Synthetic and Mechanistic Studies of Electrophilic Attack by the Cations $[Fe(CO)_3(1—5\text{-}\eta\text{-dienyl})]^+$ (dienyl = C_6H_7 or $2\text{-}MeOC_6H_6$) on Aryltrimethyl-silanes and -stannanes

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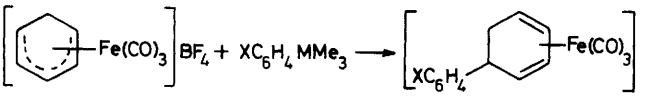
Synthetic and kinetic studies are reported for the reactions of the organometallic cations $[Fe(CO)_3(1—5\text{-}\eta\text{-dienyl})]^+$ (I) (dienyl = C_6H_7) and (III) (dienyl = $2\text{-}MeOC_6H_6$) with a wide range of aryltrimethyl-silanes and -stannanes of the type $XC_6H_4MMe_3$ (M = Si or Sn). Less extensive studies with related substrates (M = Pb or Ge), and with 2-trimethylsilyl-furan or -thiophen and allyltrimethylstannane, are also described. These provide novel routes to a variety of diene-substituted arenes and heterocycles, including the only current path to such derivatives of the less activated arenes XC_6H_5 (X = MeO, MeS, Me, F, Cl, Br, or H). The general rate law, rate = $k[Fe][XC_6H_4MMe_3]$, is rationalised in terms of electrophilic attack by cations (I) and (III) on the substrates $XC_6H_4MMe_3$. Similarly, with 2-trimethylsilylfuran the rate = $k[Fe][2\text{-}Me_3SiC_4H_3O]$. Linear free energy relationships reveal close similarities with related protiodemetallations. Rate data for the reactions of $[Fe(CO)_3(1—5\text{-}\eta\text{-}C_6H_7)]^+$ with $XC_6H_4SnMe_3$ in CH_3CN are best fitted (r = 0.98) by the Yukawa–Tsuno equation, $\log (k_X/k_H) = \rho[\sigma + 0.4(\sigma^+ - \sigma)]$, with a ρ value of −2.7. As expected, rates vary with the nature of the metal M in the order Pb ≫ Sn ≫ Ge > Si. In general, the substrates $XC_6H_4MMe_3$ are considerably more reactive towards cations (I) than are the corresponding compounds XC_6H_5. The only exceptions are the species $4\text{-}Me_2NC_6H_4MMe_3$ (M = Si or Sn), which exhibit reactivities similar to $Me_2NC_6H_5$.

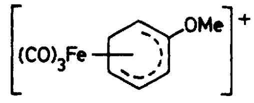
Organometallic cations such as $[Fe(CO)_3(1—5\text{-}\eta\text{-}C_6H_7)]^+$ (I) have been shown [1,2] to act as electrophiles towards a variety of activated aromatic substrates, providing novel synthetic routes to substituted arenes and heterocyclic molecules. However, cation (I) was found to be not sufficiently electrophilic to attack anisole, alkylbenzenes, or benzene itself. In attempting to extend the synthetic applications of such processes, it occurred to us that diene-substituted derivatives of the less activated arenes might be synthesised by using the reaction between (I) and the substrates $XC_6H_4MMe_3$ (M = Si or Sn). These aryltrimethyl-silanes and -stannanes are known [3] to be much more reactive towards electrophiles than the corresponding XC_6H_5 compounds.

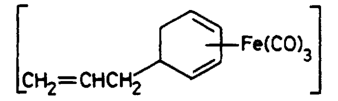
We have found that the BF_4 salt of the cation [4] (I) does indeed react readily with a range of substrates $XC_6H_4MMe_3$ according to equation (1) (M = Si, X = 4-MeO, $4\text{-}Me_2N$; M = Sn, X = H, 4-MeO, $4\text{-}Me_2N$, 4-Me, 4-SMe, 4-F, 4-Br, 4-Cl, 3-F, or $3\text{-}CF_3$; M = Ge, X = 4-MeO; M = Pb, X = H).† A preliminary account has appeared.[4] Related processes also occur between cation (I) and 2-trimethylsilylfuran, 2-trimethylsilylthiophen, and $CH_2{=}CHCH_2SnMe_3$.

Detailed kinetic studies of reactions (1) in CH_3NO_2 and CH_3CN are reported, together with more limited investigations of related processes with the cation $[Fe(CO)_3(1—5\text{-}\eta\text{-}2\text{-}MeOC_6H_6)]^+$ (III). These studies throw considerable light on the mechanisms of these novel processes, and show them to be similar to other ' demetallation ' reactions involving more normal electrophiles such as acids, halogens, acetylating agents, and sulphonating species (see ref. 3).


(I) (II)

$+ Me_3MBF_4$ (1)


(III)


(IV)

Experimental

Materials.—The BF_4 salts of (I) and (III) were prepared and purified by published procedures.[5] The substrates $XC_6H_4MMe_3$ (M = Si, Ge, Sn, or Pb) and related heterocyclic derivatives were synthesised as previously described.[6,7] Liquid substrates were generally distilled before use and their purity was checked by ^1H n.m.r. spectroscopy.

The solvents nitromethane and acetonitrile (B.D.H.) were distilled in bulk and stored over molecular sieves (size 4 Å) under dinitrogen. Immediately before preparation of the solutions, the solvents were further deoxygenated by passing a stream of dinitrogen through for 20 min.

