Kinetics of Nucleophilic Attack on Co-ordinated Organic Moieties. Part 8.† Addition of *NN*-Dimethylaniline to the Tricarbonyl(dienyl)-iron, -ruthenium, and -osmium Cations and Related Complexes

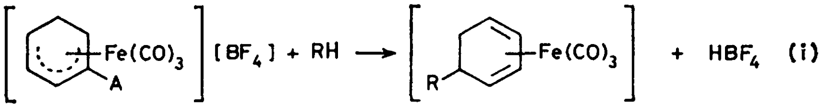
By **Glyn R. John** and **Leon A. P. Kane-Maguire,*** Chemistry Department, University College Cardiff, PO Box 78, Cardiff CF1 1XL

The complexes $[M(C_6H_7)(CO)_3][BF_4]$ (1; M = Fe, Ru, or Os) have been shown to act as electrophiles towards *NN*-dimethylaniline (RH) according to equation (I). A similar reaction occurs with $[Cr(C_9H_7)(CO)_3][BF_4]$. For

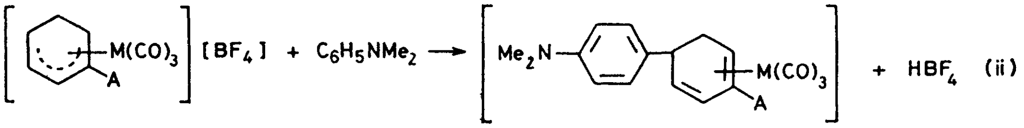
$$[M(C_6H_7)(CO)_3][BF_4] + RH \longrightarrow [M(C_6H_7R)(CO)_3] + HBF_4 \qquad (I)$$

(1; M = Fe) and $[Fe(C_6H_6OMe\text{-}2)(CO)_3][BF_4]$ the rate law, Rate = *k*[complex][RH] is observed. Preliminary kinetic investigations of the related reactions with (1; M = Ru or Os) provide the first quantitative comparison of the reactivity of cyclohexadienyl rings when co-ordinated to each of the iron triad metals, namely Fe > Os > Ru (41 : 3.6 : 1).

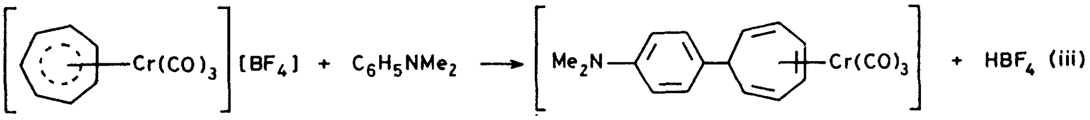
The synthetic utility of employing cationic organometallic complexes such as $[Fe(C_6H_7)(CO)_3]^+$ (1) as electrophiles towards aromatic substrates has recently been demonstrated.[1,2] Reaction (i) occurs with a wide range of heterocyclic aromatic species (RH) together with di- and tri-methoxy-substituted arenes, leading to novel diene-substituted aromatic species. More recently, derivatives of less activated arenes have been synthesised[3] in an analogous manner using the more reactive MMe_3(aryl) (M = Si or Sn) as substrates. Kinetic studies[4-6] of a variety of such reactions have confirmed that they involve electrophilic substitution by cation (1) and related complexes.



As an extension of these studies, the present paper reports the synthesis of derivatives of type (2: M = Fe, A = H or OMe; M = Os, A = H) and (3), obtained *via* direct reaction between *NN*-dimethylaniline and the appropriate organometallic cation [equations (ii) and (iii)]. A kinetic investigation of reactions (ii; M = Fe, Ru, or Os) allows the first quantitative comparison of the reactivity of dienyl rings when co-ordinated to each of the metals in the iron triad.



