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 $[Cr(CO)_5\{C(X)(C_6H_4Y)\}]$ (X = OMe or NC_4H_8; Y = *p*-OMe, *p*-Cl, or H) and ER_3H (E = Ge, R = Et or Ph; E = Sn, R = 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 (E = Si, R = Et or Ph). The variation in the rate of the reaction (E = Si < Ge $\ll$ 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 $\Delta H_2^\ddagger$ and $\Delta S_2^\ddagger$. 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 $[M(CO)_5\{C(X)(C_6H_4Y)\}]$ (M = Cr, Mo, or W; X = OMe or NC_4H_8; Y = *p*-OMe, *p*-Me, or *p*-Cl) react with Group 4 element hydrides ER_3H (E = Si, Ge, or Sn), in the presence of pyridine, to give the carbene-insertion compound $ER_3[CH(X)(C_6H_4Y)]$. In preparative studies of this reaction,[1] it was observed qualitatively that the rate of reaction increases markedly down Group 4 (E = Si < Ge < Sn). We have discussed [2] 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 $[Cr(CO)_5\{C(X)C_6H_4Y\}]$ with GeR_3H (R = Et or Ph) and SnR_3H (R = Bu^n or Ph) in hexane solution in the presence of pyridine was given by equation (1), in which the

$$\begin{aligned}\text{Rate} &= -\mathrm{d}[\mathrm{Cr}]/\mathrm{d}t \\ &= k_1[\mathrm{Cr}] + k_2[\mathrm{Cr}][\mathrm{E}] + k_3[\mathrm{Cr}][\mathrm{py}] \quad (1)\end{aligned}$$

concentrations of the chromium complex, organoelement hydride, and pyridine are represented by [Cr], [E], and [py] respectively. The principal products of the reaction were the complexes $[Cr(CO)_5(py)]$ and *cis*-$[Cr(CO)_4(py)_2]$, and the insertion compound $ER_3[CH(X)(C_6H_4Y)]$. 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 $[C(X)(C_6H_4Y)]_2$. 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 $[Cr(CO)_5\{CPh(NC_4H_8)\}]$. The values of k_1 (for E = Ge) and k_2 (for E = Ge or Sn) were determined at several temperatures in the range 260—325 K and activation parameters were obtained which are compared with those [2] 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 ($k_{obs.}$) against $[GeR_3H]$ gave a straight line with negative gradient (*i.e.* $k_{obs.} = k_1 - k_4[E]$). 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 E = Si < Ge $\ll$ Sn, the principal underlying cause being the parallel decrease in the enthalpy ($\Delta H_2^\ddagger$). In our earlier discussion [2] 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

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† 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.

increasing tendency to become five-co-ordinate[4] down the Group. We suggest that the increased reactivity of ER_3H from E = Si to Sn is probably related to this; in mechanistic terms, a concerted process becomes progressively more favourable for GeR_3H and SnR_3H. At the limit, H–C and C–Sn bond formation might occur in the activation process, simultaneously with H–Sn bond rupture, (*b*).

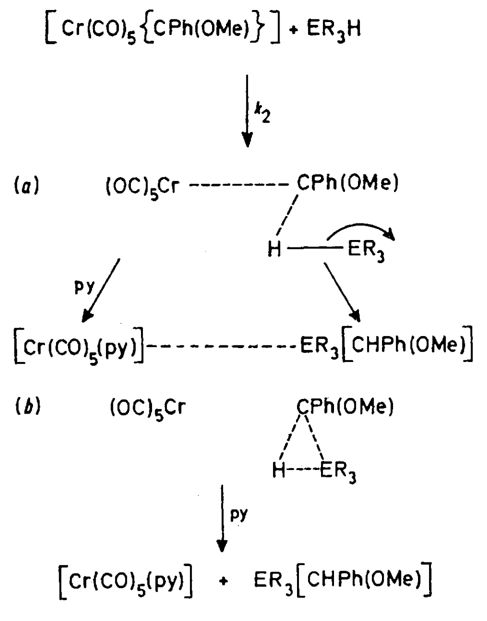
TABLE 1

Rate constants[a] and activation parameters[b] for the reaction[c] of $[Cr(CO)_5\{CPh(OMe)\}]$ with ER_3H in the presence of pyridine in hexane solution

