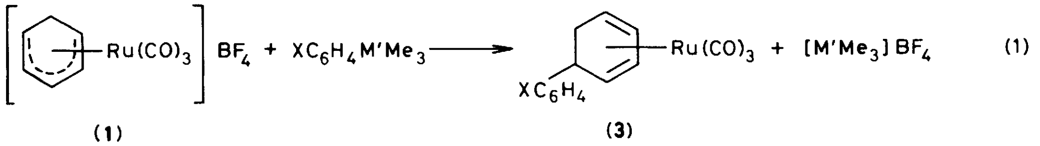
Mechanism of Addition of Aryltrimethyl-silanes and -stannanes to Tricarbonyl(cyclohexadienyl)ruthenium(II) Cation

Timothy I. Odiaka *
Inorganic Research Laboratory, University College, Cardiff CF1 1XL

Kinetic studies of the reaction between the organometallic complex $[Ru(CO)_3(1—5\text{-}\eta\text{-}C_6H_7)]BF_4$ (**1**) and aryltrimethyl-silanes and -stannanes of the type $XC_6H_4M'Me_3$ (M′ = Si or Sn; X = H, 4-NMe$_2$, 4-OMe, 1-OMe, 4-Me, 4-SMe, 4-F, 4-Cl, 4-Br, 3-F, or 3-CF$_3$) reveal the rate law, rate = $k[Ru][XC_6H_4M'Me_3]$. This rate law has been rationalised in terms of a rate-determining electrophilic attack by complex (**1**) on the $XC_6H_4M'Me_3$ substrates to form Wheland type σ-complex intermediates of the type $[Ru(CO)_3\{1—4\text{-}\eta\text{-}C_6H_7(XC_6H_4M'Me_3)\}]$ (**2**) followed by cleavage of the Me_3M–C(dienyl) bond to give the new compounds $[Ru(CO)_3\{1—4\text{-}\eta\text{-}C_6H_7(C_6H_4X)\}]$ (**3**). These reactions are of considerable synthetic interest as they offer useful routes to otherwise inaccessible substituted benzenoid derivatives. For the Sn reactions, a Hammett plot of log (k_X/k_H) *versus* σ (the standard Hammett substituent constant) is linear with a slope of −2.9 suggesting a common mechanism for each of the reactions. A plot of log (k_X/k_H) for the reactions of (**1**) with $XC_6H_4SnMe_3$ in $MeNO_2$ (at 45 °C) *versus* log (k_X/k_H) for the protiodemetallation of $XC_6H_4Sn(cyclo\text{-}C_6H_{11})_3$ by $HClO_4$ in aqueous ethanol (at 50 °C) is also linear indicating that organometallic complexes such as (**1**) behave in a similar manner to more classical electrophiles.

A wide variety of activated aromatic substrates have been shown[1–6] to add to the dienyl rings of organometallic complexes such as $[M(CO)_3(1—5\text{-}\eta\text{-}C_6H_7)]BF_4$ (M = Fe, Ru, or Os) to give novel substituted-diene products in high yields. Thus attack on $[Fe(CO)_3(1—5\text{-}\eta\text{-}C_6H_7)]BF_4$ by pyridines[7] affords products of the type tricarbonyl(1—4-η-5-*exo*-*N*-pyridiniocyclohexa-1,3-diene)iron tetrafluoroborate in yields of 60—70%. These novel reactions have recently been extended to the synthesis of diene-substituted arenes and heterocycles and to derivatives of the less activated arenes of the type XC_6H_5 (X = OMe, SMe, Me, F, Cl, Br, or H) by treatment of complexes such as $[Fe(CO)_3(1—5\text{-}\eta\text{-}C_6H_7)]BF_4$ with aryltrimethyl-silanes and -stannanes.[8] It is pertinent to note that careful oxidation of the metal atom in these tricarbonyl(substituted 1,3-diene) metal products using suitable reagents (*e.g.* Me_3NO[9,10]) leads to cleavage of the tricarbonylmetal unit and the recovery of the free substituted organic products in good yields. Reactions of complexes such as (1) with a wide variety of aryltrimethylsilanes and -stannanes would therefore afford new substituted organic derivatives which are otherwise inaccessible by conventional organic techniques.