(2)



(3)

EXPERIMENTAL

Materials.—The cations $[M(C_6H_7)(CO)_3]^+$ (M = Fe, Ru, or Os) were isolated as their tetrafluoroborate salts and purified by published methods[7-9] (Found: C, 35.4; H, 2.4. Calc. for $C_9H_7BF_4FeO_3$: C, 35.1; H, 2.3. Found: C, 31.0; H, 2.2. Calc. for $C_9H_7BF_4O_3Ru$: C, 30.8; H, 2.0. Found: C, 24.4; H, 1.5. Calc. for $C_9H_7BF_4O_3Os$: C, 24.5; H, 1.6%). Tricarbonyl(1—5-η-2-methoxycyclohexadienyl)iron tetrafluoroborate (Found: C, 35.9; H, 2.6. Calc. for $C_{10}H_9BF_4FeO_4$: C, 35.8; H, 2.7%) and tricarbonyl(η-tropylium)chromium tetrafluoroborate (Found: C, 38.2; H, 2.1. Calc. for $C_{10}H_7BCrF_4O_3$: C, 38.2; H, 2.2%) were also prepared by established procedures.[7,10]

The nitromethane, acetonitrile, and acetone solvents were purified by distillation under an atmosphere of nitrogen and stored over molecular sieves (grade 3A). Typical water contents of these solvents, as determined by the Karl Fischer method, were $MeNO_2$ (0.04% w/w), MeCN (0.005% w/w), and Me_2CO (0.02% w/w). The solvents were deoxygenated by passing a stream of nitrogen through them for 20 min immediately prior to use. *NN*-Dimethylaniline was treated with K[OH] pellets and distilled at reduced pressure before storing under nitrogen in the dark.

Reactions with NN-*Dimethylaniline*.—$[Fe(C_6H_7)(CO)_3][BF_4]$. The dienyl salt (0.20 g) was added to a solution of *NN*-dimethylaniline in MeCN (0.080 g per 10 cm^3) at 45 °C and allowed to react under nitrogen for 12 h. The reaction mixture was passed through an alumina H column, and the eluant evaporated to give a yellow oil. On washing with cold light petroleum (b.p. 40—60 °C) the product tricarbonyl[5-(4-dimethylaminophenyl)cyclohexa-1,3-diene]iron (2a) was obtained as a cream solid (0.21 g, 95%

---

* Part 7 is ref. 14.

yield), m.p. 116—117 °C. The i.r. spectrum of a liquid film showed two strong carbonyl bands at 2 045 and 1 965 cm^{-1}, while its field desorption (f.d.) mass spectrum showed a single strong parent peak at *m/e* 339 (Found: C, 60.4; H, 5.2; N, 4.0. Calc. for $C_{17}H_{17}FeNO_3$: C, 60.2; H, 5.0; N, 4.1%).

$[Fe(C_6H_6OMe\text{-}2)(CO)_3][BF_4]$. An analogous reaction with this complex (0.20 g) gave 0.15 g (70% yield) of the creamy solid product tricarbonyl[5-(4-dimethylaminophenyl)-2-methoxycyclohexa-1,3-diene]iron (2b), m.p. 69—70 °C. A liquid film exhibited two strong ν(CO) bands at 2 045 and 1 965 cm^{-1}, while its f.d. mass spectrum showed a single strong parent ion at *m/e* 369 (Found: C, 58.3; H, 5.3; N, 4.0. Calc. for $C_{18}H_{19}FeNO_4$: C, 58.5; H, 5.2; N, 3.8%).

$[Os(C_6H_7)(CO)_3][BF_4]$. The dienyl salt (0.050 g) and *NN*-dimethylaniline (0.050 g) were dissolved in acetone at 45 °C and allowed to react overnight under nitrogen. The reaction mixture was then passed through an alumina H column and the eluant evaporated to yield the product tricarbonyl[5-(4-dimethylaminophenyl)cyclohexa-1,3-diene]osmium (2c) as a light brown oil. A liquid film gave ν(CO) bands at 2 055 and 1 980 cm^{-1}, while its f.d. mass spectrum exhibited a single intense parent peak at *m/e* 473.

