Mechanism of Carbene Insertion into Hydrides of Group 4 *via* Chromium Carbene Complexes. Part I. Organosilicon Hydrides

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Measurements of the kinetics of reaction between chromium carbene complexes, $[Cr(CO)_5\{C(X)C_6H_4Y\}]$ (X = OMe or NC_4H_8; Y = *p*-OMe, H, or *p*-Cl), and organosilicon hydrides, SiR_3H (R = Et, Pr^i, Bu^n, or Ph), in hexane solution in the presence of pyridine, to give $[Cr(CO)_5(py)]$ and $SiR_3[CH(X)(C_6H_4Y)]$ as the primary products, have been made. The reactions have been studied by i.r. spectrophotometry under pseudo-first-order conditions as a function of reagent concentration and temperature. In general, a three-term rate equation is obeyed in which the kinetically significant contributions to the insertion process comprise a first-order dissociative path, which involves a major internal rearrangement of the carbene complex, and a second-order associative path in which the organosilicon hydride acts as a nucleophile. The pattern of substituent effects at the silicon atom and at the carbene-carbon atom support this picture. The reaction between $[Cr(CO)_5(py)]$ and pyridine to give *cis*-$[Cr(CO)_4(py)_2]$ is first order in $[Cr(CO)_5(py)]$ and a predominantly dissociative mechanism is indicated.

FOLLOWING cycloaddition to multiple bonds, insertion is the next most familiar mode of reaction of carbenoids.[1] Insertion of the carbene CRR′ (R = R′ = H [2] or Ph [3]; R = H, R′ = CO_2Et [3]), formed by decomposition of the diazo-compound N_2CRR', into Si–H bonds gives the corresponding alkylsilicon compound. The synthetic, and certain mechanistic, aspects of dihalogenocarbene insertion into Si–H and, to a lesser extent, Ge–H bonds of triorganosilicon and germanium hydrides using mercury compounds have been studied by Seyferth and his co-workers.[4] More recently, the insertion of 1,2,2-trifluoroethylidene, derived from the decomposition of $Si(CF_2CHF_2)F_3$, into Si–H and Si–Cl bonds has been reported.[5] In general, these reactions are thought to involve free singlet carbenes. Other carbenoid insertions have been reported which may or may not involve free carbenes.[6]

Recently we have shown that carbene complexes of the Group 6 metals, $[M(CO)_5\{C(X)(C_6H_4Y)\}]$ (M = Cr, Mo, or W; X = OMe or NC_nH_{2n} (n = 2 or 4); Y = *p*-OMe, *p*-Me, H, or *p*-Cl), react with triorganoelement hydrides of Group 4, ER_3H (R = alkyl or aryl; E = Si, Ge, or Sn), in the presence of a co-ordinating base (pyridine or acetonitrile) in hexane solution, to form the insertion product, $ER_3[CH(X)(C_6H_4Y)]$. The reaction proceeds under mild conditions and the product is obtained in good yield.[7] We now report measurements of the

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[1] W. Kirmse, ‘Carbene Chemistry,’ 2nd edn., Academic Press, New York, 1971; ‘Carbenes,’ eds. M. Jones, jun., and R. A. Moss, Wiley, New York, 1973, vol. 1; T. L. Gilchrist and C. W. Rees, ‘Carbenes, Nitrenes and Arynes,’ Nelson, London, 1969.

[2] K. Kramer and A. N. Wright, *J. Chem. Soc.*, 1963, 3604.

[3] A. Ritter and L. H. Sommer, Internat. Symp. Organosilicon Chem., Sci. Comm., Academic of Sciences, Prague, 1965, p. 279.

[4] D. Seyferth, R. Damrauer, J. Y.-P. Mui, and T. F. Jula, *J. Amer. Chem. Soc.*, 1968, **90**, 2944; L. H. Sommer, L. A. Ulland, and G. A. Parker, *ibid.*, 1972, **94**, 3469; D. Seyferth and S. P. Hopper, *J. Organometallic Chem.*, 1973, **51**, 77 and references therein.

[5] R. N. Haszeldine, A. E. Tipping, and R. O'B. Watts, *J.C.S. Perkin I*, 1974, 2391.

