

Mechanism of Carbene Insertion into Group 4 Element Hydrides *via* Chromium Carbene Complexes. Part II.† Organogermanium and Organotin Hydrides

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The kinetics of the reaction between various chromium carbene complexes $[\text{Cr}(\text{CO})_5\{\text{C}(\text{X})(\text{C}_6\text{H}_4\text{Y})\}]$ ($\text{X} = \text{OMe}$ or NC_4H_8 ; $\text{Y} = p\text{-OMe}$, $p\text{-Cl}$, or H) and ER_3H ($\text{E} = \text{Ge}$, $\text{R} = \text{Et}$ or Ph ; $\text{E} = \text{Sn}$, $\text{R} = \text{Bu}^n$ or Ph) in the presence of pyridine in hexane solution have been measured by i.r. spectrophotometry under pseudo-first-order conditions in the range 260–330 K. The results are compared with those for analogous silicon hydrides ($\text{E} = \text{Si}$, $\text{R} = \text{Et}$ or Ph). The variation in the rate of the reaction ($\text{E} = \text{Si} < \text{Ge} \ll \text{Sn}$) is explained in terms of an increasingly favourable concerted process in the second-order contribution to the rate equation, which results from the increasing ability of E to achieve five-co-ordination. This is supported by the observed variation in the activation parameters ΔH_2^\ddagger and ΔS_2^\ddagger . The influence of substituents at both the carbene carbon and the element E has been examined; it is shown that the reaction is assisted by electron withdrawal from the former and electron donation to the latter site. There is no evidence to support the intervention of free-radical intermediates in these reactions.

METAL carbene complexes of the type $[\text{M}(\text{CO})_5\{\text{C}(\text{X})(\text{C}_6\text{H}_4\text{Y})\}]$ ($\text{M} = \text{Cr}$, Mo , or W ; $\text{X} = \text{OMe}$ or NC_4H_8 ; $\text{Y} = p\text{-OMe}$, $p\text{-Me}$, or $p\text{-Cl}$) react with Group 4 element hydrides ER_3H ($\text{E} = \text{Si}$, Ge , or Sn), in the presence of pyridine, to give the carbene-insertion compound $\text{ER}_3\text{-}[\text{CH}(\text{X})(\text{C}_6\text{H}_4\text{Y})]$. In preparative studies of this reaction,¹ it was observed qualitatively that the rate of reaction increases markedly down Group 4 ($\text{E} = \text{Si} < \text{Ge} < \text{Sn}$). We have discussed² the results of a kinetic study of the chromium carbene-organosilicon hydride system and we now extend this to germanium and tin hydrides. Observation of carbene insertion into the Sn-H bond is rather uncommon,³ and the present studies provide an opportunity to compare the reactivities of Si , Ge , and Sn in detail.

RESULTS AND DISCUSSION

The rate of reaction of the chromium carbene complexes $[\text{Cr}(\text{CO})_5\{\text{C}(\text{X})(\text{C}_6\text{H}_4\text{Y})\}]$ with GeR_3H ($\text{R} = \text{Et}$ or Ph) and SnR_3H ($\text{R} = \text{Bu}^n$ or Ph) in hexane solution in the presence of pyridine was given by equation (1), in which the

$$\text{Rate} = -d[\text{Cr}]/dt = k_1[\text{Cr}] + k_2[\text{Cr}][\text{E}] + k_3[\text{Cr}][\text{py}] \quad (1)$$

concentrations of the chromium complex, organoelement hydride, and pyridine are represented by $[\text{Cr}]$, $[\text{E}]$, and $[\text{py}]$ respectively. The principal products of the reaction were the complexes $[\text{Cr}(\text{CO})_5(\text{py})]$ and *cis*- $[\text{Cr}(\text{CO})_4(\text{py})_2]$, and the insertion compound $\text{ER}_3[\text{CH}(\text{X})(\text{C}_6\text{H}_4\text{Y})]$. A reaction also occurred in the absence of Group 4 element hydride, the principal products being the two pyridine complexes already mentioned and olefins of the type $[\text{C}(\text{X})(\text{C}_6\text{H}_4\text{Y})]_2$. This also occurs as an underlying reaction when Group 4 element hydrides are present in the reaction mixture but, because of the relative rates of insertion and olefin formation, olefins are only very

minor products when the insertion reaction is carried out preparatively under the conditions used here.¹

The rate equation is identical to that for the analogous reactions with SiR_3H which were discussed in Part I.² Under the conditions employed, the k_3 term in (1) made a negligible contribution to the rate equation. We determined k_1 and k_2 under pseudo-first-order conditions of excess of pyridine (kept constant) and excess of hydride (varied). For the reactions of SnR_3H , the values of k_2 were so large that k_1 could not be determined, except for the reaction of SnBu_3H with $[\text{Cr}(\text{CO})_5\{\text{CPh}(\text{NC}_4\text{H}_8)\}]$. The values of k_1 (for $\text{E} = \text{Ge}$) and k_2 (for $\text{E} = \text{Ge}$ or Sn) were determined at several temperatures in the range 260–325 K and activation parameters were obtained which are compared with those² for organosilicon analogues in Table 1.

At temperatures above *ca.* 313 K, the reactions involving germanium hydrides started to show significant deviation from the general rate equation (1). At higher temperatures a plot of pseudo-first-order rate constant ($k_{\text{obs.}}$) against $[\text{GeR}_3\text{H}]$ gave a straight line with negative gradient (*i.e.* $k_{\text{obs.}} = k_1 - k_4[\text{E}]$). We are unable to account for this behaviour. We tested the possibility that the germanium hydrides, GeR_3H , might react independently with pyridine; GePh_3H and pyridine did not react even after prolonged heating at 325 K.