$[Cr(C_7H_7)(CO)_3][BF_4]$. The tropylium salt (0.20 g) and *NN*-dimethylaniline (0.080 g) were dissolved in $MeNO_2$ at 45 °C under nitrogen and allowed to react for several days. Evaporation yielded a red oil. This was treated with diethyl ether–water and the ether extract passed down an alumina H column. Evaporation of the eluant again gave a red oil, which was crystallised from acetone–water to give orange-red crystals (0.12 g, 55% yield) of the product (3), tricarbonyl[7-(4-dimethylaminophenyl)cyclohepta-1,3,5-triene]chromium, m.p. 132—134 °C. A liquid film exhibited three strong carbonyl bands at 1 975, 1 910, and 1 875 cm^{-1}. Its f.d. mass spectrum showed a single strong parent peak at *m/e* 347 (Found: C, 62.3; H, 5.2; N, 4.2. Calc. for $C_{18}H_{17}CrNO_3$: C, 62.2; H, 4.9; N, 4.0%).

Spectroscopic Studies.—Field desorption (f.d.) mass spectra were recorded using a Varian combined FD/FI/EI source on a CH5D mass spectrometer linked to a Varian 620 i data system. Acetone was employed as solvent, and low emitter currents were used to desorb the samples. Infrared spectra were obtained on a Perkin-Elmer 257 spectrophotometer, ^{1}H n.m.r. (90 MHz) spectra in $(CD_3)_2CO$ using a Perkin-Elmer R32 spectrophotometer.

Kinetic Studies.—Each of the reactions (ii) and (iii) was slow enough to follow by i.r. spectroscopy. The reactions were studied in the dark under nitrogen using sampling techniques previously described.[11] The disappearance of the longest-wavelength carbonyl band of the original organometallic cation {*e.g.* at *ca.* 2 110 cm^{-1} for $[M(C_6H_7)(CO)_3]^+$, M = Fe, Ru, or Os} was followed using a Perkin-Elmer 257 spectrophotometer.

Most runs were carried out employing a large excess of *NN*-dimethylaniline (0.01—0.50 mol dm^{-3}), and pseudo-first-order rate constants, $k_{obs.}$, were calculated from the gradients of plots of log A_t against time. Such plots were generally linear for at least 75% completion of reaction.

The reaction of $[Fe(C_6H_7)(CO)_3][BF_4]$ with *NN*-dimethylaniline was studied under equimolar conditions ($[Fe] = [C_6H_5NMe_2] = 6.54 \times 10^{-3}$ mol dm^{-3}) in order to obtain a conveniently slow rate. In this case the second-order rate constant, *k* was determined directly from the gradient of a plot of $x/a(a - x)$ against time (where a = initial concentration of dienyl salt, and x = concentration of product at time t). These plots were generally linear for at least 60% completion of reaction.

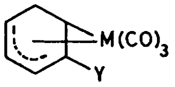
However, the runs carried out for $[Fe(C_6H_6OMe\text{-}2)(CO)_3][BF_4]$ with 1.0 mol dm^{-3} *NN*-dimethylaniline were too rapid to follow by conventional methods. A thermostatted (±0.1 °C) stopped-flow apparatus was employed using techniques previously described.[12] The progress of the reaction was monitored at 390 nm where a large decrease in absorbance occurs. Pseudo-first-order rate constants, $k_{obs.}$, were estimated from the gradients of plots of $\log(A_t - A_\infty)$ against time.

RESULTS AND DISCUSSION

During each of the reactions (ii; M = Fe, A = H or OMe; M = Ru or Os, A = H) the two carbonyl bands of the original dienyl cations at *ca.* 2 110 and 2 065 cm^{-1} are slowly replaced by strong product peaks at *ca.* 2 050 and 1 970 cm^{-1}. These product spectra are characteristic of neutral tricarbonyl(diene)metal (M = Fe, Ru, or Os) complexes. Similarly, in the related reaction (iii) the product bands at 1 975, 1 910, and 1 875 cm^{-1} are as expected for a neutral tricarbonyl(triene)chromium complex (3).

