at higher pH (10.90 and 11.39) and show no trend, although the errors are greater. We have taken $K = 5.1 \pm 0.8$ for calculation of the forward and reverse isomerization rate constants at 25° below.

In the absence of excess ethylenediamine the spectra of *cis–trans* mixtures of $Cr(en)_2(OH)_2^+$ continue to change slowly without attainment of the dihydroxo equilibrium, as noted by Woldbye. Further hydrolysis, probably with oxo-bridge formation, may be responsible; these changes were not investigated further.

Isomerization Rate.—First-order rate plots for the isomerization are shown in Fig. 1. Rate constants for the reactions

$$trans\text{-}Cr(en)_2(OH)_2^+ \underset{k_o}{\overset{k_t}{\rightleftharpoons}} cis\text{-}Cr(en)_2(OH)_2^+ \qquad (2)$$

are given in Table I. The 25° constants appear to have a small pH dependence.

TABLE I

RATE CONSTANTS FOR ISOMERIZATION OF $Cr(en)_2(OH)_2^+$

(0.10 *F* ethylenediamine, 0.10 *F* $LiClO_4$)

Temp., °C.	pH	$10^6(k_t + k_c)$, sec.$^{-1}$	10^6k_t, sec.$^{-1}$	10^6k_o, sec.$^{-1}$
25	9.95	~11[a]	~9[a]	~2[a]
	10.30	~ 8[a]	~7[a]	~1[a]
25.0	10.90	6.80 ± 0.14	5.7 ± 0.2	1.1 ± 0.2
	11.39	5.53 ± 0.11	4.6 ± 0.2	0.91 ± 0.13
35.0	10.60	28.9 ± 0.3	23 ± 1	5.7 ± 0.2

[a] Calculated by us from Woldbye's observation[2] that 46.1 and 44.6% isomerization occurs (starting with *trans*-isomer) in 21 hr. at pH 9.95 and in 27 hr. at pH 10.30, respectively, in 1 *F* $NaNO_3$.

The first and second acid dissociation constants of *cis*- and *trans*-$Cr(en)_2(OH)_2^+$ have values[2] such that less than 1% of the chromium should be present as hydroxoaquo complexes even at the lowest pH. However, the probably much greater lability of the hydroxoaquo species presumably is responsible for the small increase in observed rate constants with decreasing pH. The accuracy of the constants and the difficulty of making possible corrections for the difference in ionic strengths are such as not to warrant an attempt to deduce a quantitative rate law with a (H^+)-dependent term. Ignoring the small pH-dependence of k_t and k_c, and taking average values $10^6k_t = 5.2$ (25°), 23 (35°), $10^6k_c = 1.0$ (25°), 5.7 sec.$^{-1}$ (35°), we find $E_a \sim 27$ and ~ 32 kcal. mole^{-1} for the *trans*-to-*cis* and *cis*-to-*trans* isomerizations, respectively.

Comparison with Co Complexes.—Within 20%, $(k_t + k_c)$ found above for $Cr(en)_2(OH)_2^+$ isomerization in 0.1 *F* $LiClO_4$ (pH 10.9–11.4) at 25° is the same as observed[4,5] for isomerization of the cobalt(III) analog in 0.5–1 *F* NaOH at 25°. At 35°, $(k_t + k_c)$ is 1.5-fold smaller than the value reported[6] for the cobalt analog in 0.01–1 *F* NaOH ($\mu = 1$, $NaClO_4$). At 25°, *K* for $Cr(en)_2(OH)_2^+$ isomerization is ~6 times greater than was found[4,5] for the cobalt system.

This close similarity in isomerization behavior suggests that the isomerization mechanisms are the same for these complexes. Kruse and Taube[5] have discussed the mechanism for the cobalt case in terms of two different paths, based partly on their finding that although water exchange occurs on isomerization, the exchange corresponds to less than one molecule of water exchanged on the average per act of isomerization. They propose the possibility that one path may correspond to a $Co–OH^-$ bond scission and the other to a $Co–NH_2$ bond scission in the activated complex. Water-exchange experiments would be required for the chromium system to see if such an interpretation is permitted for that system.