Reaction of the Cation (I) *with* $4\text{-}Me_2NC_6H_4SnMe_3$.—The BF_4^- salt of (I) (0.090 g, 0.29 mmol) and (4-dimethylaminophenyl)trimethylstannane (0.080 g, 0.28 mmol) were dissolved in acetone (25 cm^3) at room temperature, and kept under dinitrogen for 2 h. The mixture was then evaporated to dryness and the product extracted with pentane from any unchanged dienyl salt. The yellow oily material was dissolved in

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† For simplicity, reactions (1)—(3) have been formulated as giving the species Me_3MBF_4. These products have not been identified in the present work, but it is well known that, for M = Si, the tetrafluoroborate, if formed, rapidly breaks down to Me_3SiF and BF_3.

a minimal volume of acetone and passed down an alumina (type H) column. Evaporation gave a cream-coloured solid, which was recrystallised from acetone–water to give the product *tricarbonyl*[5-(4-*dimethylaminophenyl*)*cyclohexa*-1,3-*diene*]*iron* (II; X = 4-Me_2N) as a cream powder (0.04 g, 40%), m.p. 116—117 °C (Found: C, 59.9; H, 5.0; N, 4.2. $C_{17}H_{17}FeNO_3$ requires C, 60.2; H, 5.0; N, 4.1%); ν_{CO} (Nujol) 2 045s and 1 965s cm^{-1}; *m*/*z* (electron impact) 339 ($[M]^+$), 311 ($[M - CO]^+$), 283 ($[M - 2CO]^+$), 255 ($[M - 3CO]^+$), and 253 ($[M - 3CO - H_2]^+$); τ (CD_3COCD_3) 3.00 (2 H, d, aromatic), 3.35 (2 H, d, aromatic), 4.35 (2 H, overlapping, H^2 and H^3), 6.30 (1 H, m, $H^{5'}$), 6.76 (2 H, overlapping, H^1 and H^4), 7.14 (6 H, s, CH_3), 7.45 (1 H, m, $H^{6'}$), and 7.70 (1 H, m, H^6).

Reaction of the Cation (I) *with* 4-$Me_2NC_6H_4SiMe_3$.—The BF_4^- salt of (I) (0.090 g, 0.29 mmol) and (4-dimethylaminophenyl)trimethylsilane (0.055 g, 0.29 mmol) were dissolved in acetonitrile (25 cm^3) at 45 °C and kept under dinitrogen for several hours until the i.r. spectrum indicated completion of the reaction. Similar work-up and recrystallisation to that already described gave the product (II; X = Me_2N) as a cream powder (0.04 g, 40%), m.p. 116—118 °C (Found: C, 60.4; H, 5.2; N, 3.9. Calc. for $C_{17}H_{17}FeNO_3$: C, 60.2; H, 5.0; N, 4.1%), identical (i.r., ^{1}H n.m.r., and electron impact mass spectra) with the product from the reaction with 4-$Me_2NC_6H_4SnMe_3$.

Reaction of the Cation (I) *with* 4-$MeOC_6H_4SnMe_3$.—The BF_4^- salt of (I) (0.18 g, 0.58 mmol) and (4-methoxyphenyl)trimethylstannane (0.25 g, 1.4 mmol) were dissolved in nitromethane (25 cm^3) at 45 °C and kept for several days under dinitrogen. At this stage the i.r. spectrum indicated the reaction to be complete. Evaporation gave a thick, yellow oil, which yielded a clear oil upon treatment with diethyl ether–water. Further treatment, with light petroleum (b.p. 40—60 °C) gave *tricarbonyl*[5-(4-*methoxyphenyl*)*cyclohexa*-1,3-*diene*]*iron* (II; X = MeO) as an off-white solid (0.10 g, 53%), m.p. 50.5 °C (Found: C, 58.7; H, 4.4. $C_{16}H_{14}FeO_4$ requires C, 58.9; H, 4.3%); ν_{CO} (film) 2 045s and 1 965s cm^{-1}; *m*/*z* (field desorption) 326 ($[M]^+$).

Reaction of the Cation (I) *with* CH_2=$CHCH_2SnMe_3$.—The BF_4^- salt of (I) (0.17 g, 0.55 mmol) and allyltrimethylstannane (0.10 g, 0.50 mmol) were kept in nitromethane (25 cm^3) at 45 °C under dinitrogen until the i.r. spectrum showed the reaction to be complete. Evaporation and extraction of the residue with pentane gave a solution which upon evaporation yielded (5-*allylcyclohexa*-1,3-*diene*)*tricarbonyliron* (IV) as a clear oil (0.08 g, 56%) (Found: C, 55.0; H, 4.3. $C_{12}H_{12}FeO_3$ requires C, 55.4; H, 4.6%); ν_{CO} (film) 2 045s and 1 965s cm^{-1}; *m*/*z* (field desorption) 520; τ (CD_3COCD_3) 4.48 (2 H, overlapping H^2 and H^3), 4.9—5.15 (3 H, overlapping, allyl CH_2=CH), 6.65—7.05 (3 H, overlapping, H^1, H^4, and $H^{5'}$), 7.5—7.9 (2 H, overlapping, 2 H^6), and 8.05 (2 H, allyl CH_2).

In situ *Investigation of the Reaction of the Cation* (I) *with other Species* $XC_6H_4MMe_3$ *and Related Substrates*.—In each of the other processes (1) investigated, ν_{CO} bands characteristic of the expected neutral tricarbonyl(substituted diene)iron products (II) were observed to grow at *ca.* 2 045 and 1 965 cm^{-1}. Similar i.r. spectra were noted for the products from the related reactions of (I) with 2-trimethylsilyl-furan or -thiophen. In all cases the reactions proceeded to completion as shown by the complete disappearance of the original dienyl ν_{CO} bands at 2 110 and 2 065 cm^{-1}.

Spectroscopic Studies.—^{1}H N.m.r. (90 MHz) spectra were recorded for solutions in $(CD_3)_2CO$ with a Perkin-Elmer R32 spectrophotometer. I.r. spectra were recorded with a Perkin-Elmer 257 spectrophotometer and matched 0.5-mm NaCl solution cells.

Kinetic Studies.—All the reactions (1) were studied in the dark under dinitrogen by using an i.r. sampling technique which has been previously described.[8] The disappearance of the highest frequency band of the initial dienyl salts {[Fe] = (5—6.5) × 10^{-3} mol dm^{-3}} at 2 110 cm^{-1} was monitored.

The majority of the kinetic runs were carried out under pseudo-first-order conditions employing a large excess of $XC_6H_4MMe_3$. Pseudo-first-order rate constants were calculated from the slopes of plots of log A_t *vs.* time. Such plots were generally linear for at least two half-lives. Duplicate k_{obs} values were determined in several cases, giving a reproducibility of ±5%.