The products (2a)—(2c) and (3) have been isolated in good yield, and further characterised by their mass and ^{1}H n.m.r. spectra. At low emitter currents the f.d. mass spectra of each of the products show base peaks corresponding to the parent molecular ions P^+. In common with other f.d. mass-spectral studies [13,14] of tricarbonyl(π-hydrocarbon)metal complexes, the only other significant peaks can be assigned to $[P + 1]^+$ ions and isotopic species. No stepwise loss of carbonyl ligands is observed. This contrasts with the electron-impact (e.i.) mass spectrum of (2a) where only a weak parent P^+ ion is observed and extensive fragmentation. The latter spectrum is typical of *exo* isomers,[15,16] showing very weak $[P - CO]^+$, $[P - 2CO]^+$, and $[P - 3CO]^+$ ions but an intense base peak at *m/e* 253 corresponding to $[P - 3CO - H_2]^+$. Other characteristic fragment ions include those at *m/e* 197 and 121 assignable to $Me_2NC_6H_4{\cdot}C_6H_5$ and $C_6H_5NMe_2$, respectively.

The ^{1}H n.m.r. spectra of the products (2a)—(2c) (Table 1) show the same basic features as those reported [7,16,17] for a variety of related substituted-1,3-diene products. Multiplets characteristic of the inner and outer diene protons are well separated at *ca.* τ 4.4 ± 0.2 and 6.9 ± 0.3, respectively. The $H^{6,6'}$ methylene protons appear between τ 7.3 and 8.0, while the H^5 protons adjacent to the dimethylaminophenyl substituent are shifted downfield to τ 6.3. The close similarity of the spectra for (2a) and (2c) suggests that the osmium product (2c) is also the *exo* isomer. The spectra are clearly inconsistent with the alternative σ,η-allyl-bonded formulations (4: Y = $C_6H_5NMe_2$).



(4)

TABLE 1

Hydrogen-1 n.m.r. spectra of neutral diene and triene products in $(CD_3)_2CO$

Complex	Proton	Chemical shift, τ *
(2a)	$H^{1,4}$	6.76 (2, m)
	$H^{2,3}$	4.35 (2, m)
	H^{5}	6.30 (1, m)
	$H^{6,6'}$	7.40 (1, m)
		7.68 (1, m)
	aromatic	3.00 (2, d),
		3.35 (2, d)
	$N-CH_3$	7.14 (6, s)
(2b)	H^{1}	6.59 (1, m)
	H^{3}	4.60 (1, m)
	H^{4}	7.24 (1, m)
	H^{5}	6.28 (1, m)
	$H^{6,6'}$	7.94 (2, m)
	$O-CH_3$	6.36 (3, s)
	aromatic	3.00 (2, d)
		3.35 (2, d)
	$N-CH_3$	7.14 (6, s)
(2c)	$H^{1,4}$	6.87 (m)
	$H^{2,3}$	4.18 (m)
	H^{5}	6.29 (m)
	$H^{6,6'}$	7.44 (s),
		7.90 (s)
	aromatic	2.90 (d),
		3.28 (d)
	$N-CH_3$	7.10 (s)
(3)	$H^{1,6'}$	6.16 (2, m)
	$H^{2,5}$	4.85 (2, m)
	$H^{3,4}$	3.69 (2, m)
	H^{7}	6.33 (1, m)
	aromatic	3.42 (2, d),
		3.80 (2, d)
	$N-CH_3$	7.18 (6, s)

* Intensities and multiplicities are given in parentheses.

