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A NEW AROMATIC METALLATION REACTION INVOLVING RHODIUM AND IRIDIUM; THE UNUSUAL REACTIVITY OF IODOBENZENE *

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Summary

Arenes (C_6H_5X) react with [$C_5Me_5IrMe_2$(DMSO)] (**1b**) to give methane and [$C_5Me_5IrMe(C_6H_4X)$(DMSO)]. The substituted phenyliridium complexes were isolated and characterised, the *m*-/*p*-isomer ratios being ca. 3/1 for X = I, Br and Cl, 2/1 for X = CF_3, 3/2 for X = CN, and 1/1 for X = NO_2, COMe and CO_2Me; only the *m*-isomer was obtained *m*- for X = NH_2. No *o*-substituted products could be detected. Reaction at higher temperature for longer times gave [$C_5Me_5Ir(C_6H_4X)_2$(DMSO)] (X = H, Cl, I), which were also characterised. The reactivity of C_6H_5X to **1b** decreases in the order X = I > NO_2 > CF_3 > CN > CO_2Me > COMe > Br > H > OMe > Cl > F > NH_2; iodobenzene is the fastest but reaction does not occur at the Ph–I bond. Deuteriation studies show that one CH_3D is formed for every **1b** reacted with C_6D_6. Complex **1b** exchanges with free DMSO and small quantities of DMSO inhibit the arylation reaction. The reaction does not appear to involve either electrophilic metal centres or free radicals. A mechanism consistent with the observations involves replacement of DMSO by the arene, oxidative addition of the aryl-H to the iridium giving an Ir^V intermediate which reductively eliminates CH_4 and recoordinates DMSO to give the observed product. The rhodium analogue [$C_5Me_5RhMe_2$(DMSO)] reacted analogously but more slowly with arenes. Reaction of [$C_5Me_5IrMe(C_6H_4NO_2)$(DMSO)] with hexachloroiridate(IV) gave nitrobenzene and a 1/1 mixture of *m*- and *p*-nitrotoluene; analogously [$C_5Me_5IrPh_2$(DMSO)] gave biphenyl.

Introduction

Aromatic metallation reactions have long been known and those involving mercury [1], thallium [2], palladium [3], and platinum [4] have been particularly well studied. In general the most common type of mechanism appears to be one where

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* With best wishes to our dear friend, Jack Halpern, on his 60th birthday.

the metal is acting as an electrophile, as judged by the substitution pattern for substituted benzenes. A typical instance is the use of mercuric acetate in the presence of strong non-coordinating acids where the active species is generally formulated as $[HgOAc]^+$ [1]. Examples where the metal centre is clearly acting as a nucleophile have also been identified [5].

A number of reactions are also known where the aryl C–H bond is oxidatively added to a metal centre in a suitably low oxidation state intermediate which is also coordinatively unsaturated (e.g. Cp_2W [6], C_5Me_5IrL [7], or C_5Me_5RhL [8]). These are all intermolecular processes where the metal centre and the aromatic moiety are not linked prior to reaction and are thus different from the cyclometallation reactions [9].

We report here a new set of intermolecular aromatic substitution reactions which do not seem to fall into any of these categories and which have a number of rather unique and unexpected features. A Preliminary communication on part of this work has been published [10].

Results and discussion

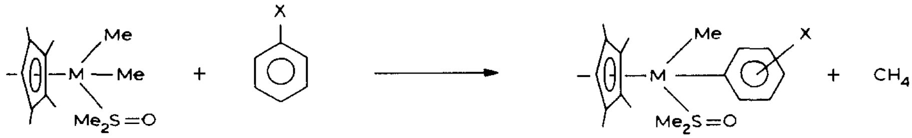
Preparation and charaterisation of mono- and di-aryl complexes

Although the recently reported and readily accessible dimethyl-rhodium and -iridium dimethyl sulphoxide (DMSO) complexes, (**1**) [11] are quite stable and easily handled (for example, in air) the DMSO ligands are very labile. Thus we observed, by ^1H NMR spectroscopy, rapid exchange of the DMSO in **1** with DMSO-d_6, the rhodium complex (**1a**) exchanging roughly three times as fast as the iridium complex (**1b**) (k_{Rh} 1.6×10^{-1} mol^{-1} s^{-1}; k_{Ir} 5.4×10^{-2} mol^{-1} s^{-1} at 35 °C).