However, because of the rapidity of the reactions of cations (I) and (III) with 4-$Me_2NC_6H_4SnMe_3$, it was more convenient to study them under equimolar conditions ([Fe] = [4-$Me_2NC_6H_4SnMe_3$] = 5.04 or 6.54 × 10^{-3} mol dm^{-3}). In these cases, second-order rate constants, *k*, were obtained directly from the gradients of plots of $x/a(a - x)$ *vs.* time (where a = initial concentration of dienyl salt, and x = concentration of product at time t). The plots were linear for 65—80% completion of reaction.

Enthalpies of activation were calculated from a least-squares fit to the Arrhenius equation. Errors quoted are the standard errors of estimate derived from the least-squares analyses. Entropies of activation were estimated using the second-order rate constants, *k*, at 45.0 °C.

Results and Discussion

Nature of the Reactions.—The nature of processes (1) has been confirmed by the isolation and characterization of products (II; X = 4-Me_2N or 4-MeO) from the reactions of cation (I) with $XC_6H_4MMe_3$ (M = Si or Sn), and by the growth in all cases of two strong product ν_{CO} bands at *ca.* 2 045 and 1 965 cm^{-1}. These latter peaks are characteristic of neutral tricarbonyl(diene)iron compounds. All the reactions proceed to completion, as shown by the complete disappearance of the original dienyl salt ν_{CO} bands at 2 110 and 2 065 cm^{-1}.

The ^{1}H n.m.r. spectra of the products (II) are fully consistent with neutral tricarbonyl(substituted 1,3-diene)iron species. In particular, the ^{1}H n.m.r. spectrum of (II; X = Me_2N) is identical with that reported[9] for this same compound produced *via* electrophilic attack by (I) upon *NN*-dimethylaniline. The aromatic regions of the spectra of the products (II) confirm that in both cases the tricarbonyl(diene)iron substituent is attached *para* to the group X. Thus, as found in earlier synthetic studies with substrates $XC_6H_4MMe_3$,[3] ready cleavage of the aryl–MMe_3 bonds leads to only one product isomer. A similar regioselectivity has been assumed for each of the other reactions (1) investigated here.

At low emitter currents, the field desorption (f.d.) mass spectra of products (II) exhibited only single strong peaks corresponding to the molecular ions (at *m*/*z* 339 and 326, respectively). As in f.d. mass spectral studies[9,10] of other tricarbonyl(π-hydrocarbon)metal complexes, no stepwise loss of carbonyl ligands is observed. In contrast, the electron impact mass spectrum of (II; X = 4-Me_2N) shows only a weak molecular ion peak at *m*/*z* 339 and extensive fragmentation. Significantly, the fragmentation pattern is typical of *exo*-isomers,[11] exhibiting only weak $[M - CO]^+$, $[M - 2CO]^+$, and $[M - 3CO]^+$ peaks, but an intense base peak at *m*/*z* 253 corresponding to $[M - 3CO - H_2]^+$. By analogy, *exo*-addition of each of the other $XC_6H_4MMe_3$ species to cations

Table 1. Kinetic results for reactions of cations $[Fe(CO)_3(1—5\text{-}\eta\text{-dienyl})]^+$ with substrates $XC_6H_4SnMe_3$; $[Fe] = 6.54 \times 10^{-3}$ mol dm^{-3}

X	Solvent	Temp. (°C)	$10[XC_6H_4SnMe_3]$/mol dm^{-3}	$10^5k_{obs}/s^{-1}$	10^5k/dm^3 mol^{-1} s^{-1}
Dienyl = C_6H_7					
4-Me_2N	CH_3NO_2	25.0	0.0504 [a]		1 530
		35.0	0.0504 [a]		4 210
		40.0	0.0504 [a]		5 930
		45.0	0.0504 [a]		10 000
		50.0	0.0504 [a]		15 300
	CH_3CN	45.0	0.0654		3 400
4-MeO	CH_3NO_2	45.0	1.00	1.77	17.3(0.4) [b]
		45.0	1.04	1.84	
		45.0	2.50	4.34	
		45.0	5.00	8.71	
		45.0	7.50	13.0	
	CH_3CN	45.0	1.04	0.680	6.60
4-Me	CH_3CN	45.0	1.00	0.221	2.21
4-MeS	CH_3CN	45.0	1.00	0.167	1.67
4-F	CH_3CN	45.0	5.00	0.218	0.435
H	CH_3CN	45.0	5.00	0.194	0.388
	CH_3NO_2	45.0	5.00	0.407	0.814
4-Br	CH_3CN	45.0	5.00	0.150	0.300
4-Cl	CH_3CN	45.0	5.00	0.149	0.298
3-F	CH_3CN	45.0	5.00	0.113	0.226
3-CF_3	CH_3CN	45.0	5.00	0.050	0.100
Dienyl = 2-$MeOC_6H_6$					
4-Me_2N	CH_3NO_2	45.0	0.0654		608

[a] $[Fe] = 5.04 \times 10^{-3}$ mol dm^{-3}. [b] *k* Value calculated by a least-squares fit to equation (4); value in brackets is the standard error of estimate.

Table 2. Kinetic results for reactions of cations $[Fe(CO)_3(1—5\text{-}\eta\text{-dienyl})]^+$ with substrates $XC_6H_4SiMe_3$; $[Fe] = 6.54 \times 10^{-3}$ mol dm^{-3}

X	Solvent	Temp. (°C)	$[XC_6H_4SiMe_3]$/mol dm^{-3}	$10^5k_{obs}/s^{-1}$	10^5k/dm^3 mol^{-1} s^{-1}
Dienyl = C_6H_7					
4-Me_2N	CH_3NO_2	25.0	0.050	24.5	490
		30.0	0.050	44.3	886
		35.0	0.10	146	1 460
		40.0	0.050	103	2 060
		45.0	0.050	171	3 420
	CH_3CN	20.0	0.104	7.80	75
		25.0	0.104	11.3	109
		30.0	0.104	20.0	192
		35.0	0.104	28.6	275
		40.0	0.104	40.4	383
		45.0	0.104	60.5	584
4-MeO	CH_3NO_2	45.0	1.50	0.634	0.422
	CH_3CN	45.0	1.00	0.107	0.107
Dienyl = 2-$MeOC_6H_6$					
4-Me_2N	CH_3NO_2	45.0	0.11	19.4	185(6) *
		45.0	0.25	50.6	
		45.0	0.50	91.6	
		45.0	0.80	149	

