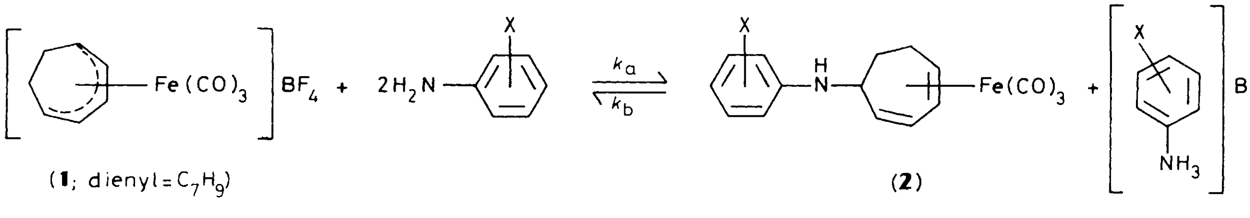
Addition of Anilines to the $[Fe(CO)_3(1—5\text{-}\eta\text{-}C_7H_9)]BF_4$ Complex, and the 'Ordered Transition State Mechanism'

Timothy I. Odiaka
Department of Chemistry, University of Ibadan, Ibadan, Nigeria

Kinetic studies of the reversible addition of anilines to the complex $[Fe(CO)_3(1—5\text{-}\eta\text{-dienyl})]BF_4$(**1**; dienyl = C_7H_9) have demonstrated the dependence of rate on the electronic and steric nature of the attacking nucleophile. A plot of $\Delta H_a^\ddagger$ *versus* $\Delta S_a^\ddagger$ for the reaction of aniline with the complexes $[Fe(CO)_3(1—5\text{-}\eta\text{-dienyl})]BF_4$ (**1**; dienyl = C_6H_7, 2-MeOC_6H_6, or C_7H_9) is linear, the slope of which gives an isokinetic temperature of 369 ± 23 K, indicating enthalpy control over the associative process. The reaction of aniline and other substituted anilines with complexes (**1**) clearly reveals the predominance of negative entropies of activation for the dissociative processes in these systems, thus providing strong support for the recently proposed 'Ordered Transition State Mechanism.'

In previous papers, the effects of variations in the steric and electronic properties of co-ordinated organic molecules on their reactivity towards a wide variety of aromatic substrates such as amines,[1–7] amides,[8] tertiary phosphines,[9–12] activated arenes,[13–15] and aryltrimethyl-silanes and -stannanes[16–17] have been examined. Some progress has also been made in establishing the influence of nucleophile basicity and its steric nature on the rate and mechanism of addition to co-ordinated organic molecules, *e.g.* anilines[3] and pyridines.[4,18] Recently, a detailed study of the addition of 4-chloroaniline to the complexes (**1**) was undertaken in order to improve understanding of the mechanism and thermodynamics of amine additions to co-ordinated organic molecules. These reactions afforded neutral products of the type [1—4-η-5-*exo*-*N*-anilinocyclohexa (or cyclohepta)-1,3-diene]tricarbonyliron in high yield and clearly demonstrated that the dissociative processes of amine additions to co-ordinated organic molecules are accompanied by large negative entropies of activation.[19] This interesting observation has been rationalised by the 'Ordered Transition State Mechanism' recently proposed by Odiaka.[19]

As an extension to these studies, this paper reports the results of a detailed kinetic study of the reaction of aniline with complex (**1**; dienyl = C_7H_9) as well as less extensive studies of the reaction of the same complex with X-substituted anilines [equation (1); X = H, 4-OMe, 3,4-Me$_2$, 3-Me, 3-OMe, 3-Cl, or 2-Cl].



