.0 ml of CH_3I to give an immediate white precipitate of (benzyl-d_1)-trimethylammonium iodide, mp 183°. The proton nmr spectrum of the salt in D_2O solution showed sharp singlets at -7.42, -4.37, and -2.97 ppm (*vs.* external $(CH_3)_4Si$) in a ratio 4:2:9. For comparison, an authentic sample of undeuterated [C_6H_5-$CH_2N(CH_3)_3$]I showed the same aryl, methylene, and methyl signals in a ratio of 5:2:9. By implication, one aromatic C–H had been replaced by deuterium.

2. *o*-Dimethylaminomethylphenyl(2,2,6,6-tetramethylheptanedionato)palladium.—A solution of 0.42 g of the title compound and 1.0 g of triphenylphosphine in 20 ml of benzene was stirred at room temperature under D_2 for 7 days. The solution became deep yellow but no solid deposited. Evaporation followed by washing with ether gave a residue of 0.25 g of tetrakis-(triphenylphosphine)palladium. Oxidation with air followed by nmr analysis of the $(C_6H_5)_3PO$ in C_6D_6 solution showed no deuterium incorporation in the aryl groups of the $(C_6H_5)_3P$.

Treatment of the distillate with methyl iodide gave (benzyl-d_1)trimethylammonium iodide. As in the preceding experiment, the aryl:CH_2:CH_3 signal intensity ratio in the nmr spectrum was 4:2:9.

Results

The phenylpalladium compound **1** is readily reduced by methanol in the presence of triphenylphosphine to give a palladium(0) complex as shown in eq 1. Under


$$[(C_6H_5)_3P]_4Pd + HCHO + C_6H_6 + \text{diketone} \quad (1)$$
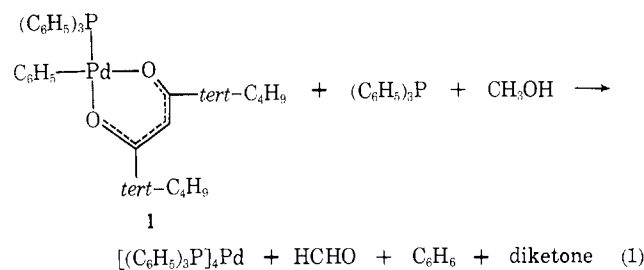
similar conditions the ortho-bonded benzyldimethylamine complex **2** and the bis-diketonate complex **3** are likewise reduced to give tetrakis(triphenylphosphine)-palladium(0) and free ligands. In each instance, formaldehyde is formed as the oxidation product of methanol. Reduction does not occur if ether is substituted for methanol.
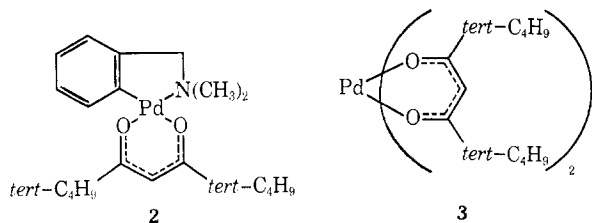
The procedure of choice for these reductions is to reflux the complex and the phosphine in excess methanol. The palladium(0) complex is insoluble and precipitates. However this procedure can be modified to use a small amount of CH_3OH in ether in order to conserve labeled methanol or to detect volatile products, such as benzene from **1**.

The benzyldimethylamine complex **2** is also reduced

by hydrogen in the presence of $(C_6H_5)_3P$ to give $[(C_6H_5)_3P]_4Pd$ and free amine. In the absence of triphenylphosphine, the amine complex is reduced to metallic palladium. The reaction is catalyzed by the metal so, after an induction period, the reaction becomes autocatalytic and rapid. Both in the presence and absence of $(C_6H_5)_3P$, hydrogenolysis of the C–Pd bond in **2** is indicated since substitution of D_2 for H_2 results in introduction of one deuterium atom into each $C_6H_5CH_2N(CH_3)_2$ ligand. In contrast to the situation with many other triphenylphosphine complexes,[8] no deuterium is incorporated in the $[(C_6H_5)_3P]_4Pd$ product. Indeed, this complex resists deuterium substitution of the aromatic rings even at 100° for several days.