[6] D. Seyferth, R. Damrauer, R. M. Turkel, and L. J. Todd, *J. Organometallic Chem.*, 1969, **17**, 367.

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

kinetics of some of these reactions and discuss possibilities for their mechanisms.

RESULTS AND DISCUSSION

The rate of reaction of the chromium carbene complexes $[Cr(CO)_5\{C(X)(C_6H_4Y)\}]$ (X = OMe or NC_4H_8; Y = *p*-OMe, H, or *p*-Cl) with various organosilicon hydrides SiR_3H (R = Et, Pr^i, Bu^n, or Ph) in hexane solution in the presence of pyridine was studied both as a function of reagent concentration and, in some cases, temperature. The principal products of the reaction are the chromium complexes $[Cr(CO)_5(py)]$ and *cis*-$[Cr(CO)_4(py)_2]$, and the insertion compound $SiR_3[CH(X)(C_6H_4Y)]$. A reaction also occurs in the absence of silane, 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 silanes are present in the reaction mixture but, because of the relative rates of insertion compared with olefin formation, under the conditions used olefins are usually only very minor products when the silane insertion is carried out preparatively.[7]

TABLE 1

Rate constants [a] and activation parameters [b] for the reactions [c] of $[Cr(CO)_5\{CPh(OMe)\}]$ with SiR_3H in the presence of pyridine in hexane solution

	$SiPh_3H$		$SiEt_3H$		$SiPr^i{}_3H$		No silane	
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
294	1.67	4.00	1.87	4.67				
304	3.25	10.0	4.03	11.1	3.56	1.55	2.96	2.70
308					4.56	2.40		
313	8.40	26.0	9.17	34.2	8.16	3.20	7.10	7.50
318					11.3	5.64	10.5	16.3
321							11.7	19.3
323	14.9	110			15.2	10.10	13.2	26.3
325			20.0	140				
328							15.5	34.8
$\Delta H^‡$/kJ mol^{-1}	59.5	88.5	64.0	85.9	62.0	75.0	56.0	96.4
$\Delta S^‡$/J K mol^{-1}	−135	−29	−118	−36	−112	−90	−145	−15

[a] Defined by equation (1); k_1 in s^{-1} and k_2 in dm^3 mol^{-1} s^{-1}; standard deviations *ca.* 3%. [b] Standard deviations: $\Delta H^‡$, 4 kJ mol^{-1}; $\Delta S^‡$, 15 J K^{-1} mol^{-1}. [c] Conditions: [Cr] = 3×10^{-3}; [py] = 3×10^{-2}; and [Si] = 3×10^{-2}—3×10^{-1} mol dm^{-3}.

For reactions of the complex $[Cr(CO)_5\{CPh(OMe)\}]$, the three-term rate equation (1) was obeyed in which

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

[Cr], [Si], and [py] represent the concentrations of carbene complex, silane, and pyridine respectively, and k_1, k_2, and k_3 are rate constants (Table 1). The reactions were carried out under pseudo-first-order conditions using excess (>10-fold) of silane and/or py. The values of, and activation parameters for, k_1 obtained for the reaction in the absence of silane are reasonably similar to those for k_1 obtained in the presence of the three silanes (Table 1). The dependence on [py] (and hence k_3) was essentially the same both in the presence and absence of silanes. The dependence on [Si] (and hence k_2) was essentially the same at various (but always excess) pyridine concentrations. We conclude that the reaction proceeds by three parallel, effectively independent, paths, each represented by one of the terms in equation (1), and we have measured the activation parameters for each.

The dependence on [py] was not measured for reactions of the other carbene complexes with various silanes (Table 2), and our observed rate law is given by equation (2). Assuming that, in fact, rate equation (1) is still valid, then $k_1' = k_1 + k_3[py]$. However, at the concentration of pyridine used, the term $k_3[py]$ is likely to be

$$-d[Cr]/dt = k_1'[Cr] + k_2[Cr][Si] \quad (2)$$

negligible (*ca.* 3% of k_1 for reactions of $[Cr(CO)_5\{CPh(OMe)\}]$). We, therefore, assumed that $k_1' \approx k_1$. These reactions were studied at one temperature only.

