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BASE CLEAVAGES OF C—Si AND C—Ge BONDS IN STUDIES OF ELECTRONIC EFFECTS IN ARENECHROMIUM TRICARBONYL COMPLEXES

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Summary

Rates of cleavage by aqueous methanolic alkali have been measured for the C—MR_3 bonds in some arenechromium tricarbonyl complexes.

The complex (h^6-PhC≡$CGeEt_3$)$Cr(CO)_3$ is 16 times as reactive as the uncomplexed PhC≡$CGeEt_3$ towards a mixture of methanol (5 vol) and aqueous alkali (1 vol) at 30°, which leads to a value of +0.84 for the σ-constant of the $Cr(CO)_3$ group. The relative rates for the complexes (h^6-XC_6H_4C≡$CGeEt_3$)-$Cr(CO)_3$ with varying X correlate excellently with those for the uncomplexed XC_6H_4C≡$CGeEt_3$ compounds, showing that the $Cr(CO)_3$ group causes no distortion of the pattern of substituent effects, but the groups X have a smaller influence on the rate in the complexed series.

The aryl—$SiMe_3$ bond of the complex (h^6-$PhSiMe_3$)$Cr(CO)_3$ is much more readily cleaved by base than that in the uncomplexed $PhSiMe_3$, but the pattern of substituent effects in (h^6-$XC_6H_4SiMe_3$)$Cr(CO)_3$ complexes is consistent with that in the series $XC_6H_4SiMe_3$.

The complex (h^6-$PhCH_2SiMe_3$)$Cr(CO)_3$ is some 3×10^5 times as reactive as $PhCH_2SiMe_3$ towards methanol (5 vol) containing aqueous alkali (1 vol) at 30°, which corresponds to an approximate value of +1.12 for the σ^--constant of the $Cr(CO)_3$ group.

Introduction

Several studies have been made of the electronic effects of the $Cr(CO)_3$ group on the physical properties and reactivities of arenechromium tricarbonyl complexes. These have mainly examined two separate factors, viz. (*a*) the direct effect of the $Cr(CO)_3$ group especially on reactivity, and (*b*) the effect of the group on the influence exerted by other ring substituents.

As far as the direct effect of the $Cr(CO)_3$ group is concerned, it is usually accepted that the group frequently has an electron-withdrawing effect rather similar to that of a p-NO_2 group, as originally proposed by Nicholls and Whiting, who found that these two groups had similar effects on the dissociation constants of benzoic and phenylacetic acid [1]. Confirmation of this proposal was provided by the observation that the rate of hydrolysis of $(h^6\text{-}C_6H_5CO_2Me)Cr(CO)_3$ in 56% aqueous acetone, a reaction strongly facilitated by electron withdrawal in the aromatic ring, was identical with that of p-$NO_2C_6H_4CO_2Me$ [2], implying a σ-constant for the $Cr(CO)_3$ group of +0.78. The validity of these conclusions from the experimental evidence has been questioned, however, notably by Ceccon and Biserni [3]. Certainly in reactions in which enhanced delocalization of electrons into suitable substituents (e.g. p-NO_2) can be involved in the transition state the $Cr(CO)_3$ group seems to have a rather variable influence, as indicated by the fact that it has (*i*) a markedly smaller effect than the p-NO_2 group on the rate of elimination from $XC_6H_4CH_2CH_2Br$ and $XC_6H_4CH_2CH_2$-$OSO_2C_6H_4Me$-p compounds (the results imply a σ^--constant of + 0.74 or + 0.82 for $Cr(CO)_3$, compared with + 1.53 and/or + 1.45 for p-NO_2)[*] [3], (*ii*) essentially the same effect as the p-NO_2 group on the reactivity of chloro- and fluorobenzene towards methoxide ion in the methanol [6], and (*iii*) a markedly larger effect than the p-NO_2 group on the ionization of phenol in water; the effect corresponds with a σ^--constant of + 1.6, compared with + 1.24 for p-NO_2 [3, 7] and a σ^--constant of + 1.57 for the $Cr(CO)_3$ group can be derived from data [9] on the ionization of phenols in 50% ethanol. Furthermore, from the PMR chemical shifts of the amino-protons of anilines, a σ^--constant of + 0.71 can be derived for the $Cr(CO)_3$ group, since it has exactly the same effect as a m-NO_2 group, and a much smaller effect than the p-NO_2 group [8].

It is clear, furthermore, that in some special situations in reactions strongly assisted by electron-releasing substituents, the complexed $Cr(CO)_3$ group can also act as a source of electrons [10, 25], (σ—π) conjugation from the arene—Cr bond and/or Cr-bridging probably being mainly responsible, at least in some cases.