	$SiEt_3H$		$SiPh_3H$		$GeEt_3H$		$GePh_3H$		$SnBu_3H$	$SnPh_3H$
T/K	10^5k_1	10^5k_2	10^5k_1	10^5k_2	10^5k_1	10^5k_2	10^5k_1	10^5k_2	10^5k_2	10^5k_2
261									80 900	
267									91 000	
277									117 000	
283					0.50	12.8	0.41	8.0		
292					1.75	48.0			163 000	2 700
294	1.87	4.67	1.67	4.00			1.88	36.0		
296										4 500
298					3.30	90.0				
304	4.03	11.1	3.25	10.0	5.40	189	4.32	85.0	221 000	6 810
313	9.17	34.2	8.40	26.0	22.5	360	8.50	208		10 800
323			14.9	110						19 100
325	20.0	140								
$\Delta H^‡$/kJ mol^{-1}	64	86	60	89	84	77	73	80	16	44
$\Delta S^‡$/J K^{-1} mol^{-1}	−118	−36	−135	−29	−48	−46	−90	−42	−194	−126

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

Compared to the two-step process postulated for the silicon compounds, (*a*, E = Si), concerted processes of



the type envisaged, (*b*), could well require a lower enthalpy of activation ($\Delta H_2^‡$), and an increase in negative entropy of activation ($-\Delta S_2^‡$) could arise from the greater degree of molecular ' organisation ' required to reach the transition state.

Substituent Effects.—The effects of varying the substituent groups, both in the carbene and the hydride, 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 $[Cr(CO)_5\{C(C_6H_4Y)(OMe)\}]$ (Table 2), k_2 decreases in the order C_6H_4Cl-4 > C_6H_5 > C_6H_4OMe-4, parallel to the variation for the analogous reactions of $SiEt_3H$. A plot of k_2 against the Hammett parameter, σ_p, had a gradient $\rho = 2.7$ [*cf.* $\rho(SiEt_3H)$ 1.9] indicating that electron withdrawal from the carbene-carbon centre assists the second-order process. For the reactions of $SnBu^n{}_3H$, changing the substituent X in $[Cr(CO)_5\{CPh(X)\}]$ from OMe to NC_4H_8 causes a substantial decrease (*ca.* 10^4) in k_2. We have commented previously that such a decrease is consistent with the probable increase in (p–p) π bonding in the carbene $C–NR_2$ bond, which could result both in a decrease in the electrophilic character of the carbene-carbon centre and a decrease in the requirement for metal–carbene ($M_d \rightarrow C_{2p}$) π donation.

TABLE 2

Rate constants * at 304 K for the reaction of SnR_3H with $[Cr(CO)_5\{C(X)Z\}]$ in the presence of pyridine in hexane solution

R	X	Z	10^5k_2/dm^3 mol^{-1} s^{-1}	10^5k_1/s^{-1}
Ph	OMe	C_6H_4OMe-4	1 720	
Ph	OMe	C_6H_5	6 810	
Ph	OMe	C_6H_4Cl-4	14 210	
Bu^n	OMe	C_6H_5	221 000	
Bu^n	NC_4H_8	C_6H_5	10	0.15

* See footnotes *a* and *c* in Table 1.

When the reaction between $[Cr(CO)_5\{CPh(OMe)\}]$ and $SnPh_3H$ in the presence of pyridine was carried out in the cavity of an e.s.r. spectrometer no signal indicating the presence of a paramagnetic intermediate was observed either at room temperature or at 120 K. The addition of

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

the radical scavenger galvinoxyl[5] to the same reaction mixture did not inhibit the reaction and caused only insignificant reduction in the rate of formation of $SnPh_3$-[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 $[Cr(CO)_5\{C(X)(C_6H_4Y)\}]$ at *ca.* 1 956 cm^{-1} (A_1' carbonyl stretching mode), under pseudo-first-order conditions ([E], [py] >10[Cr]). Details were presented[2] in Part I; in general, reactions remained essentially first order in [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 [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, Massachussetts, U.S.A. These halides were converted into the hydrides[6] by reduction with $Li[AlH_4]$ in diethyl ether. Chlorotriphenylstannane and chlorotri(n-butyl)stannane were purchased from B.D.H. and converted into the corresponding hydrides[7] 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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* 1 G = 10^{-4} T.

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

[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.