The rate of the reaction of $[Cr(CO)_5(py)]$ with pyridine to give *cis*-$[Cr(CO)_4(py)_2]$ followed a first-order equation, (3). This reaction occurred at a slower rate (*ca.* 10%)

$$\text{Rate} = d[Cr(CO)_5(py)]/dt = k_1[Cr(CO)_5(py)] \quad (3)$$

than the formation of $[Cr(CO)_5(py)]$ in the insertion reactions. Thus, the appearance of *cis*-$[Cr(CO)_4(py)_2]$ as a product of the insertion reactions is probably due to its formation from the $[Cr(CO)_5(py)]$ formed initially; the proposal[8] that the two products are formed by two separate reaction paths does not appear to be necessary.

TABLE 2

Rate constants * at 304 K for the reaction of SiR_3H and $[Cr(CO)_5\{C(X)Z\}]$ in the presence of pyridine in hexane solution

R	X	Z	10^5k_1/s^{-1}	10^5k_2/dm^3 mol^{-1} s^{-1}
Et	OMe	C_6H_5	4.03	11.10
Pr^i	OMe	C_6H_5	3.56	1.55
Bu^n	OMe	C_6H_5	3.65	48.0
Et	NC_4H_8	C_6H_5	0.2	0.1
Et	OMe	C_6H_4OMe-4	0.6	2.7
Et	OMe	C_6H_4Cl-4	2.2	16.7

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

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[8] E. O. Fischer, B. Heckl, and H. Werner, *J. Organometallic Chem.*, 1971, **28**, 359; B. Heckl, Dissertation, T. U. München, 1971.

Since the activation energy for formation of *cis*-$[Cr(CO)_4(py)_2]$ (Table 3) is greater than that for formation of $[Cr(CO)_5(py)]$ in the insertion reaction, the former product may predominate at higher temperatures, as was observed.[8] The form of rate equation (3), and the values of the activation parameters, suggest a predominantly dissociative (*D*) mechanism for this reaction.

We next consider the possible mechanisms for the reactions involving $[Cr(CO)_5\{CPh(OMe)\}]$, for which activation parameters have been obtained.

TABLE 3

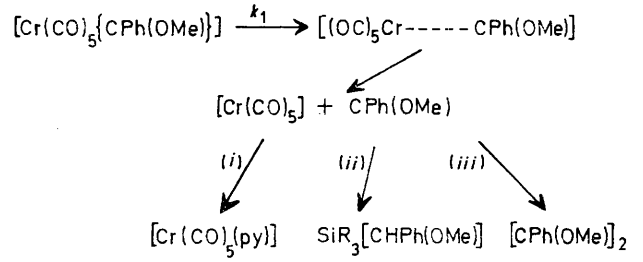
Rate constants [a] and activation parameters for the reaction [b] of $[Cr(CO)_5(py)]$ with pyridine

T/K	332	333	343	353	360
$10^5 \times$ Rate constants/s^{-1}	3.61	4.10	15.3	45.0	98.0

$\Delta H^\ddagger = 117$ kJ mol^{-1}, $\Delta S^\ddagger = 14$ J K^{-1} mol^{-1}

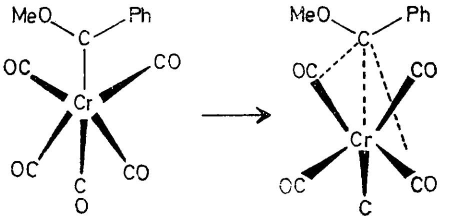
[a] Standard deviations: k, 3%; $\Delta H^\ddagger$, 3 kJ mol^{-1}; and $\Delta S^\ddagger$, 8 J K^{-1} mol^{-1}. [b] The $[Cr(CO)_5(py)]$ concentration was initially 3×10^{-3} mol dm^{-3}; pyridine concentrations were 3.0×10^{-2}, 6.0×10^{-2}, and 9.0×10^{-2} mol dm^{-3} with no significant variation in rate constant.