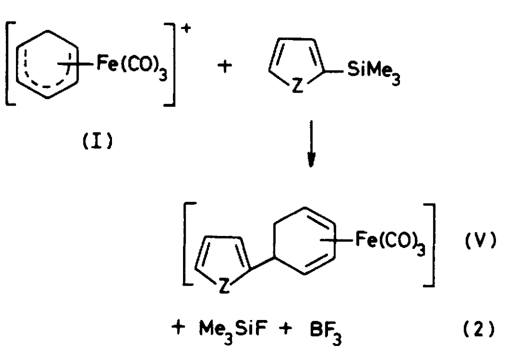
* *k* Value calculated by a least squares fit to equation (4); value in brackets is the standard error of estimate.

(I) and (III) is assumed in reactions (I). The absence of spectroscopic or kinetic evidence for intermediates (see later) further supports direct addition of $XC_6H_4MMe_3$ to the dienyl rings of cations (I) and (III).

Processes analogous to (1) were also found when the cation (I) was treated with 2-trimethylsilyl-furan or -thiophen [equation (2); Z = O or S] or allyltrimethylstannane [equation (3)]. Product (IV) from reaction (3) was isolated in 56% yield and characterised by elemental analysis and its i.r. and ^1H n.m.r. spectra. Formation of the substituted furan and thiophen derivatives (V) in reaction (2) was indicated by the appearance of two intense product ν_{CO} bands at *ca.* 2 050 and 2 070 cm^{-1} (solvent CH_3CN).

Reactions (1)—(3) reveal the wide synthetic potential of employing π-hydrocarbon cations such as (I) as electrophiles towards aryl–MMe_3 and related substrates. Except for 4-$Me_2NC_6H_4MMe_3$ (M = Si or Sn), these substrates are generally much more reactive than analogous aryl–H species towards (I) (see later). They thus provide more convenient routes to a variety of diene-substituted arenes and heterocycles, including the only current path to such derivatives of the less activated arenes XC_6H_5 (X = MeO, MeS, Me, F, Cl, Br, or H). Analogous reactions may be expected to occur with other R–MMe_3 species readily cleaved by electrophiles, such as those where R is allyl [*e.g.* equation (3)] or alkynyl.

Other cationic π-hydrocarbon metal complexes such as



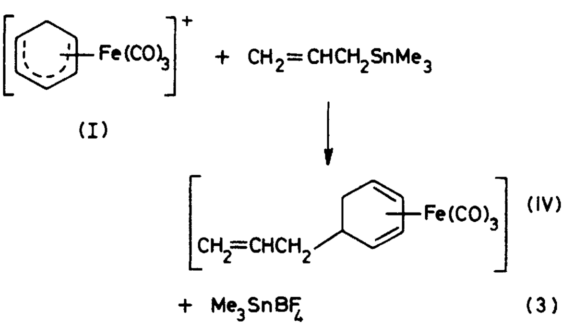
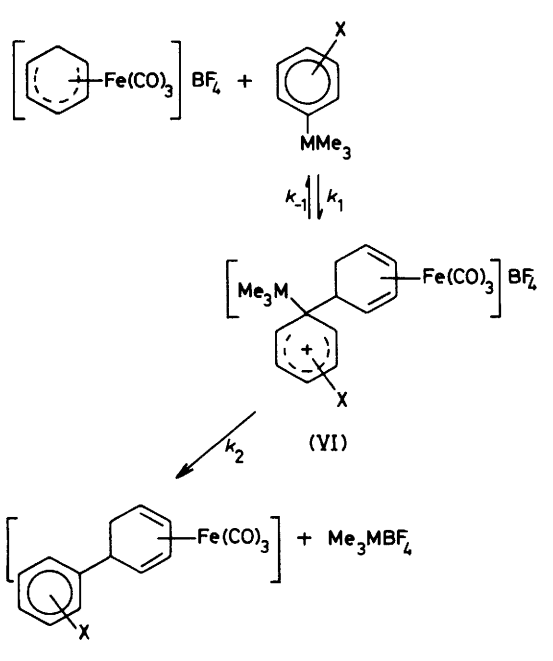


Table 3. Relative rates of attack by $[Fe(CO)_3(1—5\text{-}\eta\text{-}C_6H_7)]^+$ on $XC_6H_4MMe_3$ (M = Si, Ge, Sn, or Pb) in CH_3CN at 45.0 °C

Substrate	10^5k/ dm^3 mol^{-1} s^{-1}	k_{Sn}/k_{Si}	k_{Sn}/k_{Si} for $XC_6H_4MMe_3$ + $HClO_4$ (ref. 20)
$4\text{-}Me_2NC_6H_4SnMe_3$	3 400		
$4\text{-}Me_2NC_6H_4SiMe_3$	584	6 (3) [a]	*ca.* 20 [b]
$4\text{-}MeOC_6H_4SnMe_3$	6.60		
$4\text{-}MeOC_6H_4GeMe_3$	0.123 [c]		
$4\text{-}MeOC_6H_4SiMe_3$	0.107	62 (41) [a]	1.4×10^4
$C_6H_5PbMe_3$	358 [d]		
$C_6H_5SnMe_3$	0.388		
$C_6H_5SiMe_3$	$\ll 0.01$ [e]	≥ 40	3.5×10^5

[a] Values in brackets are for CH_3NO_2 as solvent. [b] Estimated; see text for details. [c] [Fe] = 6.5×10^{-3} mol dm^{-3}, $[4\text{-}MeOC_6H_4GeMe_3]$ = 0.50 mol dm^{-3}, $k_{obs} = 6.4 \times 10^{-7}$ s^{-1}. [d] [Fe] = 6.5×10^{-3} mol dm^{-3}, $[C_6H_5PbMe_3]$ = 0.20 mol dm^{-3}, $k_{obs} = 7.15 \times 10^{-4}$ s^{-1}. [e] No reaction observed with $[C_6H_5SiMe_3]$ = 1.0 mol dm^{-3} after 11 days in either CH_3CN or CH_3NO_2.