There is more consistency in the observations of the effect of the $Cr(CO)_3$ group on the influence of other ring substituents. In every case studied, the presence of the group markedly lowers the influence of ring substituents, and usually without any distortion from the normal pattern of substituent effects. For example, (*i*) the effects of substituents, X, in the hydrolysis of $(h^6\text{-}XC_6H_4,CO_2Me)Cr(CO)_3$ complexes correlate with σ-constants (with a slope, ρ, of +1.55) just as do those in the hydrolysis of the uncomplexed $XC_6H_4CO_2Me$ compounds (with a slope, ρ, of + 2.36) [2]; (*ii*) the PMR chemical shifts of the amino protons of $(h^6\text{-}XC_6H_4NH_2)Cr(CO)_3$ complexes correlate well with σ-, or where appropriate σ^--constants, with a markedly smaller slope than is found for the uncomplexed $XC_6H_4NH_2$ compounds [8]; (*iii*) the pK_a values of $(h^6\text{-}XC_6H_4OH)Cr(CO)_3$ complexes in 50% ethanol at 20° correlate well with σ- or σ^--constants, with a slope of 0.99, compared with one of 2.51 for the uncomplexed phenols [9]. The dampening of the influence of the X groups has

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[*] The σ^--constants derived for the p-NO_2 group by Ceccon and Biserni are markedly larger than the commonly accepted value of + 1.24. They suggested that their values represented the ability of the group to delocalize a negative charge on *carbon*, whereas the usual σ^--value is derived from reactions of phenols or amines, but we have shown that the usual σ^--constants for the p-NO_2 and other groups correlate excellently the rates of base cleavage of $XC_6H_4CH_2SiMe_3$ compounds [4, 5], in which a large degree of carbanionic character develops on the benzylic carbon atom in the transition state.

been fairly generally attributed to the large electron withdrawal by the $Cr(CO)_3$ group, which takes up so much of the negative charge developed in the transition state that relatively little is left to interact with the other substituents [2, 8]. This is equivalent to the saturation effect commonly proposed to explain departures from additivity of substituent effects in multiply substituted systems.

To obtain additional information on the electronic effects of the complexing between the aromatic ring and the $Cr(CO)_3$ group we have studied spectrophotometrically the rates of the base-cleavages of the C—M bonds in three types of system, viz. (*a*) $(h^6\text{-}XC_6H_4C{\equiv}CMR_3)Cr(CO)_3$ compounds (M = Si or Ge); (*b*) $(h^6\text{-}XC_6H_4SiMe_3)Cr(CO)_3$ compounds; and (*c*) $(h^6\text{-}PhCH_2SiMe_3)Cr(CO)_3$.

Results and discussion

(a). Cleavage of $(h^6\text{-}XC_6H_4C{\equiv}CMR'_3)Cr(CO)_3$ *compounds*

Since the acetylenic bond has been shown not to be involved in the co-ordination in $(h^6\text{-aryl-}C{\equiv}CH)Cr(CO)_3$ complexes [11], valid comparisons can be made between the effects of the substituents X in cleavage of the C—M bonds of $(h^6\text{-}XC_6H_4C{\equiv}CMR_3)Cr(CO)_3$ complexes and those in cleavage of the corresponding bonds in $XC_6H_4C{\equiv}CMR_3$ compounds.

To provide a measure of the electron-withdrawing influence of the $Cr(CO)_3$ group, the rate of cleavage of $(h^6\text{-}PhC{\equiv}CGeEt_3)Cr(CO)_3$ was first compared with that of $PhC{\equiv}CGeEt_3$ in a mixture of methanol (5 vol) and 0.20 *M* aqueous potassium hydroxide (1 vol), and it was found (see Table 1) that the complex is 16 times as reactive as the uncomplexed compound. Since a plot of log k_{rel} against σ (where k_{rel} represents the rate for the substituent compound $XC_6H_4C{\equiv}CGeEt_3$ relative to that of the parent $C_6H_5C{\equiv}CGeEt_3$) for cleavage of $XC_6H_4C{\equiv}CGeEt_3$ compounds in this medium is +1.43, the effect of the $Cr(CO)_3$ group corresponds with a σ-constant for the group of + 0.84, which is consistent with the generalization that the group has an influence rather similar to that of the p-NO_2 group ($\sigma = +0.78$) in reactions in which there is no increased demand for conjugative electron-withdrawal in the transition state, i.e. in reactions to which σ-rather than σ^--constants apply.