$$+ \; [(C_6H_5)_3P]_4Pd \; + \; \text{diketone-}d_2 \quad (2)$$
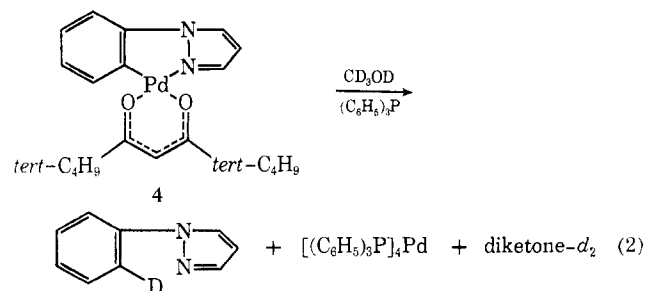
Confirmation that a similar hydrogenolysis of the C–Pd bond occurs with methanol as the reducing agent emerges from a study of the reaction of the phenylpyrazole complex **4** with deuterated methanol as in eq 2. The phenylpyrazole isolated from this reduction contains one deuterium in an ortho position, as determined from the nmr spectrum (Figure 1) in which the ortho proton signal (7.62 ppm) is reasonably well resolved. If CH_3OD is used as the reducing agent, little (<7%) deuterium is found in the recovered amine. The tetramethylheptanedione recovered from either CD_3OD or CH_3OD is dideuterated because of rapid H–D exchange between the alcohol and the enolic tautomer of the diketone.

Discussion

In previous work, cyclooctenyl[9] and π-allyl[10-12] complexes of palladium were treated with triphenylphosphine to give $[(C_6H_5)_3P]_4Pd$. The organic reaction products were those derived from coupling the allyl or cyclooctenyl radical with an anionic ligand, for example[10]

$$2[(C_6H_5)_3P]_4Pd \; + \; 2 \quad (3)$$
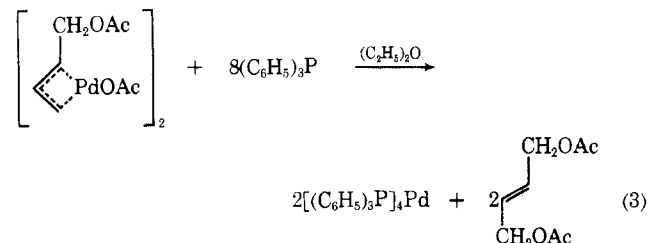
(8) G. W. Parshall, *Accounts Chem. Res.*, **3**, 139 (1970).

(9) B. F. G. Johnson, T. Keating, J. Lewis, M. S. Subramanian, and D. A. White, *J. Chem. Soc.*, 1793 (1969).

(10) B. F. G. Johnson, J. Lewis, and D. A. White, unpublished work.

(11) E. O. Fischer and H. Werner, *Chem. Ber.*, **95**, 1703 (1962).

(12) R. Hüttel and C. König, *Amer. Chem. Soc., Div. Petroleum Chem., Preprints*, **14**, B35 (1969).

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
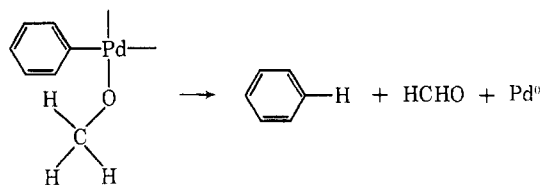
The intermediate methoxide complex is probably formed by methanolysis of the β-diketonate ligand, a selective cleavage of the O–Pd bond in preference to C–Pd like that observed with π-allylpalladium β-diketonate complexes.[13] The reduction of the C–Pd bond occurs by transfer of H from the methyl group 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

CONTRIBUTION FROM THE PRODUCT DEPARTMENT LABORATORIES,
LARKIN LABORATORY, THE DOW CHEMICAL COMPANY,
MIDLAND, MICHIGAN 48640

Dihydrotrimethylsiloxyaluminum

BY CHARLES B. ROBERTS AND DARELL D. TONER

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]

$$3LiAlH_4 + AlCl_3 \xrightarrow{(C_2H_5)_2O} 4AlH_3 \cdot (C_2H_5)_2O + LiCl\downarrow$$
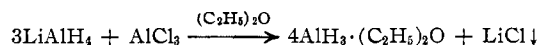
In a typical procedure, the ethereal aluminum hydride solution was prepared in a nitrogen-filled drybox. An ether solution of lithium aluminum hydride (75 ml, 1.0 M) was added to 300 ml of diethyl ether, followed by the addition of 25 ml of an ether solution of 1.0 M aluminum chloride. After stirring 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

(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).

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 $H_2AlOSi(CH_3)$.—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).