Scheme.

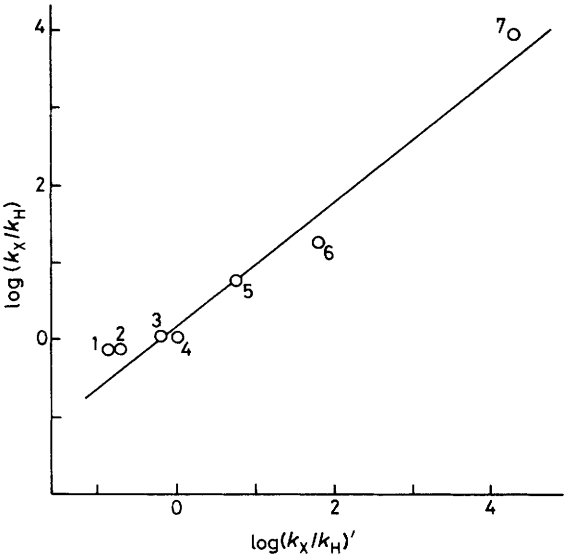


Figure 1. Plot of log (k_X/k_H) for the reaction of $XC_6H_4SnMe_3$ with $[Fe(CO)_3(1—5\text{-}\eta\text{-}C_6H_7)]^+$ in CH_3CN (at 45 °C) *vs.* log $(k_X/k_H)'$ for the protiodemetallation of $XC_6H_4Sn(C_6H_{11})_3$ by $HClO_4$ in aqueous ethanol (at 50 °C): 1, X = 4-Br; 2, X = 4-Cl; 3, X = 4-F; 4, X = H; 5, X = 4-Me; 6, X = 4-MeO; 7, X = $4\text{-}Me_2N$

$[Ru(CO)_3(1—5\text{-}\eta\text{-}C_6H_7)]^+$, $[Cr(CO)_3(\eta\text{-}C_7H_7)]^+$, and the acyclic dienyl $[Fe(CO)_3(1—5\text{-}\eta\text{-}1\text{-}Me\text{-}5\text{-}PhC_5H_5)]^+$ have also recently been shown [12,13] to function as electrophiles in a manner analogous to reactions (1); this emphasises the broad scope of such processes for the synthesis of otherwise inaccessible compounds. These studies will be the subject of subsequent publications.

Kinetics and Mechanism.—Kinetic results for the reactions of various substrates $XC_6H_4SnMe_3$ with cations (I) and (III) in CH_3NO_2 and CH_3CN are summarised in Table 1. Analogous results for species $XC_6H_4SiMe_3$ are collected in Table 2, while less extensive data for species $XC_6H_4MMe_3$ (M = Ge or Pb) species are given in Table 3. The second-order rate law (4)

$$\text{Rate} = k_{obs}[\text{complex}] = k[\text{complex}][XC_6H_4MMe_3] \quad (4)$$

is confirmed for the reactions of $4\text{-}Me_2NC_6H_4MMe_3$ (M = Si or Sn) with cations (I) and (III) and of $4\text{-}MeOC_6H_4SnMe_3$ with (I) in nitromethane as solvent. Not surprisingly, the same rate expression is maintained in acetonitrile [*e.g.* reaction of $4\text{-}Me_2NC_6H_4SnMe_3$ with (I), Table 1].

The second-order rate law (4) is most readily interpreted in terms of electrophilic attack by cations (I) and (III) on the arene ring of the substrates $XC_6H_4MMe_3$ (M = Si or Sn), as depicted in the Scheme. If we assume a steady-state concentration for the Wheland-type σ-complex intermediate (VI), this mechanism leads to the general expression (5), which is

$$\text{Rate} = \frac{k_1k_2[\text{complex}][XC_6H_4MMe_3]}{k_{-1} + k_2} \quad (5)$$