(**1**; dienyl = C_7H_9) (**2**)

(1)

These results are compared with results reported earlier for amine additions to the complexes (**1**)[7,14,19] and thus throw more light not only on the influence of the steric and electronic nature of the amine nucleophile on reaction rates but also provide additional support on the predominance of large negative entropies of activation in the dissociative processes of these systems and the consequent operation of the recently proposed 'Ordered Transition State Mechanism.'[19]

Experimental

Materials.—The complex (**1**; dienyl = C_7H_9) was synthesized and purified as described previously.[20] Aniline and substituted anilines were purchased in the purest grades available (BDH or Aldrich). The liquids were freshly distilled under a dinitrogen atmosphere and dried over molecular sieves (size 3 Å) prior to use. The solids were used as supplied. Acetonitrile (BDH) solvent was distilled in bulk and stored over molecular sieves under a dinitrogen atmosphere.

Kinetic Studies.—All of the reactions (1) in MeCN were studied under pseudo-first-order conditions using a large excess of amine nucleophile ([Fe] = 1.5×10^{-3}, [amine] = 0.01—0.20 mol dm^{-3}). The reactions were rapid and were studied using a thermostatted (±0.1 °C) stopped-flow spectrophotometer at a wavelength of 390 nm where a large decrease in absorbance was observed. The reaction traces were recorded and analysed using a rapid data-capture system (Lombardi Scientific Ltd.) employing computer programs developed jointly with Lombardi (U.K.) Ltd., and described elsewhere.[21] Pseudo-first-order rate constants, $k_{obs.}$, were calculated from the slopes of plots of $\log(A_t - A_\infty)$ *versus* time which were linear for at least two half-lives. Each $k_{obs.}$ value is the average from at least six separate runs, with an average reproducibility of ±3%. The second-order rate constants, k_a, were derived by a least-squares fit to plots of $k_{obs.}$ *versus* [amine], and the errors quoted are the standard deviations. Activation enthalpies were obtained from the slopes of Arrhenius plots of $\log k_a$ or $\log k_b$ *versus* T^{-1}, calculated by a least-squares method. The errors quoted are the standard errors of estimation from these analyses. Entropies of activation were calculated from the second-order and first-order rate constants k_a and k_b respectively.