The pseudo-first-order rate constants, *k*, for the cleavage at 50° of $(h^6\text{-}XC_6H_4C{\equiv}CGeEt_3)Cr(CO)_3$ complexes by a mixture of methanol (5 vol) and 0.20 *M* aqueous potassium hydroxide (1 vol) are listed in Table 1, along with the values of the rate constants, k_{rel}, relative to those of the parent compound having X = H. A plot of log k_{rel} against σ for the compounds (except the one *ortho*-substituted compound) gives a fairly good line, defined by least-squares analysis as $\log k_{rel} = 0.956\sigma + 0.003$, with a correlation coefficient, *r*, of 0.973. This overall correlation is deceptive, however, since it disguises the fact that all the points lie on the line except those for X = *p*-OMe, which deviates rather badly (by 0.12 σ-units) and X = *m*-OMe, which deviates rather less (by 0.07 σ-units). The plots of log k_{rel} against σ^0 ($r = 0.999$) or σ^n ($r = 0.996$) are excellent, but we suspect that this is coincidental, and certainly no clear significance can be read into the superiority of these constants over the σ-constants, since the difference arises almost entirely from the *p*-OMe substituent. A similar deviation was observed for this substituent in the plot of log k_{rel} against σ for

TABLE 1

CLEAVAGE OF $(h^6\text{-}XC_6H_4C{\equiv}CGeEt_3)Cr(CO)_3$ COMPLEXES BY A MIXTURE OF METHANOL (5 vol) AND 0.20 *M* AQUEOUS POTASSIUM HYDROXIDE (1 vol) AT 30° [a].

X	$10^3 \times k$ (min^{-1})	k_{rel}	λ [b] (nm)
m-CF$_3$	69.8	2.75	250
m-Cl	62.0	2.44	250
m-OMe	27.9	1.10	250
H	25.4	1.0	250
m-Me	21.6	0.85	250
p-OMe	17.8	0.70	250
o-Me	15.0	0.59	250

[a] For $PhC{\equiv}CGeEt_3$, values of $10^3 \times k$, k_{rel}, and λ were 1.59 min^{-1}, 0.063, and 270.5 nm, respectively.
[b] Wavelength at which rate was measured.

the uncomplexed $XC_6H_4C{\equiv}CGeEt_3$ compounds [12], and a special explanation has been suggested for it [13], based on the probability that electrophilic attack by an incipient proton from the solvent on the carbon atom of the C—GeEt$_3$ bond plays a small but significant part in the cleavage, occurring synchronously with the cleavage of the C—GeEt$_3$ bond under the influence of the hydroxide or methoxide ion, and that this electrophilic attack is specifically facilitated by *para*-substituents with strong electron-releasing resonance effects.

The more significant feature for present purposes is that a plot of log k_{rel} for the complexed series against that for the uncomplexed series is an excellent straight line, even when the point for X = *o*-Me is included, as Fig. 1 shows; every point, except possibly that for X = *m*-OMe, is effectively on the line within the limits of experimental error. Thus there is very direct evidence that the complexing does not distort the pattern of substituent behaviour, in accord with previous conclusions.

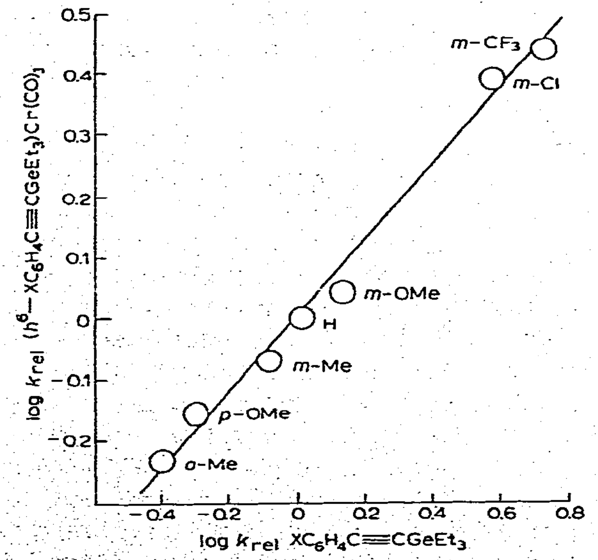

Fig. 1. Plot of log k_{rel} for the alkali cleavage of $(h^6\text{-}XC_6H_4C{\equiv}CGeEt_3)Cr(CO)_3$ versus log k_{rel} for the alkali cleavage of $XC_6H_4C{\equiv}CGeEt_3$ compounds.

