Mechanism of Methoxyphenylcarbene Insertion into Group IV Element–Hydrogen Bonds *via* a Chromium Carbene Complex

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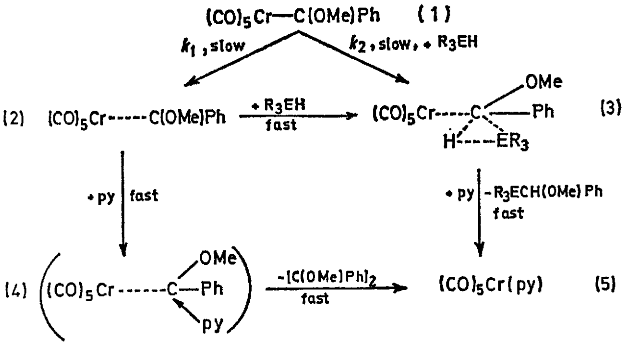
Summary Activation parameters indicate that the first-order component of the kinetic equation corresponds not to complete dissociation of the carbene ligand but rather to the production of an intermediate which is also formed in the kinetically dominant second-order process of the concerted reaction described in the title.

Triorganoelement hydrides, R_3EH (R = alkyl, aryl; E = Si, Ge, Sn), react with the chromium carbene complex, $Cr(CO)_5[C(OMe)Ph]$ (**1**), in the presence of pyridine in hexane solution to form the α-methoxybenzyl compound $R_3ECH(OMe)Ph$, as a result of insertion of [C(OMe)Ph] into the E–H bond. The chromium is isolated as $Cr(CO)_5(py)$ and *cis*-$Cr(CO)_4(py)_2$. We have studied the kinetics of this reaction by i.r. spectrophotometry using pseudo-first-order conditions in the temperature range 283—323K for the cases where E = Si, R = Et, Pr^i, Bu^n, Ph; E = Ge, R = Et, Ph; E = Sn, R = Pr^n, Ph. In each case the rate of the reaction is given by the equation, $-d[(\mathbf{1})]/dt = k_{obs}[(\mathbf{1})] = k_1[(\mathbf{1})] + k_2[(\mathbf{1})][R_3EH] + k_3[(\mathbf{1})][py]$. The value of certain rate constants and activation parameters for three examples are shown in the Table. The values of k_1 ($4 \times 10^{-5}\,s^{-1}$) and of k_3 ($2 \times 10^{-5}\,s^{-1}\,mol^{-1}\,l$) are in reasonable agreement with separate measurements on the reaction between (**1**) and pyridine, which is a parallel first- and second-order process. We also find that $Cr(CO)_5(py)$ reacts with pyridine to give *cis*-$Cr(CO)_4(py)_2$ ($k_{obs} = 4{\cdot}8 \times 10^{-5}\,s^{-1}$ at 333K) and that the activation energy for this process is *ca* 80kJ mol^{-1}.



SCHEME

The mechanism we suggest is shown in the Scheme. The activation step in the first-order (k_1) process may produce an activated species [*e.g.* (**2**)] with increased carbocationic character[2] and greater susceptibility to nucleophilic attack. Such attack, by either R_3EH or pyridine, should occur in a subsequent fast step to give either (**3**) or (**4**), respectively. The activation parameters for the slow (k_1) step suggest that the chromium–carbene bond is stretched, but *not* broken, in the transition state leading to (**2**).

The dominant reaction path leading to the product, $R_3ECH(OMe)Ph$, under our experimental conditions, is the second-order process (k_2). This could produce (**3**) directly, by nucleophilic attack on the carbocationic centre in a concerted process. The activation parameters (Table) are consistent with this view and show also that the observed increase in the rate of reaction (Si$<$Ge$<$Sn) is the result of a subtle balance of both entropy and enthalpy components in the second-order process.

TABLE

Selected rate constants and activation parameters for insertion of [C(OMe)Ph] *into* R_3EH via $Cr(CO)_5[C(OMe)Ph]$

R_3EH	$k_{obs}{}^a \times 10^5$ /s^{-1}	$k_2 \times 10^5$ /$s^{-1}\,mol^{-1}\,l$	$\Delta H^{\ddagger}{}_1$, $T\Delta S^{\ddagger}{}_1{}^b$ /kJmol^{-1}		$\Delta H^{\ddagger}{}_2$, $T\Delta S^{\ddagger}{}_2{}^b$ /kJmol^{-1}	
Et_3SiH	4·4	11	61[c]	−39[c]	77	−20
Ph_3GeH	6·7	111	61	−39	81	−11
Ph_3SnH	213	7170	(61)	(−39)	41	−38

[a] For concentrations Cr:E:py = 1:10:10 at 304K [Cr] = $3 \times 10^{-3}\,mol\,l^{-1}$. [b] T = 303K. [c] Corresponding to k_1 (303K) = $4 \times 10^{-5}\,s^{-1}$. The values in the case of Ph_3SnH are assumed.

The other second-order process (k_3) is not kinetically significant under normal conditions. It could originate from nucleophilic attack by pyridine on (**1**) to produce $Cr(CO)_5(py)$, (**5**), directly. Apart from this, the pyridine may play two distinct roles in the reaction. One is the pathway which occurs even in the absence of R_3EH, through an intermediate such as (**4**), which we postulate by analogy with the stannylene complex,[3] $Fe[SnBu^t{}_2(py)](CO)_4$ and the ylide complex,[4] $W[C(OMe)Ph(PMe_3)](CO)_5$ which were described recently. The other function of the pyridine is to assist the further reaction of (**3**), possibly through a co-ordinatively unsaturated $Cr(CO)_5$. It has been shown[5] that $Cr(CO)_5$ has a measurable life time ($>$50ns) in solution and when generated chemically in the presence of a donor ligand it is trapped very efficiently.[6]

The addition of galvinoxyl[7] to the reactions involving tin hydrides did not inhibit the reaction so that a free radical addition–dissociation–recombination sequence can be eliminated as a mechanism with some certainty. All the other features of this reaction which have been observed on a preparative scale[1] can be rationalised within the framework of the mechanism proposed. It seems likely that the principles described here will be found to apply to the mechanism of other reactions in which an α-heterocarbene is transferred from a transition-metal complex to a substrate.[8]

The insertion of dichlorocarbene from $PhHgCCl_2Br$ into R_3EH (E = Si, Ge) involves a free carbene,[9] but methylene insertion from $Hg(CH_2Br)_2$ into the same hydrides may not involve a free carbene.[10]

We thank the S.R.C. for support.

(*Received*, 7*th May* 1973; *Com.* 651.)

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