Results and Discussion

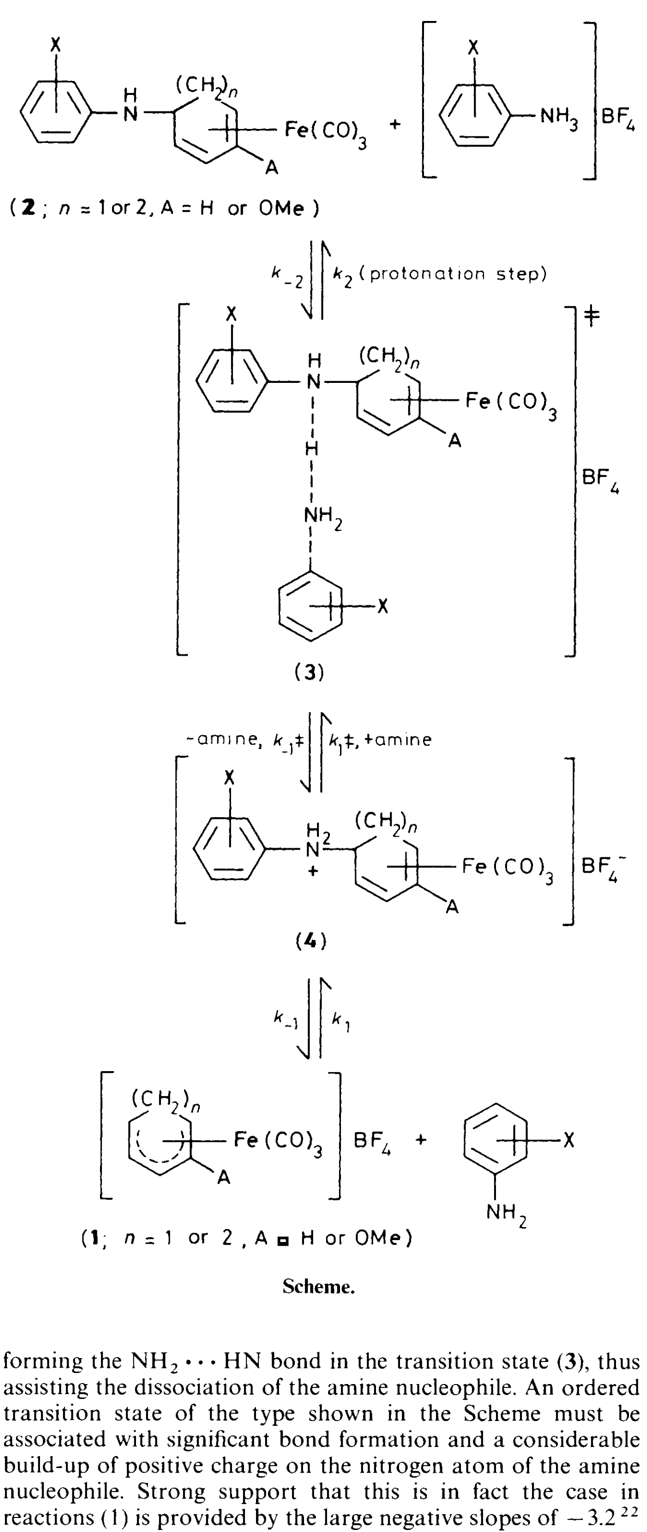
Nature of the Reactions.—The nature of the reactions between the organometallic complex (**1**; dienyl = C_7H_9) and a wide variety of anilines has been established by the isolation and characterisation of the anilinium adducts and by *in situ* i.r. and ^1H n.m.r. spectral studies.[2,3,7,19] The i.r. spectra exhibited two strong carbonyl bands at *ca.* 2 045 and 1 970 cm^{-1}. The same two ν(CO) bands were observed during the i.r. studies of reactions (1) using a large excess of amine nucleophile, indicating the formation of the same (1—4-η-5-*exo*-*N*-anilinocyclohepta-1,3-diene)tricarbonyliron complexes. The reversibility of reactions (1) was demonstrated by the addition of a few drops of trifluoroacetic acid to equilibrium mixtures as obtained from the reactions; the original organometallic compound (**1**; dienyl = C_7H_9) was regenerated quantitatively, as evidenced by the appearance of strong ν(CO) bands at 2 120 and 1 965 cm^{-1} and the disappearance of bands due to the products (**2**) at 2 045 and 1 970 cm^{-1}. The presence of the former bands in the reaction solutions of (**1**) even at infinite time further confirms that there is an equilibrium.

Kinetics and Mechanism.—Kinetic results for the addition of aniline and substituted anilines to complex (**1**; dienyl = C_7H_9) are listed in Table 1. Plots of $k_{obs.}$ *versus* [amine] are linear with non-zero intercepts, indicating the general two-term rate law (2). The separate k_a and k_b values shown in Table 1 were

$$R = k_a[\text{complex}][\text{amine}] + k_b[\text{complex}]$$
$$i.e.\ k_{obs.} = k_a[\text{amine}] + k_b \qquad (2)$$

calculated by a least-squares fit to equation (2). Rate equation (2) may be rationalised in terms of an initial amine addition to (**1**; dienyl = C_7H_9) to form the cationic diene intermediates, $[Fe(CO)_3(1\text{—}4\text{-}\eta\text{-diene}{\cdot}NH_2R)]^+$ from which the neutral products $[Fe(CO)_3(1\text{—}4\text{-}\eta\text{-diene}{\cdot}NHR)]$ are formed *via* amine-assisted proton removal.[3]