First-order Process (*Scheme* 1).—It seems likely that the rate-determining step is predominantly dissociative, where the carbene ligand, CPh(OMe), and $[Cr(CO)_5]$ are to some extent separated in the activation process, possibly with subsequent complete separation to free carbene and free $[Cr(CO)_5]$. The carbene would, presumably, react rapidly either with SiR_3H to form the insertion product, or with another carbene ligand to give the olefin. The $[Cr(CO)_5]$ would similarly be expected to react rapidly with pyridine forming $[Cr(CO)_5(py)]$. This type of dissociative (*D*) mechanism has previously been suggested for CO exchange [9] and triphenylphosphine substitution [10] with $[Cr(CO)_6]$. However, the activation parameters for the $[Cr(CO)_6]$ reactions ($\Delta H^\ddagger = 162$ and 160 kJ mol^{-1}, $\Delta S^\ddagger = 78$ and 74 J K^{-1} mol^{-1} for exchange and substitution, respectively) contrast with those for the k_1 path in the present system (average values: $\Delta H_1^\ddagger = 60$ kJ mol^{-1}, $\Delta S_1^\ddagger = -128$ J K^{-1} mol^{-1}). The enthalpy of activation is smaller than would be expected for rupture, or near rupture, of the Cr–C (carbene) bond; indeed values of $\Delta H_1^\ddagger$ for the first-order processes are smaller than $\Delta H_2^\ddagger$ for the second-order processes. These facts, together with the observed large negative entropies of activation, suggest that some sort of concerted intramolecular process is required for activation.



SCHEME 1 (*i*), py; (*ii*), SiR_3H; (*iii*), CPh(OMe)

We tentatively suggest a possible mechanism (Scheme 2) for this step. Studies of the structures of $[Cr(CO)_5(carbene)]$ complexes in the solid state typically show [11] that the chromium atom lies out of the plane of the four *cis*-carbonyl ligands, away from the *trans*-carbonyl and towards the carbene ligand. Supposing this structure to persist in solution, one mode of vibration involving principally the stretching of the Cr–C(carbene) bond moves the chromium atom towards the *cis*-carbonyl plane. An extension of this bond-stretching mode towards dissociation could move the chromium atom through the plane of the *cis*-carbonyl groups so that these in effect move towards the departing carbene ligand. Given a suitable orientation of the latter, two of the carbonyl ligands (*i.e.* a pair mutually *trans*) are in a position to interact with the carbene carbon atom and thus stabilise the transition state by the formation of carbonyl bridges, in a manner analogous to that recently described by Cotton.[12] The enthalpy of activation could thus be much lower than for an unassisted dissociative process, and such an internal rearrangement would presumably have a considerable organisational requirement and could well give rise to a negative entropy of activation.



SCHEME 2

The possibility that pyridine plays an active role in the first-order process cannot be ruled out entirely. A rapid equilibration, (4), with pyridine followed by a first-order rearrangement, (5), to give $[Cr(CO)_5(py)]$ and free carbene (which rapidly reacts further) would give

$$[Cr(CO)_5\{CPh(OMe)\}] + py \overset{K}{\rightleftharpoons} [Cr(CO)_5\{CPh(OMe)(py)\}] \quad (4)$$

$$[Cr(CO)_5\{CPh(OMe)(py)\}] \xrightarrow{k_1} [Cr(CO)_5(py)] + CPh(OMe) \quad (5)$$

the observed first-order term provided that formation of the proposed chromium–carbene–pyridine adduct in (4) was almost complete (say, >95%). In our kinetic experiments [py] > 10[Cr], and these conditions would be

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[9] G. Paiaro, F. Calderazzo, and R. Ercoli, *Gazzetta*, 1960, **90**, 1486.

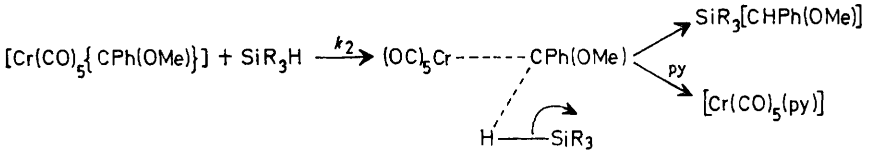
[10] H. Werner and R. Prinz, *Chem. Ber.*, 1966, **99**, 3582.

[11] D. J. Cardin, B. Cetinkaya, and M. F. Lappert, *Chem. Rev.*, 1972, **72**, 545; F. A. Cotton and C. M. Lukehart, *Progr. Inorg. Chem.*, 1972, **16**, 487; E. O. Fischer, *Angew. Chem.*, 1974, **86**, 651; J. A. Connor, *Organometallic Chem.*, 1972, **1**, 254; 1973, **2**, 302; 1975, **3**, 243; 1975, **4**, in the press.