This observation led us to seek examples of reactions that occurred as a consequence of this lability and the " vacant sites" so offered. The iridium complex **1b** was found to react readily with benzene and a variety of substituted benzenes to give methane and the aryl-methyl complexes, $[C_5Me_5Ir(C_6H_4X)Me(DMSO)]$ (Scheme 1).

The aryl-methyl complexes, $[C_5Me_5Ir(C_6H_4X)Me(DMSO)]$ (X = H, Cl, Br, I,

SCHEME 1



(**1a,b**)

(**a**, M = Rh , **b**, M = Ir)

	X
2a,b	H
4b	Cl
6b	Br
7b	I
9b	COMe
10b	CO_2Me
11b	NO_2
12b	CF_3
13b	CN
14b	NH_2

TABLE 1

YIELDS AND MICROANALYTICAL DATA

[$C_5Me_5IrR^1R^2(Me_2SO)$]			Yield (%)	Microanalyses (Found (calcd.) (%))			
R^1	R^2			C	H	S	X
Me	C_6H_5	**(2b)**	80	45.5	5.6	6.5	
				(45.9)	(5.9)	(6.4)	
C_6H_5	C_6H_5	**(3b)**	75	51.6	5.7	5.7	
				(51.5)	(5.6)	(5.7)	
Me	C_6H_4Cl	**(4b)**	75	43.1	5.4	5.9	Cl, 6.3
				(42.9)	(5.3)	(6.0)	(6.6)
C_6H_4Cl	C_6H_4Cl	**(5b)**	85	45.8	4.7	5.0	Cl, 11.0
				(45.9)	(4.7)	(5.1)	(11.3)
Me	C_6H_4Br	**(6b)**	80	39.4	4.8	5.4	Br, 13.7
				(39.6)	(4.9)	(5.6)	(13.9)
Me	C_6H_4I	**(7b)**	80	36.8	4.7	5.1	I, 20.2
				(36.6)	(4.5)	(5.1)	(20.4)
C_6H_4I	C_6H_4I	**(8b)**	80	35.8	3.7	4.1	I, 31.0
				(35.5)	(3.6)	(4.0)	(31.3)
Me	$C_6H_4CO_2Me$	**(9b)**	90	45.3	5.6	5.6	
				(45.4)	(5.6)	(5.8)	
Me	C_6H_4COMe	**(10b)**	90	46.6	5.8	6.0	
				(46.7)	(5.8)	(5.9)	
Me	$C_6H_4NO_2$	**(11b)**	90	41.5	5.3	5.8	N, 2.6
				(41.6)	(5.2)	(5.9)	(2.6)
Me	$C_6H_4CF_3$	**(12b)**	90	42.4	4.9	5.7	
				(42.5)	(5.0)	(5.7)	
Me	C_6H_4CN	**(13b)**	85	46.1	5.4	–	N, 2.7
				(46.0)	(5.4)		(2.7)
Me	$C_6H_4NH_2$	**(14b)**	75	44.3	6.0	6.3	N, 2.8
				(44.5)	(5.9)	(6.3)	(2.7)
[$C_5Me_5RhMe(Ph)(Me_2SO)$]		**(2a)**	75	55.8	7.3	7.5	
				(55.9)	(7.2)	(7.9)	

COOMe, COMe, NO_2, CF_3, CN, and NH_2), were obtained from the reactions in 80% or better isolated yields as stable yellow solids. They were identified by their microanalyses (Table 1), their IR spectra (which showed the presence of aryl bands, and also S-bonded DMSO bands at ca. 1085 cm^{-1}) and by their NMR spectra. These last showed that in nearly each case a mixture of isomers was present.

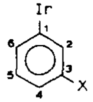
The isomers were largely identified by their ^{13}C NMR spectra at 25 MHz which showed that the *m*- and *p*-substituted benzenes were present (Table 2). The assignments were checked by applying standard substituent chemical shift differences for substituted benzenes from the literature. Thus, for example, applying the literature chemical shift differences [12] of -1.9 (*p*-), $+1.3$ (*m*-), $+0.4$ (*o*-) and $+6.2$ (*i*-) ppm for a chloro substituent on benzene to the values observed for the phenyl in **2b** (δ, *i*-, 138.6; *o*-, 139.3; *m*-, 127.3; and *p*-, 121.7) gave calculated values for the *p*-chlorophenyl resonances in very good agreement with those found (in brackets): δ, *i*-, 136.7 (136.3); *o*-, 140.6 (140.3); *m*-, 127.7 (127.1), and *p*-, 127.9 (128.3). The values for the *p*-nitrophenyl isomer were: δ, *i*-, 144.4 (144.3); *o*-, 140.2 (140.0); *m*-, 122.5 (121.1); and *p*-, 141.7 (141.3).