The complexing once again has a marked effect on the magnitude of the effects of the substituents X; the plot in Fig. 1 has a slope of 0.625, indicating that the complexing reduces substantially the influence of the X groups. We suggest that this is *not* due to a simple saturation effect arising from the electron-withdrawal by the $Cr(CO)_3$ group, since the 16-fold activation by the group [measured by the difference in reactivity between $(h^6\text{-}C_6H_5C{\equiv}CGeEt_3)$-$Cr(CO)_3$ and $C_6H_5C{\equiv}CGeEt_3$] is most unlikely in itself to cause a significant departure from additivity of substituent effects; in other words, if such an activation were caused by a simple *m*- or *p*-substituent Y, (e.g., *p*-NO_2), little, if any, departure from substituent effect additivity would be expected for the disubstituted compounds $(X)(Y)C_6H_3C{\equiv}CGeEt_3$, and thus no significant difference in the value of ρ for varying X between the series $XC_6H_4C{\equiv}CGeEt_3$ and $(X)(Y)C_6H_3C{\equiv}CGeEt_3$. It is more likely that the $Cr(CO)_3$ group acts as an electron reservoir, absorbing a substantial proportion of the electron release by an electron-supplying substituent and releasing electrons to compensate for deficiency caused by an electron-withdrawing substituent, thus dampening down the influence of the substituents. On this picture, the $Cr(CO)_3$ group would dampen the influence of substituents even in reactions which are accelerated by electron release, whereas if the saturation effect mentioned above were dominant it should markedly enhance the substituent influences in such reactions. It is thus relevant to note that the $Cr(CO)_3$ group very greatly dampens the effect of ring methyl or methoxy groups in acid-catalysed aromatic hydrogen exchange [14], a reaction which is normally strongly accelerated by electron releasing substituents, and which is powerfully retarded by the complexing [15]*.

It is rather surprising nevertheless, that little or no distortion of the pattern of substituent effects is normally brought about by the presence of the $Cr(CO)_3$ group, especially in view of the likelihood that there will be some of the synergistic interaction of σ- and π-bonding influences which normally operates in transition metal complexes. Some minor distortions have been noted for the effects of alkyl substituents on the strengths of complexed benzoic acids [18], but the only examples of substantial distortion seem to be provided by the work of Ceccon and Sartori on the rates of reaction of $(XC_6H_4CH_2Cl)Cr(CO)_3$ complexes with sodium thiocyanate in acetone, in which rather special and conflicting effects operate [25], and by the work of Klopman and Noack on the effects of substituents X on the PMR chemical shifts of the ring protons in $(h^6\text{-}XC_6H_4\text{-}CO_2Me)Cr(CO)_3$ complexes, in which substituents capable of conjugative electron release cause quite anomalous shifts at the *meta*-position [17]. Klopman and Noack suggested that π-electron donation from the lone pair of such a group would give rise to back donation by an inductive effect from the metal atom to all the positions of the ring, including the *meta*-position. Distortions arising from this effect would clearly be greatest for *meta*-substituents such as *m*-OMe

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[*] The presence of the $Cr(CO)_3$ group also greatly dampens the influence of the substituents X in the solvolysis of $(h^6\text{-}XC_6H_4CMe_2CH_2OSO_2Me)Cr(CO)_3$ complexes as compared with those in the uncomplexed $XC_6H_4CMe_2CH_2OSO_2Me$ compounds, while causing only a small overall deactivation [16]. [The free $C_6H_5CMe_2CH_2OSO_2Me$ is 1.8 times as reactive as the complexed $(h^6\text{-}C_6H_5CMe_2\text{-}CH_2OSO_2Me)Cr(CO)_3$]. Special effects operate in this system, however, the strong stabilization of the β-carbonium ion by $(\sigma\text{—}\pi)$-conjugation from the C—Cr bonds counteracting the normal electron withdrawal.

TABLE 2

CLEAVAGE OF $(h^6\text{-}XC_6H_4SiMe_3)Cr(CO)_3$ COMPLEXES BY A MIXTURE OF METHANOL (5 vol) AND AQUEOUS POTASSIUM HYDROXIDE (1 vol) AT 50°.

X	[KOH] [b] (*M*)	$10^3 \times k$ (min^{-1})	k_{rel}	λ [b] (nm)
m-Cl	0.50	10.85	62.5	270
m-OMe	0.50	0.65	3.7	285
	10.0	14.0		285
H	10.0	3.74	1.0	259.5
m-Me	10.0	2.76	0.74	275
p-OMe	10.0	1.96	0.52	281
p-Me	10.0	0.885	0.24	264

[a] Concn. of aqueous base. [b] Wavelength at which rate was measured.

in which the inductive electron withdrawal normally dominates over conjugative electron release, and Klopman and Noack expressed surprise that an unusual influence of such *meta*-groups does not upset rate correlations. It is thus noteworthy that the largest deviation from the plot of Fig. 1, while still small, is that for the *m*-OMe group.