This paper reports detailed kinetic studies of the reaction between the complex (1) and aryltrimethyl-silanes and -stannanes of the type $XC_6H_4M'Me_3$ (M′ = Si or Sn) in CH_3NO_2 [equation (1)]. The influence of the metals in $[M(CO)_3(1—5\text{-}\eta\text{-}C_6H_7)]BF_4$ (M = Fe^{II} or Ru^{II}) and $XC_6H_4M'Me_3$ (M′ = Si or Sn) on the rate and mechanisms of reactions such as (1) is discussed.



Experimental

Materials.—The complex $[Ru(CO)_3(1—5\text{-}\eta\text{-}C_6H_7)]BF_4$ (1) was prepared and purified using published procedures.[2,11] Complex (1) was obtained as an off-white solid (Found: C, 29.6; H, 2.0. $C_9H_7BF_4O_3Ru$ requires C, 30.8; H, 2.0%); m.p. 179 °C (decomp.)[lit.,[11] 180 °C (decomp.)]. I.r.: ν(CO)(CH_3NO_2), 2 130 and 2 080 cm^{-1}. Nitromethane solvent (B.D.H.) was distilled in bulk and stored over molecular sieves (size 4 Å) under a dinitrogen atmosphere. The solvent was further deoxygenated by passing a stream of dinitrogen through for 20 min immediately prior to use. The aryltrimethyl-silanes and -stannanes were kindly supplied by Professor C. Eaborn (University of Sussex). The liquid substrates were distilled and their purity was checked by ^1H n.m.r. spectroscopy.

Kinetic Studies.—The reactions (1) were all monitored in the dark under a dinitrogen atmosphere by using the i.r. sampling method described in the literature.[2,12] The disappearance of the longest-wavelength band of the original dienyl salt located at 2 130 cm^{-1} was followed using a Perkin-Elmer 257 spectrophotometer. The majority of the kinetic runs were carried out under pseudo-first-order conditions using a large excess of $XC_6H_4M'Me_3$. Pseudo-first-order rate constants, $k_{obs.}$, were calculated from the slopes of plots of log A_t *versus* time (t), which were generally linear for at least 75% completion of reaction. Activation enthalpies were calculated from the slopes of Arrhenius plots of log k *versus* $1/T$ using a least-squares method. The errors quoted are the standard errors of estimation from these analyses. Entropies of activation were calculated using the second-order rate constants, k, at 45 °C.

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* *Present address*: Department of Chemistry, University of Ibadan, Ibadan, Nigeria.

Table 1. Kinetic results for reactions of $[Ru(CO)_3(1\text{—}5\text{-}\eta\text{-}C_6H_7)]BF_4$ with $XC_6H_4SnMe_3$ in $MeNO_2$: $[Ru] = 3.02 \times 10^{-3}$ mol dm^{-3} for X = 4-NMe$_2$, 4-OMe, 4-Me, or H and 5.04×10^{-3} mol dm^{-3} others

X	Temp. (°C)	$10[XC_6H_4SnMe_3]$/mol dm^{-3}	$10^5k_{obs.}$/s^{-1}	10^5k/dm^3 mol^{-1} s^{-1}
4-NMe$_2$	25.0	0.2	38.4	
	25.0	0.3	58.6	
	25.0	0.4	78.0	2 100(50)*
	25.0	0.5	102.0	
	30.0	0.2	55.6	2 780
	35.0	0.2	76.0	3 800
	40.0	0.2	103.0	5 150
	45.0	0.2	141.1	7 050
4-OMe	45.0	0.5	1.69	33.8
	45.0	1.0	3.35	33.5
1-OMe	45.0	0.35	0.619	17.7
		0.50	0.812	16.2
4-Me	45.0	0.50	0.640	12.8
H	45.0	0.60	0.557	9.28
4-SMe	45.0	0.50	0.456	9.12
4-F	45.0	0.52	0.210	3.99(0.01)*
		1.00	0.402	
		5.00	2.00	
4-Cl	45.0	0.50	0.185	3.70
		1.00	0.344	3.44
4-Br	45.0	0.90	0.327	3.63
3-F	45.0	2.50	0.332	1.33
3-CF$_3$	45.0	2.20	0.283	1.29

* Estimated by a least-squares fit to equation (2). Values in parentheses are the standard errors of estimate.