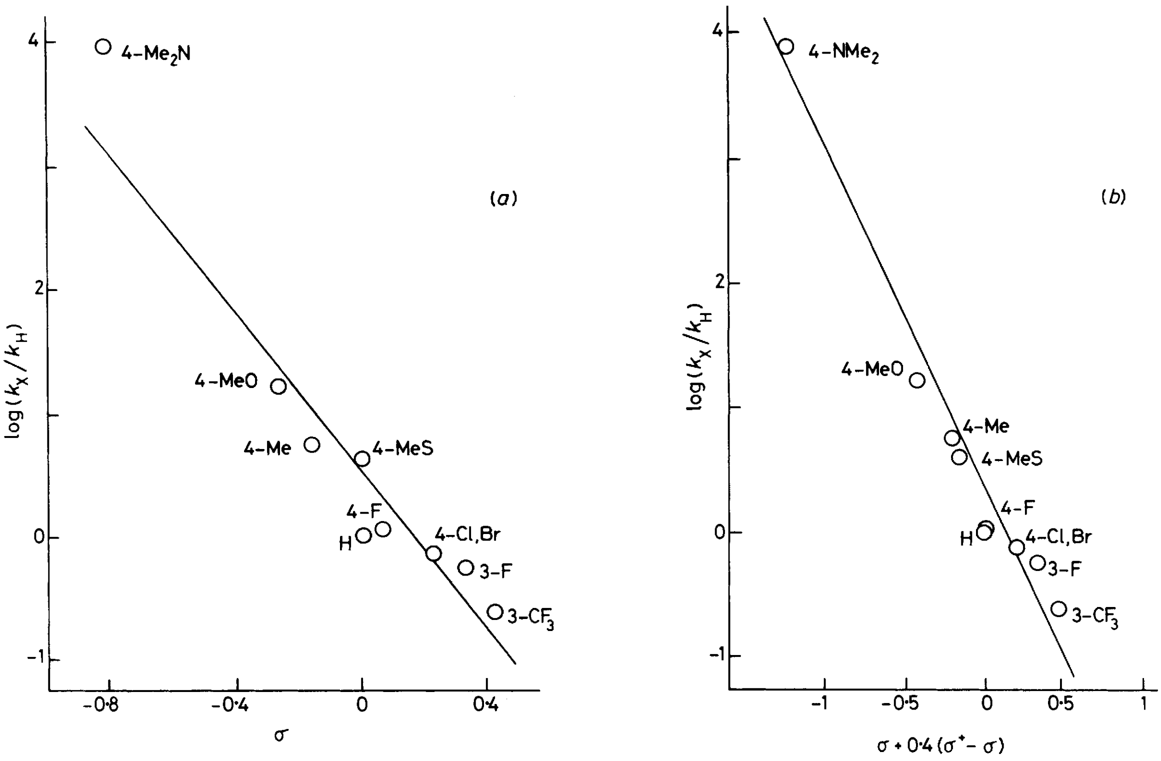


Figure 2. (*a*) Hammett plot of log (k_X/k_H) *vs.* σ for the reaction of $XC_6H_4SnMe_3$ with $[Fe(CO)_3(1—5\text{-}\eta\text{-}C_6H_7)]^+$ in CH_3CN at 45 °C; (*b*) Yukawa-Tsuno plot of log (k_X/k_H) *vs.* $\sigma + 0.4(\sigma^+ - \sigma)$ for the reaction of $XC_6H_4SnMe_3$ with $[Fe(CO)_3(1—5\text{-}\eta\text{-}C_6H_7)]^+$ in CH_3CN at 45 °C

consistent with the observed rate law (4). The rate-determining step is most probably formation of the intermediate (VI), as is believed to be the case in a variety of related demetallation reactions with more conventional electrophiles such as H^+, *e.g.* equation (6) (M = Si, Ge, Sn, or Pb).[3,14] Also sup-

$$H^+ + XC_6H_4MR_3 \longrightarrow XC_6H_4H + MR_3{}^+ \qquad (6)$$

porting a close similarity in mechanism between reactions (1) (M = Sn) and (6) (M = Sn, R = C_6H_{11}) is the good linear free energy relationship (correlation coefficient = 0.98) obtained upon plotting log (k_X/k_H) for reactions (1) (M = Sn) in CH_3CN *vs.* log (k_X/k_H)′ for the protiodemetallation of XC_6H_4-$Sn(C_6H_{11})_3$ by $HClO_4$ in aqueous ethanol (Figure 1).[15] One significant difference, however, is that while a 4-F substituent is mildly deactivating in the protiodemetallation process it is slightly activating in reaction (1) (M = Sn).

If we assume rate-determining formation of (VI) (*i.e.* $k_2 \gg k_{-1}$, k_1), the second-order rate constants, *k*, in Tables 1—3 refer to direct addition (k_1) of the substrates XC_6H_4-MMe_3 to the dienyl rings of cations (I) and (III). [An alternative one-step mechanism in which (VI) is simply the activated state would also equate the *k* values with k_1.] Consistent with such additions are the large negative $\Delta S^\ddagger$ values estimated for the reactions of 4-$Me_2NC_6H_4MMe_3$ (M = Si or Sn) with (I) (Table 5). Further support for direct addition is the assignment (see before) of an *exo*-configuration to the aryl substituent in the product (II; X = 4-Me_2N) obtained from reactions (1) (X = Me_2N; M = Si or Sn).

Rate constants, k_1, for the reactions of $XC_6H_4SnMe_3$ with the cation (I) in CH_3CN (Table 1) vary with X in the order: 4-Me_2N $\gg$ 4-MeO > 4-Me > 4-MeS > 4-F $\geqslant$ H > 4-Cl $\sim$ 4-Br > 3-F > 3-CF_3. This reactivity order generally follows the predicted substituent effects. The slight activation of the aromatic ring by the 4-F substituent (in contrast to 4-Cl and 4-Br) has precedent in molecular halogenation and detritiation processes.[16,17] The somewhat lower activating effect of the 4-MeS substituent as compared with a 4-Me group parallels the behaviour observed in protiodestannylation, but contrasts with protiodesilylation where 4-SMe activates some three times as much as the 4-Me group.[18]

The substrate selectivity of reactions (1) (M = Sn), expressed by the *k*(4-Me_2N)/*k*(4-Br) value of 1.1×10^4, is somewhat lower than that previously found [15] for the acid cleavage of the related compounds $XC_6H_4Sn(C_6H_{11})_3$ (1.4×10^5). Only limited data are available [15] on the directly comparable protiodemetallations of substrates $XC_6H_4SnMe_3$, but similar selectivities are evident for reactions (1) (M = Sn) and (6) (M = Sn, R = Me) in view of the very similar *k*(4-Me)/*k*(4-Cl) values of 7.4 and 8.9, respectively. However, the implications of such comparisons in terms of intimate mechanism are difficult to assess in view of the different solvents involved.

Further insight into the nature of the transition state in processes (1) (M = Sn) comes from a consideration of the Hammett-type plots in Figure 2(*a*) and (*b*). While there is a seemingly fair overall correlation between log (k_X/k_H) and the ordinary Hammett σ-constants as reflected in the correlation coefficient (0.96), the point for X = NMe_2 is badly off the best least-squares line, which, moreover, misses the origin by a substantial amount [Figure 2(*a*)]. The corresponding plot against σ^+ (not shown) gives a similar overall correlation (*r* = 0.96), but the points for the 4-Me_2N and 4-MeS substituents lie well off the line, and that for the 4-MeO substituent also deviates substantially. The most satisfactory correlation is obtained by use of a Yukawa–Tsuno plot of log (k_X/k_H) against [$\sigma + r(\sigma^+ - \sigma)$] with *r* = 0.4 [correction coefficient 0.98, Figure 2(*b*)] (though it should be appreciated that the point for 4-Me_2N receives a heavy weighting, and if this point is omitted the correlation coefficient is 0.95).