(b) Cleavages of $(h^6\text{-}XC_6H_4SiMe_3)Cr(CO)_3$ compounds

Base cleavage of aryl—MMe_3 bonds, where M = Si or Sn, is known to be strongly facilitated by electron withdrawal in the aryl group [13, 19], and thus it was not surprising to find that for $(h^6\text{-}XC_6H_4SiMe_3)Cr(CO)_3$ complexes rates could be measured for cleavages by a mixture of methanol (5 vol) and aqueous potassium hydroxide (0.20 *M*) at 50°, in which the reactions of the uncomplexed $XC_6H_4SiMe_3$ compounds are much too slow for study. Results for the complexes are shown in Table 2, in which the observed pseudo-first-order rate constants are shown along with the rates, k_{rel}, relative to those for $(h^6\text{-}C_6H_5SiMe_3)Cr(CO)_3$. A plot of log k_{rel} against σ (not shown) is an excellent straight line, except for the point for the *p*-OMe substituent. (The correlation coefficient, *r*, has a value of 0.997 if the *p*-OMe point is omitted). Better overall plots which include the *p*-OMe point are obtained by use of σ^0 ($r = 0.983$) or σ^n ($r = 0.990$), but again we believe that no direct significance should be attached to the superiority of the use of σ^0- or σ^n-constants since it arises wholly from the behaviour of the *p*-OMe compound. We have shown previously that the *p*-OMe group, and other *para*-substituents capable of strong conjugative electron release, have abnormal effects in this type of reaction, in which they specifically facilitate the electrophilic attack at the carbon atom of the C—MMe_3 bond [13]. While direct comparison cannot be made with cleavage of uncomplexed $XC_6H_4SiMe_3$ compounds in the medium used, in terms of the analysis we have previously made [13] the deviation of the *p*-OMe point from the log k_{rel}—σ plot is fully consistent with results for uncomplexed $XC_6H_4SiMe_3$ and $XC_6H_4SnMe_3$ compounds in other media, and thus once again the powerful activation by the

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[*] Using the symbolism defined in ref. 13, the results in Table 2 satisfactorily fit the relationship log $k_{rel} = \rho[\sigma + r\cdot\Delta^-]$, with approximate ρ and *r* values of 4.8 and 0.5 respectively, only the point for X = *p*-Me deviating significantly from the line; little significance can be attached to the *r* value, however, since it depends so heavily on the result for the *p*-OMe group.

$Cr(CO)_3$ group is not accompanied by any substantial distortion of substituent effects.

We attempted to measure the effect of the $Cr(CO)_3$ group on the reactivity by direct comparison of $(h^6\text{-PhSiMe}_3)Cr(CO)_3$ and $PhSiMe_3$ in a medium of dimethyl sulphoxide (6 vol) and 0.10 *M* aqueous potassium hydroxide (1 vol) at 30°, but the reaction was effectively complete for the complex in the time, viz. 2 min, required for the first measurement, whereas a half life of > 300 min would be expected for the uncomplexed phenyltrimethylsilane. The rate enhancement by the $Cr(CO)_3$ group is thus at least 500-fold, and is probably substantially larger.

It is appropriate at this point to note that Brown and Raju [6] initially took the powerful activation by the $Cr(CO)_3$ group in base-catalysed aromatic hydrogen exchange in liquid ammonia containing potassium amide [20] as providing support for the conclusion, based on theoretical calculations, that the $Cr(CO)_3$ group should be able to facilitate electrophilic, and not only nucleophilic, aromatic substitution [21], but later Brown and Hughes observed that the base-catalysed exchange must be regarded as nucleophilic rather than electrophilic aromatic substitution [22]. In fact the base-catalysed aromatic hydrogen-exchange and the base cleavage of aryl—MMe_3 compounds are indeed, by definition, electrophilic substitutions, in that the carbon atom retains the electrons of the broken C—H or C—MMe_3 bond in forming the new C—H bond. The transition states are, however, very different from the positively-charged Wheland intermediates which are involved in common electrophilic aromatic substitutions, and which Brown used as transition state models in his calculations [21]. We believe that electrophilic attack at carbon does, in fact, play a significant if minor role in these reactions [13] (though others have regarded the slow step of the hydrogen-exchange as involving direct proton abstraction to give the aryl carbanion [23]), but the dominant influence is the nucleophilic attack on the hydrogen or metal atom of the C—H or C—MMe_3 bond, and both reactions are very strongly facilitated by electron-withdrawal in the aromatic ring. (In the hydrogen-exchange in liquid ammonia containing potassium amide, the value of ρ, based on *meta*-substituents only [13], is ca. +9.9). The $Cr(CO)_3$ group thus facilitates these reactions by its usual powerful electron-withdrawal rather than by the electron release which would be required to facilitate common electrophilic aromatic substitutions. The $Cr(CO)_3$ group is normally thought to deactivate the ring towards ordinary electrophilic aromatic substitutions [1, 24, 26, 27], although Brown and Hughes question the validity of deductions based on acetylation results [22]. The very large reduction in the case of acid-catalysed hydrogen exchange on going from arenes to the corresponding $(h^6\text{-arene})Cr(CO)_3$ complexes [14, 15] suggests strongly that the $Cr(CO)_3$ group will normally deactivate markedly in the common types of electrophilic aromatic substitution.