Table 2. Kinetic results for reactions of $[Ru(CO)_3(1\text{—}5\text{-}\eta\text{-}C_6H_7)]BF_4$ with $XC_6H_4SiMe_3$ in $MeNO_2$: $[Ru] = 3.02 \times 10^{-3}$ mol dm^{-3} for X = 4-NMe$_2$ and 5.04×10^{-3} mol dm^{-3} for others

X	Temp. (°C)	$10[XC_6H_4SiMe_3]$/mol dm^{-3}	$10^5k_{obs.}$/s^{-1}	10^5k/dm^3 mol^{-1} s^{-1}
4-NMe$_2$	25.0	0.20	0.383	
	25.0	0.40	0.751	22.0(0.4)*
	25.0	0.80	1.69	
	25.0	1.00	2.11	
	30.0	1.00	3.46	34.6
	35.0	1.00	4.76	47.6
	45.0	1.00	11.0	110.0
4-OMe	45.0	5.00	0.175	0.350
	45.0	8.06	0.283	0.351
4-Me	45.0	5.00	0.130	0.260
	45.0	6.99	0.174	0.249

* Estimated by a least-squares fit to equation (2). Value in parentheses is the standard error of estimate.

Results and Discussion

Nature of the Reactions.—The nature of the reactions (1) has been established[8] from i.r., ^1H n.m.r., mass spectral, and microanalytical measurement of the iron analogue of product (3) (X = 4-NMe$_2$ or 4-OMe) obtained from the reactions of $[Fe(CO)_3(1\text{—}5\text{-}\eta\text{-}C_6H_7)]BF_4$ with $4\text{-}Me_2NC_6H_4SnMe_3$, $4\text{-}Me_2NC_6H_4SiMe_3$, and $4\text{-}MeOC_6H_4SnMe_3$. These latter products are stable cream solids exhibiting two strong i.r. ν(CO) bands at *ca.* 2 045 and 1 965 cm^{-1}. During each reaction (1) (M′ = Si or Sn) the two carbonyl bands of the original dienyl salt at 2 130 and 2 080 cm^{-1} are slowly replaced by two strong product bands at *ca.* 2 050 and 1 975 cm^{-1} ($MeNO_2$), characteristic of neutral tricarbonyl(substituted 1,3-diene)-ruthenium complexes, (3). Interestingly the product $[Ru(CO)_3\{1\text{—}4\text{-}\eta\text{-}C_6H_7(C_6H_4NMe_2\text{-}4)\}]$ (**4**), isolated[2] as brown needle-like crystals from the reaction of complex (**1**) with *N,N*-dimethylaniline, shows two strong i.r. ν(CO) bands at 2 050 and 1 975 cm^{-1} in $MeNO_2$ indicating the formation of identical 1,3-diene products as the reactions (1) involving $XC_6H_4M'Me_3$. In particular, the ^1H n.m.r. spectrum of (**4**) is identical to those of the products isolated[8] from the reactions of $[Fe(CO)_3(1\text{—}5\text{-}\eta\text{-}C_6H_7)]BF_4$ with $4\text{-}Me_2NC_6H_4M'Me_3$ (M′ = Si or Sn) substrates. In all three cases, the aromatic regions of the spectra show two doublets at *ca.* τ 3.0 and 3.4 indicating that electrophilic attack by the $[M(CO)_3(1\text{—}5\text{-}\eta\text{-dienyl})]BF_4$ (M = Fe or Ru) complexes has occurred at C(4) of the $4\text{-}Me_2NC_6H_4M'Me_3$ and $4\text{-}Me_2NC_6H_5$ substrates, *para* to the substituent group. This is the normal position for electrophilic attack on such substrates as predicted from simple electrostatic and steric considerations.[13] Thus, as recently reported[8] in the literature for the analogous reactions of $[Fe(CO)_3(1\text{—}5\text{-}\eta\text{-}C_6H_7)]BF_4$ with $XC_6H_4M'Me_3$ substrates, cleavage of the $XC_6H_4\text{–}M'Me_3$ bonds leads to only the *exo* isomer for the products (3). However, it should be noted that in the reactions of complex (1) with some of the less reactive tin substrates such as $C_6H_5SnMe_3$, the expected product bands occurred at *ca.* 2 050 and 1 975 cm^{-1} but their final intensity is sometimes as low as 50% of the anticipated value. This indicates that the products in these cases undergo a slow subsequent decomposition which may be either thermal or due to the introduction of small