The Second-order Process.—The rate constants (k_2) and activation parameters for the second-order process show considerable variation with changes in the Group 4 element (Table 1). In particular, for analogous reactions, k_2 increases in the order $\text{E} = \text{Si} < \text{Ge} \ll \text{Sn}$, the principal underlying cause being the parallel decrease in the enthalpy (ΔH_2^\ddagger). In our earlier discussion² of the mechanism of this process we suggested nucleophilic attack by the hydride hydrogen atom at the carbene carbon in the activation step, (*a*), followed by the establishment of a bond between this carbon atom and E . These elements show, in their general chemistry, an

† Part I is ref. 2.

¹ J. A. Connor, P. D. Rose, and R. M. Turner, *J. Organometallic Chem.*, 1973, **55**, 111.

² J. A. Connor, J. P. Day, and R. M. Turner, *J.C.S. Dalton*, 1976, 108.

³ M. Lesbre and R. Buisson, *Bull. Soc. chim. France*, 1957, 1204; D. Seyferth, J. M. Burlitch, H. Dertouzos, and H. D. Simmons, *J. Organometallic Chem.*, 1967, **7**, 405.

have been described ² for the silane reactions. The same qualitative observations have been made for germanium and tin hydrides. For the reactions of SnPh_3H with $[\text{Cr}(\text{CO})_5\{\text{C}(\text{C}_6\text{H}_4\text{Y})(\text{OMe})\}]$ (Table 2), k_2 decreases in the order $\text{C}_6\text{H}_4\text{Cl-4} > \text{C}_6\text{H}_5 > \text{C}_6\text{H}_4\text{OMe-4}$, parallel to the

Rate constants ^a and activation parameters ^b for the reaction ^c of [Cr(CO)₅(CPh(OMe))]₂ with ER₃H in the presence of pyridine in hexane solution

^a Defined by equation (1); k_1 in s^{-1} , k_2 in $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$; standard deviations *ca.* 4%. ^b Standard deviations: ΔH^\ddagger , 5 kJ mol^{-1} ; ΔS^\ddagger , 20 J $\text{K}^{-1} \text{mol}^{-1}$. ^c Conditions: $[\text{Cr}] = 3 \times 10^{-3}$; $[\text{py}] = 3 \times 10^{-2}$; and $[\text{E}] = 3 \times 10^{-2} - 3 \times 10^{-1} \text{mol dm}^{-3}$ ($\text{E} = \text{Si, Ge, or Sn}$).

⁴ F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' 3rd edn., Wiley, London, 1972.

the radical scavenger galvinoxyl⁵ to the same reaction mixture did not inhibit the reaction and caused only insignificant reduction in the rate of formation of $\text{SnPh}_3\text{[CHPh(OMe)]}$. Taken together, these results provide no evidence to support the intervention of free-radical intermediates in these reactions.

EXPERIMENTAL

Kinetic Measurements.—Reactions were followed by i.r. spectrophotometry, by measurement of the absorbance due to the carbene complex $[\text{Cr}(\text{CO})_5\{\text{C}(\text{X})(\text{C}_6\text{H}_4\text{Y})\}]$ at ca. 1956 cm^{-1} (A_1' carbonyl stretching mode), under pseudo-first-order conditions ($[\text{E}], [\text{py}] > 10[\text{Cr}]$). Details were presented² in Part I; in general, reactions remained essentially first order in $[\text{Cr}]$ for 2–3 half-lives and k_{obs} was calculated over the first half-life of the reaction. The rate constants k_1 and k_2 were obtained from the intercept and gradient, respectively, of plots of k_{obs} against $[\text{E}]$ in which at least two determinations of k_{obs} were made at each of at least five concentrations of Group 4 element hydride.

Materials and Methods.—Triethyliodogermane and bromotriphenylgermane were purchased from Strem Chemicals Inc., Danvers, Massachusetts, U.S.A. These halides were

* 1 G = 10^{-4} T.

⁵ P. D. Bartlett and T. Funahashi, *J. Amer. Chem. Soc.*, 1962, **84**, 2596.

converted into the hydrides⁶ by reduction with $\text{Li[AlH}_4\text{]}$ in diethyl ether. Chlorotriphenylstannane and chlorotri(n-butyl)stannane were purchased from B.D.H. and converted into the corresponding hydrides⁷ in the same way. The hydrides were purified by distillation or recrystallisation as appropriate, and characterised by microanalysis and i.r. and n.m.r. spectroscopy. The pure compounds were stored under nitrogen, in the dark, at low temperature. The chromium carbene complexes and other materials were prepared as outlined in Part I.

All experiments and manipulations and the kinetic measurements were carried out in oxygen-free dry nitrogen atmospheres. All glassware was thoroughly washed in water, acetone, and hexane and dried at 420 K prior to use.

E.s.r. spectra were recorded on a Varian V4502 spectrometer at 34.4 MHz. The magnetic field was varied from 10 to 14 kG.* The attenuator was varied from 0 to 60 dB.

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⁶ D. H. Johnson, W. H. Nebergall, and D. M. Harris, *Inorg. Synth.*, 1957, **5**, 76; J. Satgé, *Ann. Chim. (France)*, 1961, **6**, 519.

⁷ H. G. Kuivila and O. F. Beumel, *J. Amer. Chem. Soc.*, 1961, **83**, 1246; G. J. M. van der Kerk, J. G. Noltes, and J. G. A. Luijten, *J. Appl. Chem.*, 1957, **7**, 366.