Similarly, the ^{1}H n.m.r. spectrum of product (3) is as expected for a substituted 1,3,5-triene. From the aromatic portion of each of the above spectra (Table 1) it is also clear that the $[Fe(dienyl)(CO)_3]^+$ and $[Cr(C_7H_7)(CO)_3]^+$ cations have attached to *NN*-dimethylaniline at C^4, *para* to the dimethylamino-group. This is the normal position for electrophilic attack as predicted from simple electrostatic and steric considerations.[18]

TABLE 3

Kinetic data for reactions of other organometallic cations with *NN*-dimethylaniline

Cation	Solvent	θ_c/°C	$10^2[C_6H_5NMe_2]$/ mol dm^{-3}	$10^4k_{obs.}$/s^{-1}	10^3k/ dm^3 mol^{-1} s^{-1}
$[Fe(C_6H_7)(CO)_3]^{+\,a}$	MeCN	21.3	0.654		4.90
		35.0	0.654		13.6
		45.0	0.654		28.4
		57.0	0.654		65.2
	$MeNO_2$	45.0	0.654		51.3
$[Ru(C_6H_7)(CO)_3]^{+\,b}$	$MeNO_2$	45.0	10.1	1.24	1.23 ^{c}
$[Os(C_6H_7)(CO)_3]^{+\,b}$	$MeNO_2$	45.0	5.0	2.25	4.51 ^{c}

^{a} [Fe] = 6.54 × 10^{-3} mol dm^{-3}. ^{b} [Ru] or [Os] = 6.0 × 10^{-3} mol dm^{-3}. ^{c} Calculated assuming equation (iv).

The kinetic data in Table 2 for the reaction of $[Fe(C_6H_6OMe\text{-}2)(CO)_3][BF_4]$ with *NN*-dimethylaniline in a variety of solvents show close adherence to the second-order rate law (iv) over the concentration range $[C_6H_5NMe_2] = 0.01 - 1.0$ mol dm^{-3}.

$$k_{obs.} = k[Fe][C_6H_5NMe_2] \qquad \text{(iv)}$$

This rate law is consistent with electrophilic attack by the $[Fe(dienyl)(CO)_3]^+$ cation on *NN*-dimethylaniline, as outlined in the general mechanism below (Scheme 1). A similar mechanism has recently been proposed[5] for the analogous reactions with the aromatic heterocycles pyrrole and furan. From the kinetic evidence it is not possible to distinguish between rate-determining formation of a π complex (5) (*i.e.* $k_{obs.} = k_1[C_6H_5NMe_2]$) and rate-determining formation of the Wheland-type σ complex (6) with no significant contribution from a π-complex intermediate. Rapid proton loss (k_3) is not surprising in view of the electron-withdrawing character of the $[Fe(C_6H_6A)(CO)_3]$ moiety.[19]

TABLE 2

Kinetic data for the reaction of $[Fe(C_6H_6OMe\text{-}2)(CO)_3][BF_4]$ with *NN*-dimethylaniline in various solvents at 45.0 °C. [Fe] = 3.0 × 10^{-3} mol dm^{-3}

Solvent	$10^2[C_6H_5NMe_2]$/ mol dm^{-3}	$10^4k_{obs.}$/s^{-1}	$10^2k\,^a$/dm^3 mol^{-1} s^{-1}
$MeNO_2$	1.0	1.20	1.20
	2.0	2.27	1.14
	3.0	3.61	1.20
	6.0	7.18	1.20
	8.0	9.64	1.20
	10.0	12.3	1.23
	100 ^{b}	121	1.21
MeCN	3.0	2.22	0.740
	6.0	4.83	0.806
	10.0	7.77	0.776
Me_2CO	3.0	1.73	0.577
	6.0	3.50	0.583
	8.0	4.88	0.609
	10.0	5.88	0.588
	100 ^{b}	60.1	0.601

^{a} Derived from equation (iv), $k_{obs.} = k[C_6H_5NMe_2]$. ^{b} *via* Stopped-flow technique.

The reaction of $[Fe(C_6H_7)(CO)_3][BF_4]$ with $C_6H_5NMe_2$ also obeys the second-order rate law (iv) (Table 3). The large negative $\Delta S^{\ddagger}$ value of -99 ± 10 J K^{-1} mol^{-1} estimated for this latter reaction in MeCN solvent is expected for Scheme 1, and is similar to the $\Delta S^{\ddagger}$ values previously found with pyrrole and indole as substrates (Table 4). The somewhat slower reaction with $C_6H_5NMe_2$ is seen to arise largely from a significantly higher enthalpy of activation, $\Delta H^{\ddagger}$. Table 4 also indicates that $C_6H_5NMe_2$ is much more susceptible towards electrophilic attack than the fundamental five-membered heterocyclic aromatics furan and thiophen.