Table 3. Rate and activation parameters for reactions of $[M(CO)_3(1\text{—}5\text{-}\eta\text{-}C_6H_7)]BF_4$ (M = Fe or Ru) with $4\text{-}Me_2NC_6H_4M'Me_3$ (M′ = Si or Sn) in $MeNO_2$

Substrate	M	$10^5k_{45\,^\circ C}$/dm³ mol⁻¹ s⁻¹	$\Delta H^\ddagger$/kJ mol⁻¹	$\Delta S^\ddagger$/J K⁻¹ mol⁻¹
$4\text{-}Me_2NC_6H_4SnMe_3$	Fe[a]	10 000	70.7 ± 1.5	−43 ± 5
	Ru[b]	7 050	45.5 ± 0.8	−125 ± 3
$4\text{-}Me_2NC_6H_4SiMe_3$	Fe[a]	3 140	72.3 ± 3.2	−46 ± 8
	Ru[b]	110	60.4 ± 1.6	−112 ± 5

[a] Results from ref. 8. [b] This work.

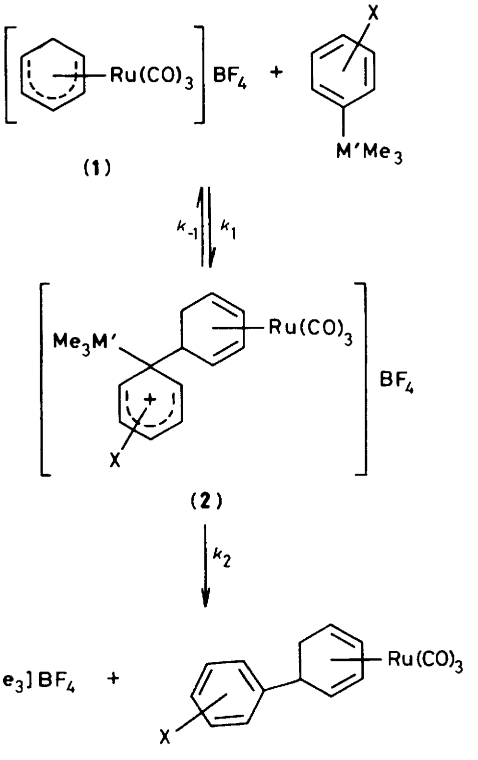
amounts of oxygen during sampling. Since the reactions were studied kinetically by monitoring the decrease of the ν(CO) band due to the original dienyl salt at 2 130 cm⁻¹ no interference is expected from this subsequent decomposition.

Kinetics and Mechanism.—Kinetic results for the reaction of complex (**1**) with the various $XC_6H_4SnMe_3$ and $XC_6H_4SiMe_3$ substrates in nitromethane are summarised in Tables 1 and 2 respectively. These results show close adherence to the second-order rate law (2) as confirmed for the reactions of $4\text{-}Me_2NC_6H_4M'Me_3$ (M′ = Si or Sn) and $4\text{-}FC_6H_4SnMe_3$ with complex (**1**) (Tables 1 and 2).