Table 2 lists the activation enthalpies and entropies determined to date for the addition of anilines to complexes (**1**) in MeCN, and clearly reveals the predominance of large negative entropies of activation for the dissociative processes of these systems. Although the addition of 4-methylaniline to complexes (**1**) has been reported,[2] a detailed study of the reverse dissociation step is being investigated and will appear in subsequent publications. Large negative entropies of activation have also recently been observed in the reverse step of the addition of 2-ethylpyridine to complexes (**1**; dienyl = 2-Me-OC_6H_6 or C_7H_9).[6] Such large negative entropies of activation are thus common features in the dissociative processes of amine additions to organometallics of type (**1**) and have recently been rationalised by the 'Ordered Transition State Mechanism' proposed by Odiaka[19] (Scheme). The proposed mechanism involves the formation of an ordered transition state (**3**) which results from a rather tight bonding and undergoes an internal S_N2 process in reforming the starting dienyl complexes (**1**) (dissociative process) or protonation to the anilinium salt and the products (**2**) (associative process). It is pertinent that 2 mol of amine are used up per mol of complex in the formation of the product (**2**) [equation (1)]. Such a novel mechanism would no doubt give rise to the observed negative entropies of activation (Table 2). Thus part of the energy necessary to effect breaking of the amine-carbon (diene) bond in complex (**4**) to form the starting dienyl complexes (**1**) is supplied by that produced in forming the $NH_2 \cdots HN$ bond in the transition state (**3**), thus assisting the dissociation of the amine nucleophile. An ordered transition state of the type shown in the Scheme must be associated with significant bond formation and a considerable build-up of positive charge on the nitrogen atom of the amine nucleophile. Strong support that this is in fact the case in reactions (1) is provided by the large negative slopes of −3.2[22] and −2.7[14] determined from the plots of log k_1 *versus* δ (the Hammett coefficient for various X-substituted anilines) for the reaction of anilines with (**1**; dienyl = C_6H_7 and 2-$MeOC_6H_6$ respectively) in MeCN. The k_1 values of 6 470 ± 260, 1 010 ± 5, and 386 ± 5 $dm^3\ mol^{-1}\ s^{-1}$ found respectively for addition of 4-methylaniline in MeCN at 0 °C to complexes (**1**) (diene = C_6H_7, 2-$MeOC_6H_6$ and C_7H_9) compare favourably with the corresponding values of 11 000 ± 443, 3 130 ± 280, and 560 ± 49 $dm^3\ mol^{-1}\ s^{-1}$ in $MeNO_2$ at the same temperature.[14] The results clearly suggest that solvation effects



Scheme.

Table 1. Kinetic results for reactions of $[Fe(CO)_3(1-5\text{-}\eta\text{-}C_7H_9)]BF_4$ (1.5×10^{-3} mol dm^{-3}) with anilines in MeCN

Nucleophile	θ_c/°C	10^2[amine]/ mol dm^{-3}	$k_{obs.}$/s^{-1}	k_a*/dm^3 mol^{-1} s^{-1}	k_b*/s^{-1}
H_2NPh	0.0	1.0	1.97		
	0.0	2.0	3.44		
	0.0	4.0	6.63		
	0.0	6.0	9.50		
	0.0	8.0	12.5	151 (1)	0.482 (0.054)
	8.5	1.0	3.20		
	8.5	2.0	5.60		
	8.5	4.0	10.2		
	8.5	6.0	15.1		
	8.5	8.0	19.6	235 (2)	0.873 (0.064)
	15.7	1.0	4.80		
	15.7	2.0	8.21		
	15.7	4.0	15.2		
	15.7	6.0	21.3		
	15.7	8.0	28.2	332 (4)	1.58 (0.21)
	20.0	1.0	6.01		
	20.0	2.0	10.2		
	20.0	4.0	18.1		
	20.0	6.0	25.6		
	20.0	8.0	34.1	397 (4)	2.11 (0.17)
$H_2NC_6H_4OMe$-4	0.0	1.0	6.24		
	0.0	1.5	9.64		
	0.0	2.0	11.7		
	0.0	3.0	18.0	578 (20)	0.563 (0.411)
$H_2NC_6H_3Me_2$-3,4	0.0	1.0	4.00		
	0.0	2.0	8.43		
	0.0	3.0	12.1		
	0.0	4.0	16.2		
	0.0	5.0	20.4	406 (5)	0.06 (0.15)
$H_2NC_6H_4Me$-3	0.0	1.0	2.16		
	0.0	2.0	4.33		
	0.0	4.0	8.18		
	0.0	6.0	12.1		
	0.0	8.0	16.2	199 (1)	0.237 (0.061)
$H_2NC_6H_4OMe$-3	0.0	1.0	1.81		
	0.0	2.0	3.60		
	0.0	4.0	6.80		
	0.0	6.0	9.81		
	0.0	8.0	13.0	158 (2)	0.35 (0.31)
$H_2NC_6H_4Cl$-3	0.0	2.5	1.34		
	0.0	5.0	2.02		
	0.0	10.0	3.39		
	0.0	15.0	4.66		
	0.0	20.0	6.24	27.7 (0.4)	0.62 (0.06)
$H_2NC_6H_4Cl$-2	0.0	2.5	1.15		
	0.0	5.0	1.20		
	0.0	10.0	1.29		
	0.0	15.0	1.42		
	0.0	20.0	1.51	2.09 (0.06)	1.09 (0.01)