[12] F. A. Cotton and J. M. Troup, *J. Amer. Chem. Soc.*, 1974, **96**, 1233.

fulfilled if the equilibrium constant, K, was greater than 10 $dm^3\ mol^{-1}$. Such an association would probably involve nucleophilic attack of pyridine at the carbene carbon atom, by analogy with the reactions of other donors such as phosphines[13] and $N(CH_2)_3N$[14] in which adducts have been isolated. However, we have not been able to detect the proposed association with pyridine by i.r., u.v., or ^{13}C n.m.r. spectroscopy and we feel that the mechanism represented by (4) and (5) is unlikely.

Second-order Process (*Scheme* 3).—Here, an associative process in the rate-determining step seems likely, and the activation parameters for k_2 (Table 1) are consistent with this. We envisage that the nucleophile, either the hyrdide, SiR_3H, or pyridine, interacts with the carbene carbon atom so that the Cr–C(carbene) bond is considerably weakened and lengthened in the transition state. Rapid internal rearrangement and reaction of the $[Cr(CO)_5]$ moiety with pyridine gives the observed products. Support for the view that the hydride acts as a nucleophile and attacks the electrophilic carbene carbon centre comes from a consideration of substituent effects.



SCHEME 3

Substituent Effects.—Of the factors which might influence the overall rate of the insertion reaction, the effect of varying the substituent groups, both on the carbene (X,Z) and silane (R), has been studied. A comparison of the reactivities of the hydrides, (E = Si, Ge, or Sn) will be made in a later paper.[15]

Lengthening of the alkyl chain in SiR_3H (R = Et or Bu^n; Table 2) increases the value of k_2, possibly through increased nucleophilic character of the hydridic hydrogen following from the greater electron-donor (positive-inductive) effect of Bu^n compared with Et. The substitution of Pr^i for Et (Tables 1 and 2) decreases the value of k_2 as a result of a large increase in $-\Delta S_2^{\ddagger}$, which might reasonably be ascribed to steric effects (increased crowding of the transition state). Indeed $\Delta H_2^{\ddagger}$ is lower for $SiPr^i_3H$ than for $SiEt_3H$, in line with the relative electron-donating abilities, Et < Pr^i. However, comparison of Et with Ph shows similar values of both $\Delta H_2^{\ddagger}$ and $\Delta S_2^{\ddagger}$ (and, consequently, of k_2), suggesting that electronic effects are less important than steric effects.

The heterosubstituent X (OMe or NC_4H_8) at the carbene carbon atom has been shown to exert a dominant influence on the physical properties and chemical reactions of carbene complexes of this type.[11] In line with this, the rate of insertion decreases markedly from $[Cr(CO)_5\{CPh(OMe)\}]$ to $[Cr(CO)_5\{CPh(NC_4H_8)\}]$ as shown by the values of k_1 and k_2. This is consistent with the probable increase in (p–p) π bonding in the carbene $C{-}NR_2$ bond which might 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.[11,16] Moreover, the greater thermal stability with respect to decomposition of aminocarbene complexes[17] over their alkoxycarbene analogues fits into the same pattern as the rate measurements reported here (especially k_1), namely that the M–C(carbene) bond is more difficult to disrupt in the aminocarbene complex. The large decrease in the value of k_2 for the reaction of the aminocarbene complex with $SiEt_3H$ is also what would be expected from a decrease in the electrophilicity of the carbene carbon with respect to the SiR_3H nucleophile in the second-order process.

Turning to the influence of the substituent, Y, on the values of k_1 and k_2 for reaction with $SiEt_3H$, this relatively remote *para*-substituent exerts a marked effect. The value of k_1 decreases in the order $C_6H_5 > C_6H_4Cl\text{-}4 > C_6H_4OMe\text{-}4$ in line with the increase in mesomeric donation from the substituent to the carbene centre which could serve to inhibit the extension of the Cr–C(carbene) bond in an analogous manner to that described for the aminocarbene substituent. In contrast to this, the value of k_2 decreases in the order $C_6H_4Cl\text{-}4 > C_6H_5 > C_6H_4OMe\text{-}4$, which is the same as the order of decrease of the Hammett substituent constant, σ_p. A plot of k_2 against σ_p gave a straight line of gradient $\rho = +1.9$, which indicates that the bimolecular reaction is accelerated by electron withdrawal from the reaction centre; *i.e.*, by increasing the electrophilic character of the carbene carbon it is made more susceptible to bimolecular nucleophilic attack by SiR_3H.

