

*p*-chlorostyrenes, the above procedure performed under reduced pressure was repeated twice to complete the exchange reaction by supplying the alcohol evaporated during the first cycle. All of these complexes had no water of crystallization, and their acetone-*d*<sub>6</sub> solutions remained unchanged for 1 day at least. These complexes were all prepared in solution previously by Joy and Orchin<sup>17</sup> by cleavage of the respective dimers. However, they were not isolated or characterized.

The nmr spectra were obtained using a JNM-3H-60 spectrometer at 60 Mc and 25° and calibrated by the usual audiomodulation side-band technique. At least 10 sweeps were recorded for each spectrum, and 0.3 *M* solutions in acetone-*d*<sub>6</sub> were used with TMS as internal standard.

**Acknowledgments.**—The authors are pleased to acknowledge valuable discussions with Professor Y. Kato. Expenses for the purchase of the spectrometer were defrayed by the Ministry of Education.

(17) J. R. Joy and M. Orchin, *J. Am. Chem. Soc.*, **81**, 305 (1959).

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## Reaction of Aluminum Trimethyl with Halomethylsilanes

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The reaction of trialkylaluminum compounds with the halides of groups III–VI of the representative elements has been extensively reported in the literature.<sup>1</sup> In all cases where the reaction proceeds, it occurs readily on mixing the reactants at ambient temperature. If the reaction does not go at ambient temperature, heating to the boiling point of the reactants has no effect. The presence of sodium or potassium chloride has been found to make the reaction more satisfactory by complexing the aluminum chloride formed. Inert diluents such as hexane, benzene, and mineral oil have been used to moderate the reaction and to absorb the heat of reaction. During a series of preparative reactions of the group IV tetramethyl compounds, it was found that silicon tetrachloride did not react with aluminum chloride under the usual reaction conditions. A search of the literature showed reference<sup>2</sup> only to the reaction being carried out at 300° in an autoclave. Since aluminum trimethyl decomposes below this temperature, the latter reaction appears to be a free-radical attack of the methyl group, different from the ambient temperature mechanism. As a result of the unexpected inertness of silicon tetrachloride, the reactivity of a number of chloro- and bromo-substituted methylsilanes was studied. These are listed in Table I with the indicated result. Of the compounds studied only trimethylchlorosilane showed reactivity.

(1) (a) K. Zeigler, "Organometallic Chemistry," H. Zeiss, Ed., Reinhold Publishing Corp., New York, N. Y., 1960; (b) L. I. Zakharkin and O. Yu Okhobystin, *Zh. Obshch. Khim.*, **31**, 3662 (1961); (c) R. Koster, *Ann.*, **618**, 31 (1958).

(2) H. Jenkner, German Patent 1,034,174 (July 1958).

TABLE I

REACTION OF  $\text{Al}(\text{CH}_3)_3$  WITH HALOMETHYLSILANES

Compound	Results
$\text{SiCl}_4$	No reaction
$\text{SiBr}_4$	No reaction
$\text{Si}(\text{CH}_3)_2\text{Cl}_2$	No reaction
$\text{Si}(\text{CH}_3)_2\text{Br}_2$	No reaction
$\text{Si}(\text{CH}_3)_3\text{Cl}$	63% yield of TMS

The unreactivity of the silicon halides is not due to thermodynamic factors since the free energies are strongly favorable for all of the reactions. It would appear that the difficulty is in the formation of a transition state. Since both trimethylaluminum and more highly halogenated silanes are strong Lewis acids, the intermediate cannot be a Lewis salt. Trimethylchlorosilane is sufficiently basic to form a complex with trimethylaluminum and the reaction can proceed. It is unlikely that steric factors are important since methyl groups are larger than chlorine. Similarly the electronegativity difference between chlorine and bromine is not sufficient to affect the reactivity.

The difference in reactivity between silicon tetrachloride and the remaining group IV chlorides suggests an electronic factor may be important. The published spectroscopic energy level data for these atoms<sup>3</sup> show only small differences between corresponding energy states, varying no more than 5000 in 70,000  $\text{cm}^{-1}$ . However, silicon differs from the heavier elements of the group in the absence of ( $n - 1$ )d orbitals. Such orbitals are not so greatly different in energy from the *ns* and *np* orbitals to preclude their participation in transition states. The present work is part of a continuing study on the reactivity of the group IV halides and alkylaluminum compounds.

### Experimental Section

**Materials.**—Trimethylaluminum was obtained from the Ethyl Corp. as an 8% solution in a heavy mineral oil. This is a convenient concentration since it is not pyrophoric but only oxidizes slowly. All of the silicon compounds except silicon tetrabromide and dimethyldibromosilane were obtained from commercial sources and were used as received or diluted with mineral oil. Silicon tetrabromide was prepared by the reaction of the elements in a Vycor tube followed by distillation.<sup>4</sup> The fraction boiling at 151–153° was taken as product.