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

are not important in the transition states of these reactions and cannot be responsible for the large negative entropies of activation found in the dissociative processes of such systems. In addition the formation of an *endo*-MeCN intermediate would be expected to give rise to *endo* products and not the well known *exo* derivatives already established for products (**2**).[2,3,7,14,19]

A plot of $\Delta H_a^\ddagger$ *versus* $\Delta S_a^\ddagger$ for the reaction of aniline with complexes (**1**; dienyl = C_6H_7, 2-$MeOC_6H_6$, or C_7H_9) (see Table 2) is linear, the slope of which gives an isokinetic temperature of 369 ± 23 K (which is much higher than the temperature range of 273—293 K in which the aniline reactions were studied for all three organometallics) indicating enthalpy control over the associative process.

Influence of Nucleophile Basicity.—The results in Tables 1 and 3 clearly reveal the dependence of rate on nucleophile basicity as previously established (see for example refs. 3 and 4). One interesting observation is that 3-methylaniline is more

Table 2. Activation parameters for amine additions to $[Fe(CO)_3(1\text{—}5\text{-}\eta\text{-dienyl})]BF_4$ complexes in MeCN

Dienyl	Amine	$\Delta H_a^\ddagger$/kJ mol^{-1}	$\Delta S_a^\ddagger$/J K^{-1} mol^{-1}	$\Delta H_b^\ddagger$/kJ mol^{-1}	$\Delta S_b^\ddagger$/J K^{-1} mol^{-1}
C_6H_7	Aniline[a]	8.2(0.2)	−150(4)	27.2(1.7)	−118(7)
	2-Methylaniline[a]	35.3(0.7)	−60(3)	37.8(2.2)	−85(8)
	4-Chloroaniline[b]	23.7(1.6)	−103(6)	35.8(1.4)	−89(5)
	2,6-Dimethylaniline[c]	20.8(0.8)	−119(3)	126(5.4)	220(19)
2-MeOC_6H_6	Aniline[a]	17.1(1.9)	−132(4)	61.2(2.6)	−9(9)
	2-Methylaniline[a]	45.1(1.9)	−45(7)	40.9(2.2)	−79(8)
	4-Chloroaniline[b]	39.0(5.8)	−64(21)	46.3(7.1)	−58(25)
C_7H_9	Aniline[d]	30.1(1.1)	−92(4)	46.6(1.4)	−79(3)
	2-Methylaniline[a]	29.7(0.1)	−104(2)	35.2(1.7)	−115(6)
	4-Chloroaniline[b]	28.7(1.0)	−106(3)	38.5(1.2)	−101(4)
	2,6-Dimethylaniline[c]	34.6(0.8)	−96(3)	54.0(1.0)	−43(3)

[a] Results from ref. 14. [b] Results from ref. 19. [c] Results from ref. 7. [d] This work.

Table 3. Variation of rates with amine basicity for the reactions of anilines with $[Fe(CO)_3(1\text{—}5\text{-}\eta\text{-}C_7H_9)]BF_4$ in MeCN at 0 °C

Amine	k_1/dm^3 mol^{-1} s^{-1}	pK_a[a] (H_2O)
$H_2NC_6H_4OMe\text{-}4$	578	5.34
$H_2NC_6H_4Me\text{-}4$[b]	386	5.08
$H_2NC_6H_4Me\text{-}3$	199	4.73
$H_2NC_6H_4OMe\text{-}3$	158	4.23
H_2NPh	151	4.63
$H_2NC_6H_4Me\text{-}2$[b]	43.0	4.44
$H_2NC_6H_4Cl\text{-}3$	27.7	3.46
$H_2NC_6H_4Cl\text{-}2$	2.09	2.65

[a] From Handbook of Chemistry and Physics, 61st edn., Rubber Company, Washington, 1980—1981. [b] Rate constants from ref. 14.