(c). Cleavage of $(h^6\text{-PhCH}_2SiMe_3)Cr(CO)_3$

To provide a measure of the influence of the $Cr(CO)_3$ group in a reaction known to be very strongly accelerated by electron withdrawing groups and to require the use of σ^--constants, we examined the relative ease of cleavage of $(h^6\text{-PhCH}_2SiMe_3)Cr(CO)_3$ and $PhCH_2SiMe_3$. A direct comparison was not possible because of the large reactivity difference, and so we compared the

TABLE 3

CLEAVAGE OF m-$ClC_6H_4CH_2SiMe_3$ AND (h^6-$PhCH_2SiMe_3$)$Cr(CO)_3$ BY A MIXTURE OF METHANOL (5 vol) AND AQUEOUS POTASSIUM HYDROXIDE (1 vol) AT 30°.

Compound	[KOH] [a] (M)	$10^3 \times k$ (min^{-1})	Rel. rate [b]	λ [c] (nm)
m-$ClC_6H_4CH_2SiMe_3$	10.0	0.56	1	280
(h^6-$PhCH_2SiMe_3$)-$Cr(CO)_3$	0.50	125	880	325

[a] Concn. of the aqueous alkali. [b] A linear relationship between rate and alkali concn. is assumed. [c] Wavelength at which rate was measured.

rate of cleavage of the complex (h^6-$PhCH_2SiMe_3$)$Cr(CO)_3$ with that of the uncomplexed m-$ClC_6H_4CH_2SiMe_3$, in a mixture of methanol (5 vol) and aqueous alkali (1 vol) at 30°. The results are shown in Table 3, from which it will be seen that the complex is 4.5×10^3 times as reactive as the m-chloro-compound at 30°. The latter is 57.3 times as reactive as the parent benzyltrimethylsilane in this medium at 50°, and from activation energies derived for these two compounds in a rather similar medium [4] we can calculate that the value of k_{rel} for the m-chloro-compound would be raised to 66 at 30°, which corresponds to a value of ρ of 4.9. The complex (h^6-$PhCH_2SiMe_3$)$Cr(CO)_3$ reacts 3.0×10^5 times as rapidly as $PhCH_2SiMe_3$ at 30°, which leads to a value of ca. +1.12 for the σ^--constant for the $Cr(CO)_3$ group, and while there are approximations involved in this derivation they are unlikely to give rise to an error of as large as 0.05 σ-units. In this reaction, then, the $Cr(CO)_3$ group activates somewhat less effectively than the p-NO_2 group (for which $\sigma^- = +1.24$, a value which accurately correlates the effect of the group in this reaction [4]). It is clear, however,

TABLE 4

(h^6-$XC_6H_4C{\equiv}CMR_3$)$Cr(CO)_3$ COMPLEXES PREPARED FROM $XC_6H_4C{\equiv}CMR_3$ COMPOUNDS AND $Cr(CO)_6$

X	MR_3	M.p. (°C)	Analysis found (calcd.) (%) C	H	IR (cm^{-1}) $\nu(C{\equiv}O)$ vs		$\nu(C{\equiv}C)$ w
H	$SiEt_2Me$	52—53	56.6 (56.8)	5.5 (5.3)	1918	1982	2162
p-Me	$SiEt_3$	53—54	58.7 (59.0)	6.0 (6.0)	1918	1980	2150
p-Me	$SiMe_3$	77.5—78.5	55.5 (55.6)	5.0 (4.9)	1915	1981	2165
H	$GeEt_3$	44—45	51.5 (51.4)	5.15 (5.1)	1915	1980	2156
m-Me	$GeEt_3$	81—81.5	52.3 (52.6)	5.5 (5.4)	1913	1977	2130
o-Me	$GeEt_3$	22—24	53.1 (52.6)	5.6 (5.4)	1920	1982	2153
m-OMe	$GeEt_3$	71—72	50.4 (50.6)	5.4 (5.2)	1919	1984	2156
m-Cl	$GeEt_3$	46.5—47.5	47.5 (47.3)	4.7 (4.4)	1930	1990	2160
m-CF_3 [a]	$GeEt_3$		49.2 (49.7)	4.3 (4.4)	1938	1998	2158

[a] The identity of the product, obtained as a yellow oil which could not be induced to crystallise, was confirmed by its mass spectrum (M^+ 466; other peaks at m/e 438, 410, 382, 354, 326, 298, with expected isotope pattern).