**Dimethyldibromosilane.**—This compound was prepared by the reaction of dimethoxydimethylsilane (Dow Z-6072) and acetyl bromide. The reaction was carried out in a 500-ml three-necked flask equipped with condenser, stirrer, and addition funnel. The acetyl bromide (99.4 g) was added to 38.8 g of dimethoxydimethylsilane with stirring. After the addition, the system was arranged for distillation using a Vigreux column and methyl acetate removed first followed by 42.1 g of dimethyldibromosilane, bp 108–109°, 57% theory.

**Reaction of  $(\text{CH}_3)_3\text{Al}$  and Silicon Halides.**—All of the reactions were run in a similar manner and therefore only one is described to illustrate a convenient means of handling the reactants. The reaction was carried out in a 1-l. three-necked flask equipped with stirrer, condenser and bubbler, and a 250-ml addition funnel, fitted with a Y tube leading to a nitrogen source and connecting to the trimethylaluminum cylinder. Ini-

(3) "Atomic Energy Levels," National Bureau of Standards Circular 467, U. S. Government Printing Office, Washington, D. C., 1900.

(4) G. Brauer, "Handbuch der Preparativen Anorganischen Chemie," Vol. I, F. Enke, Stuttgart, 1960, p 609.

tially 40 g of potassium chloride (oven dried) was placed in the flask and carefully heated with a yellow gas flame under flowing nitrogen. Before attaching the "Tygon" tubing line to the trimethylaluminum cylinder, the line was carefully purged with nitrogen. The nitrogen inlet was then clamped off and 500 ml of trimethylaluminum solution was allowed to run into the reaction vessel. With the storage vessels used there was enough cylinder pressure to force the liquid out but as a precaution an auxiliary nitrogen line was connected to the gas phase of the cylinder to force solution out. It was found convenient to measure the solution volume with a calibrated addition funnel. After the alkylaluminum solution was added to the reaction vessel, the remaining liquid was drained from the tubing, the nitrogen inlet was unclamped, and the addition funnel was purged for about 30 min to remove the last traces of aluminum compound. The alkylaluminum line was then clamped in two places and cut with a pliers to remove the cylinder from the system. Trimethylchlorosilane, 108 g, was placed in the addition funnel with a syringe and was then added to the reaction mixture dropwise under a slow nitrogen flow. After the addition was complete, the system was set up for distillation by removal of the addition funnel between the nitrogen inlet and flask and replacement of the reflux condenser with a distillation head, condenser, and flask. In all reactions of this type it has been found necessary to heat the reaction mixture strongly while stirring to force the reaction to completion and to distill the product. The product in the reaction being tetramethylsilane made it necessary to cool the receiver in ice. In order to free the product from traces of the trimethylaluminum, the product was redistilled to yield 55 g of product boiling at 27°, 63% yield.

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### A Chromatographic Study of the Diamine-Exchange Reaction between *trans*-Dichlorobis(diamine)cobalt(III) Compounds

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Suggested procedures for the preparation of the mixed diamine complexes *trans*-[Co(en)(pn)Cl<sub>2</sub>]Cl<sup>1</sup> and *trans*-[Co(en)(tn)Cl<sub>2</sub>]Cl<sup>2</sup> (where en = ethylenediamine, pn = propylenediamine, and tn = trimethylenediamine) call for treatment of the corresponding dinitro complexes with concentrated hydrochloric acid. Recent advances in the chromatography of diamine-cobalt(III) complexes<sup>3</sup> have stimulated a more thorough

examination of the products obtained in a preparative reaction of the type mentioned above. We have found that treatment of Co(en)(NH<sub>3</sub>)(NO<sub>2</sub>)<sub>2</sub> with an aqueous solution of propylenediamine (1:1) followed by concentrated HCl results in the formation of *trans*-[Co(en)<sub>2</sub>Cl<sub>2</sub>]Cl, *trans*-[Co(en)(pn)Cl<sub>2</sub>]Cl, and *trans*-[Co(pn)<sub>2</sub>Cl<sub>2</sub>]Cl.<sup>4</sup> Furthermore, some *trans*-[Co(en)(pn)Cl<sub>2</sub>]Cl is obtained on equilibration of a mixture of *trans*-[Co(en)<sub>2</sub>Cl<sub>2</sub>]Cl and *trans*-[Co(pn)<sub>2</sub>Cl<sub>2</sub>]Cl in aqueous HCl or methanol. In both instances a statistical distribution of diamine ligands is attained at equilibrium.<sup>5</sup> For the complexes under investigation, *trans* to *cis* isomerization and inner-sphere displacement of chloride by solvent are significant reactions in aqueous solution. Because these reactions are stoichiometrically insignificant in methanol, it was selected as the solvent for the exchange study.