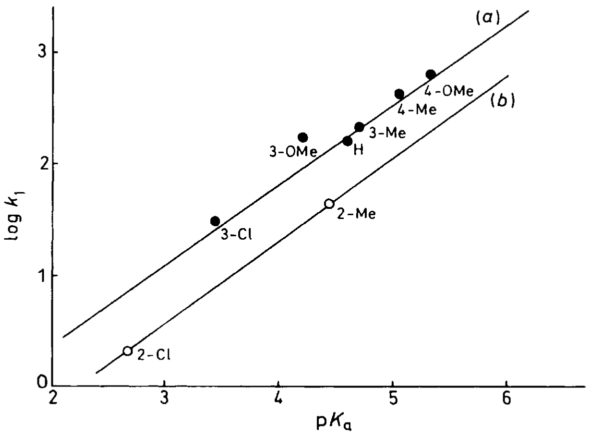


Figure. Brönsted plots for the reaction of $[Fe(CO)_3(1\text{—}5\text{-}\eta\text{-}C_7H_9)]BF_4$ in MeCN at 0 °C with (*a*) non-sterically hindered anilines and (*b*) anilines with 2-Me or 2-Cl groups

Table 4. Steric effects on rates of addition of anilines to $[Fe(CO)_3(1\text{—}5\text{-}\eta\text{-}C_7H_9)]BF_4$ in MeCN at 0 °C

Amine	k_1/dm^3 mol^{-1} s^{-1}	Relative k_1
H_2NPh[a]	151	12
$H_2NC_6H_4Me\text{-}2$[b]	43.0	3
$H_2NC_6H_3Me_2\text{-}2,6$[b]	12.7	1

[a] This work. [b] Rate constants from refs. 7 and 14.

reactive than 3-methoxyaniline whereas the reverse is the case for the 4-substituted analogues (Table 3). This is almost certainly due to the mesomeric influence of the methoxy group whose effect at the 3 position of the aniline nucleophile is to deactivate the N nucleus, thus considerably reducing its nucleophilicity. A Brönsted plot of log k_1 *versus* pK_a of the amine conjugate acid in water (Figure) gave a slope, α, of 0.67 ± 0.20 for addition of non-sterically crowded anilines to (**1**; dienyl = C_7H_9). A similar plot for addition of anilines to (**1**; dienyl = 2-MeOC_6H_6) gave an α value of 1.0,[3] revealing the much greater electrophilicity of the 2-MeOC_6H_6 complex compared to the C_7H_9 analogue, attributed to the increased steric hindrance caused by the extra methylene group in the latter if one assumes approach of the anilines from above the dienyl rings. This much higher α value also indicates the much greater accumulation of positive charge in the transition states of aniline reactions with the 2-MeOC_6H_6 complex than in their analogous reactions with the C_7H_9 complex.

Steric Influence of Nucleophile.—The steric effects of aniline additions to complex (**1**; dienyl = C_7H_9) is clearly demonstrated in the Figure and in Table 4 ($H_2NC_6H_5 > H_2NC_6H_4Me\text{-}2 > H_2NC_6H_3Me_2\text{-}2,6$; relative rates 12:3:1). The two straight lines shown in the Figure are plots of log k_1 *versus* pK_a of the amine conjugate acid for (*a*) non-sterically hindered anilines and (*b*) anilines blocked with methyl or chloride groups at the 2 position. The distance of *ca*. 0.5 log units between graphs (*a*) and (*b*) indicates a three-fold rate decrease due to steric blocking at the 2 position of the aniline nucleophile. Addition of pyridines to the same C_7H_9 complex resulted in a 10-fold rate decrease due to steric blocking at the 2 position of the pyridine nucleophile.[18] This observation is not surprising since it is obvious that the N reaction centre in pyridines is considerably more sterically masked by *ortho* substituents than is the N atom in the related anilines.