TABLE 5

$(h^6XC_6H_4SiMe_3)Cr(CO)_3$ COMPLEXES PREPARED FROM $XC_6H_4SiMe_3$ COMPOUNDS AND $Cr(CO)_6$

X	M.p. (°C)	Analysis found (calcd.) (%)		IR (cm^{-1})	
				$\nu(C{\equiv}O)$ vs	
		C	H		
H	70—71 [a]			1910	1978
m-Me	64—65.5	52.0 (52.0)	5.6 (5.3)	1905	1975
p-Me	88.5—89.5	52.0 (52.0)	5.6 (5.3)	1905	1975
m-OMe	57—57.5	49.3 (49.4)	5.0 (5.1)	1900	1974
p-OMe	93.5—94.5	49.4 (49.4)	5.0 (5.1)	1904	1975
m-Cl	57—58.5	45.1 (44.9)	4.4 (4.1)	1924	1988

[a] Lit., [11] m.p. 72—73°.

that the $Cr(CO)_3$ group can, by delocalizing an excess of negative charge conjugated with the aromatic ring, withdraw electrons substantially more effectively than would be expected from its σ-constant, which seems to have a value in the range 0.75—0.85.

Nothing in our results seems to us to throw further light on the question of whether the effect of the $Cr(CO)_3$ group on the aromatic ring is exerted mainly through the σ-system [3, 28] or mainly through the π-system [2, 17, 23].

Carbonyl stretching frequencies in (h^6-$XC_6H_4C{\equiv}CGeEt_3$)$Cr(CO)_3$ complexes

Carbonyl stretching frequencies were measured for some of the (h^6-$XC_6H_4C{\equiv}CGeEt_3$)$Cr(CO)_3$ complexes, with the results shown in Table 5. The variations are small, but the frequencies generally increase with increasing electron withdrawal by X, as would be expected from previous work [8, 17, 29].

Experimental

General

Infrared spectra were recorded on solutions by use of 1 mm cells in conjunction with a Perkin—Elmer 257 grating spectrophotometer. Mass spectra were recorded on a Hitachi—Perkin—Elmer RU6 instrument.

Preparation of arenechromium tricarbonyl complexes

(h^6-$PhC{\equiv}CSiMe_3$)$Cr(CO)_3$. In a typical preparation, a 25 ml flask fitted with an air condenser surmounted by a water-cooled condenser was charged with $PhC{\equiv}CSiMe_3$ (1.74 g, 0.01 mole), $Cr(CO)_6$ (2.2 g, 0.01 mole) and 1,2-dimethoxyethane (10 ml), (freshly distilled from sodium). The system was degassed by a series of freezing-evacuation cycles then filled with oxygen-free nitrogen, and the flask was heated in an oil bath (125—135°) for 12 h. During this period any chromium hexacarbonyl which sublimed on to the walls of the air condenser was returned mechanically to the reaction vessel. The mixture, which gradually turned yellow, with precipitation of solid, was cooled, then diluted with light petroleum (100 ml, b.p. 40—60°) and filtered. Volatile mate-

rial was removed from the filtrate under reduced pressure and the residual yellow-brown oil was chromatographed on a 45 cm column of silica gel (B.D.H. 60—120 mesh) with protection from sunlight, light petroleum/diethyl ether being used for elution. The solid remaining after concentration of product-rich eluent fractions was recrystallised from n-pentane to give the complex (h^6-PhC$\equiv$CSiMe$_3$)Cr(CO)$_3$ (36.5%); m.p. 73—74° (lit. [11] m.p. 75—76°); IR (CCl$_4$): ν(C$\equiv$O), 1920 (vs), 1985 (vs), ν(C$\equiv$C), 2162 (w) cm^{-1}.

Details of other new (h^6-XC$_6$H$_4$C$\equiv$CMR$_3$)Cr(CO)$_3$ complexes prepared in the same way are given in Table 4. The complex (h^6-PhCH$_2$SiMe$_3$)Cr(CO)$_3$ (nc) also prepared in this way from benzyltrimethylsilane had m.p. 143—144° (Found: C, 52.3; H, 5.1. $C_{13}H_{16}CrO_3Si$ calcd.: C, 52.0; H, 5.3%). IR (CCl$_4$): ν(C$\equiv$O) 1903 (vs), 1973 (vs) cm^{-1}. New (h^6-XC$_6$H$_4$SiMe$_3$)Cr(CO)$_3$ complexes (Table 5) were synthesised by the same method except that the reaction mixture was heated at 130—140° for 48 h.