Table 4. Kinetic results for reactions of $[Fe(CO)_3(1\text{—}5\text{-}\eta\text{-}C_6H_7)]^+$ with other substrates at 45 °C; [Fe] = 6.54×10^{-3} mol dm^{-3}

Substrate	Solvent	$[RSiMe_3]$/ mol dm^{-3}	10^5k_{obs}/s^{-1}	10^5k/dm^3 mol^{-1} s^{-1}
2-Trimethylsilylfuran	CH_3NO_2	0.10	1.10	10.1 (0.4) *
		0.25	2.49	
		0.50	4.64	
		0.80	8.39	
		1.00	10.0	
	CH_3CN	0.52	7.23	13.9
2-Trimethylsilylthiophen	CH_3NO_2	1.00	0.200	0.200
	CH_3CN	0.52	0.100	0.193
CH_2=$CHCH_2SnMe_3$	CH_3CN	6.54×10^{-3}		17 100

* k Value calculated by a least-squares fit to equation (8); value in brackets is the standard error of estimate.

Table 5. Relative rate constants for reactions of $[Fe(CO)_3(1\text{—}5\text{-}\eta\text{-}C_6H_7)]^+$ with various substrates in CH_3NO_2 at 45.0 °C

Substrate	10^5k/dm^3 mol^{-1} s^{-1}	Relative rate [a]	$\Delta H^\ddagger$/kJ mol^{-1}	$\Delta S^\ddagger$/J K^{-1} mol^{-1}	Ref.
$Me_2NC_6H_5$	6 060	1	53.3(1.3)	−102(4)	26
$4\text{-}Me_2NC_6H_4SnMe_3$	10 000	1.7	70.7(1.5)	−43(5)	This work
$4\text{-}Me_2NC_6H_4SiMe_3$	3 420	0.56	72.3(2.3) [b]	−46(8) [b]	This work
Furan	0.64	1			25
2-Trimethylsilylfuran	10.2	16			This work
Thiophen	0.028	1			25
2-Trimethylsilylthiophen	0.200	7			This work

[a] k_{Si}/k_H or k_{Sn}/k_H. [b] Corresponding parameters in CH_3CN are: $k = 5.84 \times 10^{-3}$ dm^3 mol^{-1} s^{-1}; $\Delta H^\ddagger = 61.4(1.9)$ kJ mol^{-1}; $\Delta S^\ddagger = -95(7)$ J K^{-1} mol^{-1}.

The correlation in Figure 2(*b*) is not surprising in the light of the plot shown in Figure 1, since the rate data for the protiodestannylation also fit the Yukawa–Tsuno equation (7) with $r = 0.4$.[15] The slope, ρ, of −2.7 calculated for reactions (1) (M = Sn) in CH_3CN is considerably lower than that

$$\log (k_X/k_H) = \rho[\sigma + r(\sigma^+ - \sigma)] \qquad (7)$$

reported[15] for the protiodemetallation of $XC_6H_4Sn(C_6H_{11})_3$ by $HClO_4$ in aqueous ethanol ($\rho = -3.8$). However, it is similar to the ρ value of −2.2 ($r = 0.4$) calculated, albeit from limited data, for the more strictly comparable reactions (6) (M = Sn, R = Me). This similarity in ρ values between reactions (1) (M = Sn) and (6) (M = Sn, R = Me) is probably even closer when consideration is taken of the more polar solvent involved in the protiodemetallations. In view of earlier conclusions[15,19] regarding reactions (6) (M = Sn), these observations indicate a relatively early transition state for the reactions of cation (I) with $XC_6H_4SnMe_3$, with only moderate carbon–carbon bond formation and positive charge build-up in the transition state.

The more limited results in Table 2 show that arylsilicon substrates are generally attacked less readily by cations (I) and (III) than are their tin analogues. Similar behaviour has been reported[20] for the protiodemetallations (6). Also, as noted previously for acid cleavage, the k_{Sn}/k_{Si} values for reactions (1) are markedly dependent on the substituent X. Table 3 summarises some of these k_{Sn}/k_{Si} values. They are seen to increase markedly with decreasing reactivity of the substrates $XC_6H_4MMe_3$, in accord with the reactivity–selectivity principle.[21] Unfortunately, no direct literature comparisons are available for the protiodemetallations of substrates $4\text{-}Me_2NC_6H_4MMe_3$ (M = Si or Sn). However, extrapolation of a Yukawa–Tsuno plot for the M = Sn reactions provides a very approximate k_{Sn}/k_{Si} value of *ca.* 20 (Table 3). This value thus appears somewhat larger than that of 6 found here for reactions (1) (X = $4\text{-}Me_2N$) in CH_3CN. The lower sensitivity of processes (1) to the nature of M is even more striking when X = 4-MeO, in which case k_{Sn}/k_{Si} values of 62 and 1.4×10^4 are observed for reactions (1) and (6) (R = Me), respectively. Exact comparisons, however, are complicated by the observed sensitivity of k_{Sn}/k_{Si} to changes in solvent. For example, in reactions (1) (X = $4\text{-}Me_2N$), k_{Sn}/k_{Si} decreases from 6 to 3 upon changing the solvent from CH_3CN to CH_3NO_2 (Table 3). The small k_{Sn}/k_{Si} value in CH_3NO_2 is seen from Table 5 to arise from very similar $\Delta H_1^\ddagger$ and $\Delta S_1^\ddagger$ values for the silicon and tin reactions.

As expected on the basis of the reactivity–selectivity principle,[21] the less reactive arylsilicon substrates in reactions (1) show a greater rate variation with X than do analogous aryltin compounds. For example, the $k(4\text{-}Me_2N)/k(4\text{-}MeO)$ value of 8 100 for the species $XC_6H_4SiMe_3$ in CH_3NO_2 is to be compared with a value of only 520 for the tin analogues (see Tables 1 and 2). Similar behaviour has been previously observed in the protiodemetallations (6) (M = Si or Sn).[16,22] These differences probably reflect the involvement of a ‘ later ’ transition state in reactions (1) (M = Si) than in the related aryltin processes.