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Trimethylsilyl-, Trimethylgermyl-, and Trimethylstannylbenzene Chromium Tricarbonyl

BY DIETMAR SEYFERTH[1a] AND DAVID L. ALLESTON[1b]

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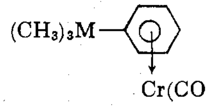
In connection with our study of germanium-containing transition metal organic compounds[2] we have prepared the trimethylsilyl-, trimethylgermyl-, and trimethylstannylbenzene tricarbonyl derivatives of chromium (I, II, and III) by the reaction of the



I, M = Si
II, M = Ge
III, M = Sn

trimethylphenyl compounds of silicon, germanium, and tin with chromium hexacarbonyl. This general procedure has been reported previously by several research groups.[3-5] The infrared spectrum of I has been reported,[6] but details concerning its preparation and physical properties were not given.

We investigated briefly the possibility of carrying out a transmetalation reaction between III and phenyllithium in ether at low temperature, since selective attack by the lithium reagent at the tin–phenyl linkage could give a chromium carbonyl complex of phenyllithium. Carbonation of the reaction mixture, however, gave no benzoic acid chromium tricarbonyl, and it is thus likely that attack by phenyllithium occurred

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[2] D. Seyferth, H. P. Hofmann, R. Burton, and J. F. Helling, *Inorg. Chem.*, **1**, 227 (1962).

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[5] M. C. Whiting and B. Nicholls, *Proc. Chem. Soc.*, 152 (1958); *J. Chem. Soc.*, 551 (1959).

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at the carbonyl groups rather than at the tin–carbon bond.

Experimental[7]

Preparation of Starting Materials.—Trimethylphenylgermane was prepared in 75% yield by the reaction of C_6H_5MgBr with $(CH_3)_3GeI$ in an ether–toluene solvent system; b.p. 182–184° (lit.[8] 182°), $n^{25}\text{D}$ 1.5045.

Anal. Calcd. for $C_9H_{14}Ge$: C, 55.49; H, 7.24. Found: C, 55.65; H, 7.20.

Trimethylphenyltin was prepared in 78% yield by the reaction of CH_3MgBr with $C_6H_5SnCl_3$ (Metal & Thermit Corp.) in tetrahydrofuran; b.p. 76.5° at 0.9 mm., $n^{25}\text{D}$ 1.5330. This compound was prepared previously[9] in 35% yield, but no physical constants were recorded.

Trimethylsilylbenzene Chromium Tricarbonyl.—A mixture of $Cr(CO)_6$ (2.2 g., 10 mmoles) and 10 ml. of $(CH_3)_3SiC_6H_5$ was maintained at 170–175° for 36 hr. under an argon atmosphere in a flask equipped with an air condenser topped with a water-cooled condenser. During this time the $Cr(CO)_6$ which sublimed into the air condenser was periodically pushed back into the reaction flask with a long spatula. A yellow color developed slowly in the reaction mixture, and a small amount of solid formed. The mixture then was cooled and diluted with 100 ml. of ether. Filtration through a short column of deactivated alumina was followed by removal of volatiles at reduced pressure. The yellow crystalline residue was recrystallized from aqueous ethanol to give 0.56 g. (20%) of I, m.p. 72–73°. An analytical sample was sublimed at 60–65° at 0.01 mm.

Anal. Calcd. for $C_{12}H_{14}O_3SiCr$: C, 50.33; H, 4.93. Found: C, 50.83; H, 4.86.