Kinetic measurements

Rates of cleavage of ethynyl—germanium and —silicon bonds and of benzyl—silicon bonds in *m*-chlorobenzyl(trimethyl)silane and in the complex (h^6-PhCH$_2$SiMe$_3$)Cr(CO)$_3$ were determined by the spectrophotometric method previously described [4]. For measurements at 50°, methanol (10 ml) and aqueous potassium hydroxide (2 ml) of appropriate strength were thoroughly mixed, and samples were transferred to 1 cm stoppered cells which were left for 10 min in a thermostatted cell-holder. A small quantity of a methanol solution of the appropriate organometallic compound (sufficient to give a concentration of ca. 10^{-4} *M* in the cleavage medium) was injected from a microsyringe. The cell was removed, shaken quickly, and replaced in the cell holder. For measurements at 30°, a ca. 10^{-4} *M* solution of the complex in methanol (10 ml) was mixed with aqueous potassium hydroxide (2 ml) and a portion transferred to the sample cell.

Optical densities, D_t, were then recorded at appropriate times, t, and suitable wavelength, λ, up to 75% of reaction. Slow decomposition of the product complexes (h^6-ArC$\equiv$CH)Cr(CO)$_3$ in the reaction media led to a drift in the 'infinity' value of optical density, D_∞, (i.e., after ten half-lives), and so first order rate constants, k_1, were evaluated by a computer programme which continuously adjusts D_∞ until the correlation coefficient for a least-squares analysis of the experimental readings, D_t expressed in the rate equation form $\log_{10}(D_t - D_\infty) = k_1 \cdot t + C$, is maximal. Rates were measured in triplicate for most compounds; because of the low overall optical density change in some of the cleavages the uncertainty in the values of the rate constants is ± 5%.

The following technique was used for most of the (h^6-XC$_6$H$_4$SiMe$_3$)-Cr(CO)$_3$ complexes. A sample of the complex (ca. 0.1 g) was dissolved in a mixture (60 ml) of methanol and aqueous potassium hydroxide of the composition specified in Table 2, contained in a 100 ml flask fitted with a rubber suba seal cap. The flask and contents were thermostatted at 50° for 10 min, and 5 ml aliquots were then withdrawn at appropriate intervals by means of a syringe and shaken with water (25 ml), dilute hydrochloric acid (5 ml), and spectroscopic grade n-hexane (10 ml). The hexane layer was separated, dried (MgSO$_4$), and irradiated for 45 min with a Hanovia 100 watt UV lamp. It was then centrifuged, and its optical density recorded at 25° at an appropriate wavelength. For runs of long half-lives, e.g., with X = *p*-OMe, and *p*-Me, separate 5 ml samples of the solution of the complex in the aqueous methanolic alkali were sealed into glass ampoules which were then placed in the thermostat.

The reliability of the method was checked in the following way. A sample of the complex (h^6-PhSiMe$_3$)Cr(CO)$_3$ (0.10 g, 0.35 mmol) in hexane (50 ml) was irradiated for 45 min and then centrifuged. The UV spectrum of the supernatant solution was recorded and found to be identical with that of a solution of trimethyl(phenyl)silane (0.35 mmol) in hexane (50 ml). Irradiation of the sample for a further 2h caused no further change in the spectrum. The work-up procedure was checked by dissolving (h^6-PhSiMe$_3$)Cr(CO)$_3$ (0.035 mmol) in a mixture of methanol (10 ml) and water (2 ml), acidifying and extracting into hexane as described above. Comparison of the UV spectrum of the dried hexane solution with that of a solution of (h^6-PhSiMe$_3$)Cr(CO)$_3$ of known strength in hexane, showed that the extraction was essentially complete in a single step.

Preparative scale cleavage

Confirmation of the nature of the base cleavage was obtained in a representative case, as follows. To a solution of the (h^6-PhC≡CSiMe$_3$)Cr(CO)$_3$ complex (0.1 g, 2.4 mmol) in methanol (50 ml) was added 0.1 *M* aqueous potassium hydroxide (20 ml) and aqueous 0.025 *M* borax (50 ml). The resulting homogeneous mixture was kept at 30° for 2 h, then water (100 ml) was added, and the organic products were extracted with ether (3 × 50 ml). The ether extracts were dried (MgSO$_4$), concentrated by evaporation, and the residue was recrystallised from n-pentane to give (h^6-PhC≡CH)Cr(CO)$_3$ (51%); m.p. 67—69° (lit., [11] m.p. 70—71°); IR (CCl$_4$): ν(C≡O), 1990 (vs), 1930 (vs), ν(C≡C), 2118 (w) cm^{-1}. NMR (CCl$_4$): τ(C$_6$H$_5$) 4.5—4.8 (5H m); (C≡C—H) 7.16 (1H, s).

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