We have found that the exchange of diamine between *trans*-dichlorobis(diamine)cobalt(III) compounds is relatively rapid in aqueous and methanolic solutions. This finding seriously alters the concept that the diamine ligands in such systems are nonlabile.

#### Experimental Section

Co(en)(NH<sub>3</sub>)(NO<sub>2</sub>)<sub>2</sub> and [Co(en)(pn)(NO<sub>2</sub>)<sub>2</sub>]NO<sub>2</sub> were prepared as described by Werner.<sup>6,7</sup> *trans*-[Co(en)<sub>2</sub>Cl<sub>2</sub>]Cl and *trans*-[Co(pn)<sub>2</sub>Cl<sub>2</sub>]Cl were obtained by the procedures of Bailar.<sup>8</sup> ACS reagent grade methanol containing about 0.05% water was used without drying.<sup>9</sup> Solutions of sodium methoxide in methanol were standardized by titration with aqueous HCl.

The similarities of the visible and ultraviolet spectra of the three dichlorodiamine complexes made a direct spectrophotometric determination of the extent of diamine exchange impossible. Therefore, a paper chromatographic method was developed for the separation and semiquantitative estimation of the three *trans*-dichlorodiamine complexes. A convenient total concentration of cobalt complexes in the samples to be analyzed chromatographically was 10<sup>-2</sup> M. The methanolic solutions in 1.5 × 10<sup>-2</sup> ml portions were spotted on Whatman No. 1 acid-washed paper. After evaporation of the methanol, the paper was coiled into a cylinder 25 cm long and stapled. The chromatogram was developed by standing it in a shallow container filled with 85% ethanol-15% water under a bell jar. When the solvent approached the top of the paper (6-7 hr), the chromatogram was removed from the bell jar and dried rapidly. The spots on the developed chromatogram were located by use of ultraviolet light in a darkroom. The R<sub>f</sub> values<sup>10</sup> determined for *trans*-[Co(en)<sub>2</sub>Cl<sub>2</sub>]Cl and *trans*-[Co(pn)<sub>2</sub>Cl<sub>2</sub>]Cl were 0.32 ± 0.04 and 0.60 ± 0.02, respectively. Differences of 10% in sample concentrations could be distinguished by visual comparison of the spots on a developed chromatogram. *trans*-[Co(en)<sub>2</sub>Cl<sub>2</sub>]Cl could not be differentiated from *trans*-[Co(pn)<sub>2</sub>Cl<sub>2</sub>]Cl by spot intensity. There-

(4) Contrary to the findings of Mathieu,<sup>1</sup> who reported only *trans*-[Co(en)<sub>2</sub>Cl<sub>2</sub>]Cl and *trans*-[Co(pn)<sub>2</sub>Cl<sub>2</sub>]Cl products.

(5) The statistical distribution of 1:2:1 was based on equal spot intensities for *trans*-[Co(en)<sub>2</sub>Cl<sub>2</sub>]Cl and *trans*-[Co(pn)<sub>2</sub>Cl<sub>2</sub>]Cl in the same sample and for *trans*-[Co(en)(pn)Cl<sub>2</sub>]Cl when this sample was diluted to half the original concentration. These spots were processed on the same chromatogram. In concentrated HCl at ~100° the half-time for the exchange is about 30 min.

(6) A. Werner, *Helv. Chim. Acta*, **1**, 10 (1918).

(7) L. A. P. Kane-Maguire and T. E. MacDermott, *Inorg. Chem.*, **7**, 769 (1968), have recently shown the material reported by Werner<sup>6</sup> as [Co(en)(pn)(NO<sub>2</sub>)<sub>2</sub>]NO<sub>2</sub> to consist of bisethylenediamine and bispropylenediamine complexes as well as the mixed diamine complex.

(8) J. C. Bailar, Jr., *Inorg. Syn.*, **2**, 222 (1946).

(9) Attempts to dry the methanol with magnesium resulted in an undesirable increase in basicity, which repeated distillations failed to reduce.

(10) R<sub>f</sub> is defined as the ratio of the distance the spot moved up the paper to the maximum height reached by the solvent. The initial points for both solvent and complex were taken as the center of the original spot as placed on the paper.

(1) J. P. Mathieu, *Ann. Phys. (Paris)*, **19** (11) 340 (1944).

(2) J. C. Bailar, Jr., and J. B. Work, *J. Am. Chem. Soc.*, **68**, 234 (1946).

(3) See, for example, F. P. Dwyer, *et al.*, *ibid.*, **86** 590 (1964), and earlier papers in that series.