Conclusion.—Although the detailed pattern is more complex, the kinetically significant contributions to the insertion process are a minor first-order dissociative path, which probably involves a major internal rearrangement of the carbene complex, and a major second-order associative path in which the organosilicon hydride acts as a nucleophile and attacks at the carbene-carbon atom. The pattern of substituent effects both at silicon and at the carbene-carbon atom fully support this picture. The question of the intervention of a free carbene species in the first-order reaction appears to be rather semantic.

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[13] H. Fischer, E. O. Fischer, C. G. Kreiter, and H. Werner, *Chem. Ber.*, 1974, **107**, 2459.

[14] F. R. Kreissl and E. O. Fischer, *Chem. Ber.*, 1974, **107**, 183.

[15] J. A. Connor, J. P. Day, and R. M. Turner, in preparation.

[16] J. A. Connor, E. M. Jones, E. W. Randall, and E. Rosenburg, *J.C.S. Dalton*, 1972, 2419; G. M. Bodner, S. B. Kahl, K. Bork, B. N. Storhoff, J. F. Wuller, and L. J. Todd, *Inorg. Chem.*, 1973, **12**, 1071.

[17] J. A. Connor and J. P. Lloyd, *J. Chem. Soc.* (*A*), 1970, 3237.

A free carbene does not appear to be involved in the second-order reaction.

EXPERIMENTAL

Standard methods [11] were used to prepare the chromium carbene complexes from $[Cr(CO)_6]$. Triethylsilane was purchased from P.C.R. Inc., Gainesville, Florida, U.S.A; the other silanes were prepared by standard methods [18] from $SiCl_3H$. The complex $[Cr(CO)_6]$ was purchased from Strem Chemicals Inc., Danvers, Massachussetts, U.S.A; $SiCl_3H$ was a generous gift from I.C.I. Ltd., Organics Division. All reagents and solvents were carefully purified and characterised. Preparations and kinetic measurements were carried out in oxygen-free nitrogen atmospheres.

Kinetic Measurements.—Reactions were followed by i.r. spectrophotometry in the 2 100—1 800 cm^{-1} region, using a Perkin-Elmer model 221 (grating-interchange) spectrophotometer with digital readout and automatic data logging on punched tape. Two methods were used. For slower reactions above room temperature, reaction solutions were prepared in a Schlenk tube immersed in a thermostat and samples withdrawn at intervals by syringe. These were injected, under nitrogen, into a solution cell (0.1 mm sodium chloride plates) in the sample beam of the spectrophotometer, a matched cell in the reference beam containing the pure solvent (usually hexane). For faster reactions, and those below room temperature, a temperature-controlled i.r. cell was used in a system similar to that previously described.[19] In this case, absorbance readings were obtained automatically (maximum rate, two per second) giving usually *ca.* 300 readings per half-life of reaction. Pseudo-first-order conditions were used throughout ([Si], [py] $>$ 10[Cr]), and measurement was of the absorbance due to $[Cr(CO)_5\{CX(C_6H_4Y)\}]$ (the carbonyl-stretching mode, A_1', at *ca.* 1 956 cm^{-1}, which was in all cases entirely free from interference by other absorption bands). The data were treated by a least-squares procedure to give the optimum straight line for ln $(A_t - A_\infty)$ against time (A_t = absorbance reading at time t), for which the gradient = $-k_{obs.}$ (pseudo-first-order rate constant). The Fortran program RATEK-60 includes checks for deviation from linearity and finally calculates the rate constant over the first half-life of the reaction. The second-order rate constants (k_2 and k_3) were obtained from gradient of plots of $k_{obs.}$ against [Si] or [py], and the first-order rate constant (k_1) was obtained by extrapolation to [py] = [Si] = 0. Activation parameters were calculated for transition-state theory, plotting $\Delta G^\ddagger$ against T, using a standard least-squares procedure (Fortram program ARRHENIUS-4).

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