Limited data for substrates $XC_6H_4MMe_3$ (M = Ge or Pb) are also summarised in Table 3. With X = MeO, the reactivity order Sn ≫ Ge ⩾ Si (62 : 1.2 : 1) is observed towards cation (I) in CH_3CN. The k_{Ge}/k_{Si} value of 1.2 is considerably smaller than the corresponding value (15) found[20] for related protiodemetallations. On the other hand the k_{Pb}/k_{Sn} value of 920 observed here for reactions (1) (X = H) (Table 3) is similar to that (*ca.* 600) noted previously[20] for reactions (6) (R = Et, X = H). Overall the results in Table 3 reveal the expected rate trend Pb ≫ Sn ≫ Ge > Si for processes (1).

Changing the solvent from CH_3CN to CH_3NO_2 has only a small effect on the rates of reactions (1). Rate constants in

CH_3NO_2 are 2—6 times greater than those in CH_3CN (Tables 1 and 2). In the case of $4\text{-}Me_2NC_6H_4SiMe_3$, the activation parameters in Table 4 show that this small rate difference (factor of 6) arises from a play-off between enthalpy and entropy effects. Thus, the greater rate in CH_3NO_2, despite a significantly higher $\Delta H^\ddagger$ value, is due to the much less negative $\Delta S^\ddagger$ value of -46 J K^{-1} mol^{-1}.

The cation (I) is seen from Tables 1 and 2 to be 16—18 times more electrophilic than (III) towards $4\text{-}Me_2NC_6H_4MMe_3$ (M = Sn or Si). This is expected on the basis of the mesomeric influence of the 2-methoxy substituent in $[Fe(CO)_3(1\text{—}5\text{-}\eta\text{-}2\text{-}MeOC_6H_6)]^+$, which will delocalise electron density on to the dienyl ring of (III).[23] A similar lower reactivity of (III) than (I) has been previously observed in other reactions with nucleophiles such as acetylacetone, tertiary phosphines, and pyridines.[24] The electrophilicity of the cation (I) may also be compared with that of oxonium ions. Towards the common substrate $C_6H_5SnMe_3$, $HClO_4$ and $[Fe(CO)_3(1\text{—}5\text{-}\eta\text{-}C_6H_7)]BF_4$ exhibit second-order rate constants, k, of 5.2×10^{-4} dm^3 mol^{-1} s^{-1} (50 °C; aqueous ethanol) [16] and 3.88×10^{-6} dm^3 mol^{-1} s^{-1} (45 °C; CH_3CN; Table 1), respectively. Allowing for the difference in temperature, (I) is seen to be *ca.* 100 times less electrophilic than the oxonium ion in ethanolic perchloric acid. On the other hand, examination of data with $4\text{-}Me_2NC_6H_4SiMe_3$ as a common substrate indicates similar electrophilicities for the oxonium ion and (I).

Table 4 summarises kinetic results for the related demetallation processes (2) and (3). The second-order rate law (8) is confirmed for the reaction of 2-trimethylsilylfuran with (I). These reactions may also be interpreted as S_E2 processes.

$$\text{Rate} = k_{obs}[\text{complex}] = k[\text{complex}][2\text{-}Me_3SiC_4H_3O] \quad (8)$$

As has been found previously with other electrophiles, the demetallation processes examined here with cation (I) are generally more rapid than analogous deprotonations. This is strikingly illustrated by the failure to observe any reaction between (I) and the substrates XC_6H_5 (X = 4-MeO, 4-Me, or H). Table 5 makes quantitative comparisons where these are possible. Thus, desilylations of 2-trimethylsilyl-furan and -thiophen by (I) are 16 and 7 times more rapid than deprotonations [25] of furan and thiophen, respectively. (Since furan is more reactive than thiophen, one might have expected, contrary to observations, a larger k_{Si}/k_H ratio for thiophen than for furan.) The greater reactivity of aryl–MMe_3 (M = Si or Sn) as compared with aryl–H towards electrophiles has been rationalised in terms of stabilization of the incipient Wheland intermediate *via* electron donation from the MMe_3 groups.[3]

The only exceptions to the above generalisation are the reactions of $4\text{-}Me_2NC_6H_4MMe_3$ (M = Si or Sn) with (I). In nitromethane as solvent, the M = Sn substrate is seen (Table 5) to be only 1.7 times as reactive as $Me_2NC_6H_5$,[26] while the M = Si compound is slightly less reactive ($k_{Si}/k_H = 0.56$). These unusually small differences arise from a play-off between enthalpy and entropy effects. Thus, while the substrates $4\text{-}Me_2NC_6H_4MMe_3$ have unfavourably high enthalpies of activation ($\Delta H^\ddagger = 70.7-72.3$ kJ mol^{-1}) as compared with $Me_2NC_6H_5$ ($\Delta H^\ddagger = 53.3$ kJ mol^{-1}), this is counterbalanced by their much less negative $\Delta S^\ddagger$ values (Table 5).

This behaviour with the species $4\text{-}Me_2NC_6H_4MMe_3$ is even more apparent in acetonitrile as solvent, where k_{Sn}/k_H and k_{Si}/k_H values of 1.2 and 0.2 are noted for reactions with cation (I). These marked differences as compared with other substrates $XC_6H_4MMe_3$ may reflect changes in mechanism. It is possible that formation of the Wheland-type intermediate (VI) with the more basic substrates $4\text{-}Me_2NC_6H_4MMe_3$ is preceded by a pre-equilibrium involving either a π-complex or an intermediate in which the nitrogen atom of the $4\text{-}Me_2NC_6H_4MMe_3$ is directly associated with (I) (*via* the dienyl ring, the iron centre, or a CO ligand).

However, the above observations are not inconsistent with a common mechanism of the type shown in the Scheme for all substrates $XC_6H_4MMe_3$. Benzene is undoubtedly much less reactive than $C_6H_5MMe_3$ towards electrophiles such as (I) or the oxonium ion. Thus, on the basis of the reactivity–selectivity principle,[21] one would expect a much higher ρ (or ρ^+) value for the XC_6H_5 series than for $XC_6H_4MMe_3$. Consequently, for some value of σ (or σ^+) the Hammett plots must, in principle, cross. This could conceivably account for the unusually low k_{Sn}/k_H and k_{Si}/k_H values for X = $4\text{-}Me_2N$.

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