Choice of solvent has a small influence on the rate of reaction (ii; M = Fe), which decreases by a factor of two along the series $MeNO_2 > MeCN > Me_2CO$ (Tables

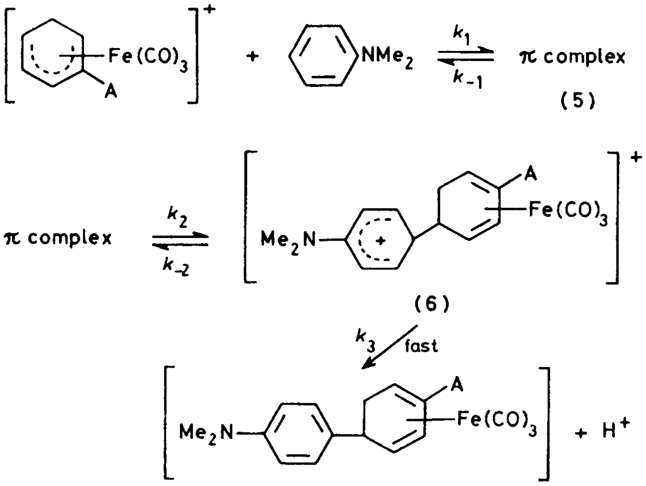
TABLE 4

Rate and activation parameters for reaction of $[Fe(C_6H_7)(CO)_3][BF_4]$ with aromatic substrates

RH	Relative k (45 °C)	$\Delta H^‡$/ kJ mol^{-1}	$\Delta S^‡$/ J K^{-1} mol^{-1}
Pyrrole [a]	3.2×10^6	47.2 ± 2.9	-96 ± 8
Indole [a]	2×10^6	43.5 ± 0.4	-113 ± 4
$C_6H_5NMe_2$	1.2×10^5 [b]	55.8 ± 0.8 [c]	-99 ± 10 [c]
Furan [a]	23		
Thiophen [a]	1		

[a] Ref. 5, $MeNO_2$ solvent. [b] This work, $MeNO_2$ solvent. [c] This work, MeCN solvent.

2 and 3). Interestingly, this order contrasts with that previously observed for the analogous reactions with heterocyclic aromatic substrates,[5] where the rates in MeCN were 2—7 times faster than in $MeNO_2$. These differences must reflect variations in the intimate mechanism (Scheme 1) with the nature of the aromatic substrate.



SCHEME 1

Finally, preliminary kinetic data for reaction (ii; A = H, M = Ru or Os) in Table 3 provide the first quantitative comparison of the reactivity of dienyl rings when co-ordinated to each of the metals Fe, Ru, and Os. Assuming a common mechanism, the electrophilicity of the C_6H_7 ligand is seen to decrease in the order $Fe > Os > Ru$ (41 : 3.6 : 1). Interestingly, although the order $Fe > Ru$ is now established with a variety of nucleophiles, the Fe/Ru rate quotient varies markedly with the nature of the nucleophile. For example, Fe/Ru quotients of 4 300, 134, and 18 have been found for reactions (ii) with RH = pyrrole,[5] indole,[4] and 2-methylfuran,[5] respectively. These different relative rates are not explicable in terms of the 'reactivity–selectivity' principle,[20] which would predict the largest ratio with the least reactive substrate, namely 2-methylfuran. Rate comparisons between iron and related ruthenium and osmium complexes may in some cases be complicated by changes in mechanism down the triad.[4,15,16]