$$\text{Rate} = k\,[\text{complex}][XC_6H_4M'Me_3]$$

$$k_{\text{obs.}} = k\,[XC_6H_4M'Me_3] \qquad (2)$$

The rate law (2) is the same as that found recently[8] for the analogous reactions of these substrates with $[Fe(CO)_3(1\text{—}5\text{-}\eta\text{-}dienyl)]BF_4$ (**5**) in both nitromethane and acetonitrile solvents, and supports a common mechanism for all reactions. Rate law (2) may be rationalised in terms of a rate-determining electrophilic attack by complex (**1**) on the $XC_6H_4M'Me_3$ substrates to form Wheland type σ-complex intermediates of the type (**2**) (Scheme) followed by cleavage of the Me_3M'–C(dienyl) bond to give the products (**3**). This Scheme is the same as that reported[8] for the analogous iron complex $[Fe(CO)_3\{1\text{—}5\text{-}\eta\text{-}dienyl)]$ (**5**) and suggests a common mechanism for addition of $XC_6H_4M'Me_3$ (M = Si or Sn) substrates to complexes (**1**) and (**5**). Hammett plots of log k_X/k_H *versus* σ (the standard Hammett substituent constant) for the reaction of complexes (**1**) and (**5**) with the Sn substrates at 45 °C are linear with slopes, ρ, of −3.4 for Fe and −2.9 for Ru, suggesting a common mechanism for each of the reactions. However, the lower value found here for the Ru complex indicates an earlier transition state for reactions (1) than in the analogous Fe reactions. This view is consistent with the significantly lower $\Delta H^\ddagger$ values obtained for the reactions of the Ru complex with $4\text{-}Me_2NC_6H_4M'Me_3$ (M′ = Si or Sn) compared with the iron analogue (Table 3). In addition, plots of log k_X/k_H for the reaction of complexes (**1**) and (**5**) with the Sn substrates at 45 °C *versus* log k_X/k_H for the protiodemetallation of $XC_6H_4Sn(cyclo\text{-}C_6H_{11})_3$ by $HClO_4$ in aqueous ethanol (at 50 °C)[14] are also linear indicating that these organometallic complexes behave in a similar manner to more classical electrophiles. As found earlier for the Fe reactions, one significant difference is the deactivating property of a 4-F substituent in the protiodemetallation process while it is slightly activating in reaction (1). Further support for a relatively early transition state for reaction (1) (M′ = Sn) comes from a Yukawa–Tsuno plot[15] of log k_X/k_H (M = Ru) *versus* $\sigma + r(\sigma^+ - \sigma)$ if an *r* value of 0.3 is chosen. The slope, ρ, of −2.3 is again lower than that calculated for the analogous Fe reactions (ρ = −2.8, *r* = 0.3). It is also lower than the ρ value of −3.8 reported[14] for the cleavage of $XC_6H_4Sn(cyclo\text{-}C_6H_{11})_3$ substrates by perchloric acid (*r* = 0.4), indicating that the transition state in reaction (1) (M′ = Sn) is also earlier than for these latter protiodemetallations. Perhaps the strongest support for the similarity in mechanism between the reactions of the iron and ruthenium organometallics with the $XC_6H_4SnMe_3$ substrates is confirmed by the excellent linear free-energy relationship obtained from the plot of log k_X/k_H (M = Ru) *versus* log k_X/k_H (M = Fe) at 45 °C (Figure). It also reveals that for the reactions of both complexes with the Sn substrates, the rate trend generally follows the expected substituent effects in the order 4-NMe₂ > 4-OMe > 4-Me > H > 4-F > 4-Cl ~ 4-Br > 3-F > 3-CF₃ with an overall reactivity range of *ca.* 5 × 10³ for the Ru reactions in MeNO₂ at 45 °C.



Scheme. X = 4-NMe₂ or 4-OMe

The effect of variation of the metal (M′) in the $XC_6H_4M'Me_3$ substrates can be seen from the comparative results in Table 4. Generally the rate trend Sn > Si is observed for both $[M(CO)_3(1\text{—}5\text{-}\eta\text{-}C_6H_7)]BF_4$ (M = Fe or Ru) complexes. Interestingly, the k_{Sn}/k_{Si} ratio is larger for the Ru complex than for Fe. For example, with $4\text{-}Me_2NC_6H_4M'Me_3$ substrates, k_{Sn}/k_{Si} is 3 for Fe and 64 for Ru. This observation may be rationalised from the activation parameters shown in Table 3.