The importance of basicity and steric properties in determining amine nucleophilicity towards co-ordinated organic substrates in organometallics of the type (**1**) has been clearly established,[3,4] and it has been shown that the degree of accumulation of positive charge in the transition state of these systems depends on the nature of the co-ordinated organic moiety.[22] The transition-state species in these systems are believed to be highly ordered, thus allowing some internal S_N2 process in which Fe–C(diene) bond making accompanies carbon (diene)–amine bond breaking as explained with 4-chloroaniline in Odiaka's 'Ordered Transition State Mechanism'[19] and in the Scheme for other anilines. It is therefore not surprising that the dissociative processes of amine additions to organometallics of type (**1**) are usually associated with large negative entropies of activation (Table 2).

Acknowledgements

I am very grateful to Professor R. D. Gillard of University College, Cardiff for permitting the use of his laboratories, and to the University of Ibadan authorities for permission for study leave at Cardiff.

References

1 L. A. P. Kane-Maguire, T. I. Odiaka, S. Turgoose, and P. A. Williams, *J. Organomet. Chem.*, 1980, **188**, C5.
2 L. A. P. Kane-Maguire, T. I. Odiaka, and P. A. Williams, *J. Chem. Soc., Dalton Trans.*, 1981, 200.
3 L. A. P. Kane-Maguire, T. I. Odiaka, S. Turgoose, and P. A. Williams, *J. Chem. Soc., Dalton Trans.*, 1981, 2489.
4 T. I. Odiaka and L. A. P. Kane-Maguire, *J. Chem. Soc., Dalton Trans.*, 1981, 1162.
5 T. I. Odiaka and L. A. P. Kane-Maguire, *J. Organomet. Chem.*, 1985, **284**, 35.
6 T. I. Odiaka, *J. Chem. Soc., Dalton Trans.*, 1986, 2707.
7 T. I. Odiaka, *Inorg. Chim. Acta*, 1988, **145**, 267.
8 T. I. Odiaka and J. I. Okogun, *J. Organomet. Chem.*, 1985, **288**, C30.
9 M. Gower, G. R. John, L. A. P. Kane-Maguire, T. I. Odiaka, and A. Salzer, *J. Chem. Soc., Dalton Trans.*, 1979, 2003.
10 T. I. Odiaka, *Inorg. Chim. Acta*, 1985, **103**, 9.
11 G. R. John and L. A. P. Kane-Maguire, *J. Chem. Soc., Dalton Trans.*, 1979, 873.
12 A. L. Burrows, Ph.D. Thesis, University of Cambridge, 1978.
13 T. I. Odiaka and L. A. P. Kane-Maguire, *Inorg. Chim. Acta*, 1979, **37**, 85.
14 T. I. Odiaka, Ph.D. Thesis, University of Wales, 1980.
15 T. G. Bonner, K. A. Holder, P. Powell, and E. Styles, *J. Organomet. Chem.*, 1977, **131**, 105.
16 G. R. John, L. A. P. Kane-Maguire, T. I. Odiaka, and C. Eaborn, *J. Chem. Soc., Dalton Trans.*, 1983, 1721.
17 T. I. Odiaka, *J. Chem. Soc., Dalton Trans.*, 1985, 1049.
18 T. I. Odiaka, *J. Organomet. Chem.*, 1988, **345**, 135.
19 T. I. Odiaka, *J. Organomet. Chem.*, 1987, **321**, 227.
20 M. A. Hashmi, J. D. Munro, and P. L. Pauson, *J. Chem. Soc. A*, 1967, 240.
21 J. G. D. M. Atton, Ph.D. Thesis, University of Wales, 1982.
22 T. I. Odiaka, *Inorg. Chim. Acta*, 1989, in the press.

Received 21st March 1988; *Paper* 8/01160E