Despite such problems considerable progress has now been made in establishing the relative reactivity of organometallic cations towards nucleophiles. In particular, the following reactivity order is indicated for reaction with *NN*-dimethylaniline: $[Mn(C_7H_8)(CO)_3]^+ >$ $[Fe(C_4H_4)(CO)_2(NO)]^+$ (ref. 21) $> [Fe(C_6H_7)(CO)_3]^+ >$ $[Fe(C_6H_6OMe\text{-}2)(CO)_3]^+ > [Os(C_6H_7)(CO)_3]^+ >$ $[Ru(C_6H_7)(CO)_3]^+ > [Cr(C_7H_7)(CO)_3]^+$ (ref. 22) (relative rates *ca.* 10 000 : 230 : 100 : 20 : 10 : 2.5 : 1). A similar order has recently been reported[23] for reaction with tertiary phosphines, although the range of reactivities was *ca.* 30 times smaller than with the less reactive *NN*-dimethylaniline.

We thank the S.R.C. for the award of a Studentship (to G. R. J.), and D. A. Sweigart for helpful discussions.

[8/1572 *Received*, 31*st August*, 1978]

REFERENCES

[1] L. A. P. Kane-Maguire and C. A. Mansfield, *J.C.S. Chem. Comm.*, 1973, 540.

[2] C. A. Mansfield, K. M. Al-Kathumi, and L. A. P. Kane-Maguire, *J. Organometallic Chem.*, 1974, **71**, C11.

[3] G. R. John, L. A. P. Kane-Maguire, and C. Eaborn, *J.C.S. Chem. Comm.*, 1975, 481.

[4] L. A. P. Kane-Maguire and C. A. Mansfield, *J.C.S. Dalton*, 1976, 2192.

[5] G. R. John, C. A. Mansfield, and L. A. P. Kane-Maguire, *J.C.S. Dalton*, 1977, 574.

[6] G. R. John, L. A. P. Kane-Maguire, and C. Eaborn, unpublished work.

[7] A. J. Birch, P. E. Cross, J. Lewis, D. A. White, and S. B. Wild, *J. Chem. Soc.* (*A*), 1968, 332.

[8] R. G. Cowles, Ph.D. Thesis, University College, London, 1969.

[9] E. G. Bryan, A. L. Burrows, B. F. G. Johnson, J. Lewis, and G. M. Schiavon, *J. Organometallic Chem.*, 1977, **129**, C19.

[10] J. D. Munro and P. L. Pauson, *J. Chem. Soc.*, 1961, 3475.

[11] L. A. P. Kane-Maguire, *J. Chem. Soc.* (*A*), 1971, 1602.

[12] L. A. P. Kane-Maguire and C. A. Mansfield, *J.C.S. Dalton*, 1976, 2192.

[13] D. E. Games, A. H. Jackson, L. A. P. Kane-Maguire, and K. Taylor, *J. Organometallic Chem.*, 1975, **88**, 345.

[14] G. R. John and L. A. P. Kane-Maguire, *J.C.S. Dalton*, 1979, 873.

[15] E. G. Bryan, A. L. Burrows, B. F. G. Johnson, J. Lewis, and G. M. Schiavon, *J. Organometallic Chem.*, 1977, **129**, C19 and refs. therein.

[16] A. Burrows, Ph.D. Thesis, Cambridge University, 1977.

[17] M. A. Hashmi, J. D. Munro, P. L. Pauson, and J. M. Williamson, *J. Chem. Soc.* (*A*), 1967, 240.

[18] P. Sykes, 'Mechanism in Organic Chemistry,' 3rd edn., Longman, 1970, ch. 6.

[19] J. M. Landesberg and L. Katz, *J. Organometallic Chem.*, 1971, **33**, C15.

[20] H. C. Brown and K. L. Nelson, *J. Amer. Chem. Soc.*, 1953, **75**, 6292.

[21] D. A. Sweigart, personal communication.

[22] L. Al-Dugaither and L. A. P. Kane-Maguire, unpublished work.

[23] D. M. Birney, A. M. Crane, and D. A. Sweigart, *J. Organometallic Chem.*, 1978, **152**, 187.