The infrared spectrum (10% solution in cyclohexane) showed carbonyl absorption at 1987 and 1911 cm.$^{-1}$ (lit.[6] 1982 and 1911 cm.$^{-1}$), bands due to the trimethylsilyl group (1250, 840, and 757 cm.$^{-1}$), and a band characteristic of the Si–phenyl linkage at 1105 cm.$^{-1}$.[10]

Trimethylgermylbenzene Chromium Tricarbonyl.—Chromium hexacarbonyl (10 mmoles) and $(CH_3)_3GeC_6H_5$ (1.95 g., 10 mmoles) were heated under argon in anhydrous ethylene glycol dimethyl ether (10 ml.) at 155° for 26 hr., and the sublimed hexacarbonyl was returned to the flask in the usual manner. A green solid formed slowly. The residue obtained by filtration and evaporation of the filtrate at reduced pressure was recrystallized from ethanol-water. Yellow crystals of II, 1.12 g. (34%), m.p. 79–79.5°, were obtained. Sublimation (70°, 0.001 mm.) gave pure material, m.p. 79.5–80°.

Anal. Calcd. for $C_{12}H_{14}O_3GeCr$: C, 43.56; H, 4.27. Found: C, 43.37; H, 4.26.

Its infrared spectrum showed carbonyl absorption at 1985 and 1910 cm.$^{-1}$ and a band due to the Ge–phenyl linkage at 1082 cm.$^{-1}$.[10]

Trimethylstannylbenzene Chromium Tricarbonyl.—The procedure described above was used in the reaction of 10 mmoles of $Cr(CO)_6$ and 3.61 g. (15 mmoles) of $(CH_3)_3SnC_6H_5$ in 10 ml. of anhydrous ethylene glycol dimethyl ether. The heating period (155°) was 43 hr., and again green solid was formed. The crude residue was recrystallized from ethanol–water and from petroleum ether at −40° to give 1.28 g. (34%) of shiny yellow crystals of III, m.p. 77–77.5°. Further purification by slow sublimation at 65–70° at 0.001 mm. raised the m.p. to 78.5–79°.

Anal. Calcd. for $C_{12}H_{14}O_3SnCr$: C, 38.23; H, 3.74. Found: C, 38.25; H, 3.83.

The infrared spectrum of the product showed carbonyl absorption at 1984 and 1908 cm.$^{-1}$ and a band characteristic of the tin–phenyl system at 1066 cm.$^{-1}$.[10]

III, as well as its silicon and germanium analogs, appeared to be stable in air in the solid state. In solution, however, all three compounds were decomposed by air. None was very stable thermally; during the sublimations mentioned above, some decomposition always appeared to occur.

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[7] All reactions were carried out under an atmosphere of argon or prepurified nitrogen. Melting points are uncorrected. Analyses by the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y., and by A. Schoeller, Kronach, Ofr.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF
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The Cleavage of Hexamethyldisiloxane and Hexamethyldigermoxane by Methyllithium: A Convenient Preparation of Lithium Trimethylsilanolate and Lithium Trimethylgermanolate[1]

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Although the cleavage of organosiloxanes by organolithium reagents is known,[3] this reaction has found no synthetic application to the preparation of lithium silanolates.

$$R_3SiOSiR_3 + R'Li \longrightarrow R_3SiOLi + R_3SiR'$$

In the examples reported,[3] the siloxanes and lithium reagents used did not constitute a system favorable for synthetic purposes, since a tetraorganosilane of relatively high molecular weight also was formed in the reaction.

It seemed to us that this apparently general reaction could find synthetic utility, especially in the preparation of lithium trimethylsilanolate. None of the procedures for preparing alkali metal silanolates is wholly satisfactory.[4] Thus some methods are based on the use of trimethylsilanol, a silicon intermediate which is not commercially available, while the best method for sodium trimethylsilanolate based on the commercially available hexamethyldisiloxane requires a reaction in liquid ammonia.

We find that the cleavage of hexamethyldisiloxane with one molar equivalent of methyllithium in an

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[1] Presented in part at the Colloque International de Chimie Organique du Centre de la Recherche Scientifique, Paris, Sept. 24–28, 1962.

[2] (a) Alfred P. Sloan Research Fellow; (b) Fellow of the M.I.T. School for Advanced Study, 1961–1962.

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