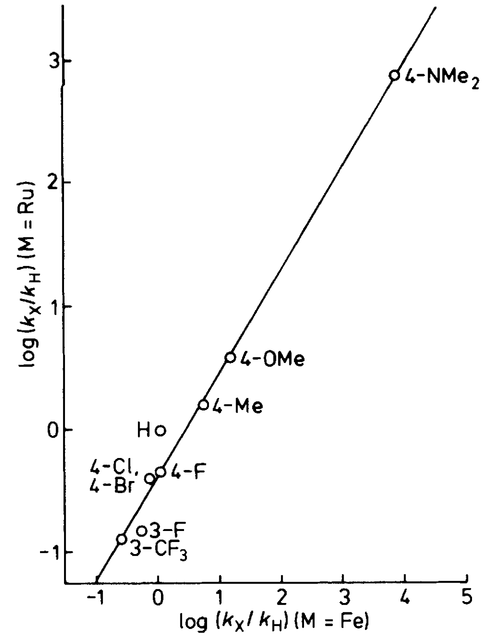


Figure. Plot of log (k_X/k_H) for the reaction of $XC_6H_4SnMe_3$ with $[Ru(CO)_3(1\text{—}5\text{-}\eta\text{-}C_6H_7)]^+$ in $MeNO_2$ (at 45 °C) *versus* log (k_X/k_H) for the reaction of the same substrates with $[Fe(CO)_3(1\text{—}5\text{-}\eta\text{-}C_6H_7)]^+$ in MeCN (at 45 °C)

For the Fe reactions, the small k_{Sn}/k_{Si} ratio of 3 is seen to arise from very similar $\Delta H^\ddagger$ and $\Delta S^\ddagger$ values for both processes while for the analogous Ru reactions a much larger k_{Sn}/k_{Si} ratio of 64 is associated with a significantly lower $\Delta H^\ddagger$ value for the Sn substrate (45.5 ± 0.8 kJ mol^{-1}) compared with the Si analogue (60.4 ± 1.6 kJ mol^{-1}). On the other hand the Sn reaction has a more negative entropy of activation than for Si [$\Delta S^\ddagger(Sn) = -125 \pm 3$ J K^{-1} mol^{-1}, $\Delta S^\ddagger(Si) = -112 \pm 5$ J K^{-1} mol^{-1}], indicating enthalpy control over the k_{Sn}/k_{Si} ratio.

Finally the greater reactivity of the iron complex compared with (**1**) (Table 4) suggests that the effective overall electron-donating property of the $M(CO)_3$ group to the π-hydrocarbon ligands decreases in the order $Ru(CO)_3 > Fe(CO)_3$, resulting in an increasingly positive dienyl ring for complex (**5**). A similar rate trend has been observed[2] for the reactions of $[M(CO)_3(1\text{—}5\text{-}\eta\text{-}C_6H_7)]BF_4$ (M = Fe, Ru, or Os) complexes with *N,N*-dimethylaniline where the effective overall electron-donating property of the $M(CO)_3$ group was found to decrease in the order $Ru(CO)_3 > Os(CO)_3 > Fe(CO)_3$. The much smaller k_{Fe}/k_{Ru} ratio for the Sn reactions compared with their Si analogues [*e.g.* 1.4 (Sn) and 31 (Si) for the $4\text{-}Me_2NC_6H_4M'Me_3$ substrates, Table 4] is in agreement with the reactivity-selectivity principle[16] since the $XC_6H_4SnMe_3$ substrates are generally more reactive than their Si analogues.

Table 4. Effect of metal on rate of reactions between $[M(CO)_3(1\text{—}5\text{-}\eta\text{-}C_6H_7)]BF_4$ (M = Fe or Ru) and $4\text{-}Me_2NC_6H_4M'Me_3$ (M' = Si or Sn) substrates in $MeNO_2$ at 45 °C

Complex	Substrate	k/dm^3 mol^{-1} s^{-1}	k_{Sn}/k_{Si}
Fe^a	$4\text{-}Me_2NC_6H_4SnMe_3$	10.0×10^{-2}	3
	$4\text{-}Me_2NC_6H_4SiMe_3$	3.42×10^{-2}	
Ru^b	$4\text{-}Me_2NC_6H_4SnMe_3$	7.05×10^{-2}	64
	$4\text{-}Me_2NC_6H_4SiMe_3$	0.11×10^{-2}	

^{a} Results from ref. 8. ^{b} This work. k_{Fe}/k_{Ru} = 1.4 (Sn), 31 (Si).

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