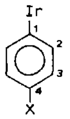
In each case (except for aniline) the ^1H NMR spectra (Table 3) again showed the presence of two types of C_5Me_5 and two Ir-methyls. As in the ^{13}C spectra, the

(Continued on p. 121)

TABLE 2

^{13}C NMR SPECTRA ^{a} (δ, ppm)





$[C_5Me_5IrR^1R^2(DMSO)]$ R^1	R^2	$C_5\mathit{Me}_5$	C_5Me_5	Me(Ir)	Me_2SO	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)
Me	C_6H_5	8.5	94.3	−16.6	42.3 45.7	138.6	139 3	127.3	121.7	–	–
C_6H_5	C_6H_5	9.3	96.9	–	44.1	137.2	142.0	127.0	121.8	–	–
Me	m-C_6H_4Cl	8.4	94.3	−16.4	42.3 45.6	141.4	138.2	132.4	121.7	128.2	137.7
Me	p-C_6H_4Cl	8.4	94.3	−16.6	42.3 45 6	136.3	140.3	127.1	128.3	–	–
C_6H_4Cl	m-C_6H_4Cl	9.3	97.2	–	44.3	139.3	139.6	128.1	122.2	132.5	141.0
C_6H_4Cl	p-C_6H_4Cl	8.6	94.4	–	44.5	134.7	142.8	127.3	128.8	–	–
Me	m-C_6H_4Br	8.5	94.4	−16.4	42.5 45.7	142.2	140.6	121.8	124.7	128.8	138.7
Me	p-C_6H_4Br	8.5	93.2	−16.6	39.8 45.2	137.3	141.0	130.1	116.7	–	–
Me	m-C_6H_4I	8.5	94.4	−16.3	42.5 45.7	143.0	146.7	95.6	130.7	129.3	139.2
Me	p-C_6H_4I	8.5	94.4	−16.7	42.5 45.7	138.5	141.8	136.0	n.o.	–	–

C_6H_4I	*m*-C_6H_4I	9.2	97.1	–	44.2	141.1	150.0	95.3	131.0	129.1	140.3
C_6H_4I	*p*-C_6H_4I	9.2	97.1	–	44.2	136.7	143.9	136.1	88.9	–	–
Me	*m*-$C_6H_4NO_2$	8.5	94.8	−16.2	42.6 45.9	n.o.	132.2	156.8	117.3	127.4	147.2
Me	*p*-$C_6H_4NO_2$	8.5	94.7	−16.4	42.6 45.9	144.3	140.0	121.1	141.3	–	–
Me	*m*-$C_6H_4CO_2Me$ [b]	8.3	94.3	−16.6	42.4 45.6	n.o.	139.3	128.1	123.2	126.8	144.9
Me	*p*-$C_6H_4CO_2Me$ [b]	8.3	94.3	−16.5	42.2 45.5	150.8	139.4	127.4	123.6	–	–
Me	*m*-C_6H_4COMe [c]	8.2	94.3	−16.7	42.1 45.5	138.9	144.9	135.8	121.8	127.0	152.2
Me	*p*-C_6H_4COMe [c]	8.2	94.2	−16.7	42.1 45.5	138.5	139.4	126.2	131.4	–	–
Me	*m*$C_6H_4CF_3$	8.4	94.5	−16.5	42.5 45.7	146.2	134.8 [d]	n.o.	118.5 [d]	126.9	139.5
Me	*p*-$C_6H_4CF_3$	8.4	93.2	−13.1	42.4 45.1	n.o.	143.5	123.2 [d]	n.o.	–	–
Me	*m*-C_6H_4CN [e]	8.4	94.5	−16.4	42.4 43.8	132.7	141.6	110.7	125.7	127.2	145.1
Me	*p*-C_6H_4CN [e]	8.4	94.6	−16.4	42.4 43.8	140.5	140.3	129.7	104.8	–	–
Me	*m*-$C_6H_4NH_2$	8.5	94.4	−16.5	42.4 45.7	139.1	126.8	145.2	109.7	127.7	132.8

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[a] In $CDCl_3$ solution. [b] *C*O$_2$Me 168.2 (*m*-) 168.4 (*p*-); CO$_2$*Me* 51.5 (*m*-) and 51.3 (*p*-). [c] CO*Me* 26.0 (*m*-), 26,5 (*p*-); *C*OMe 198.5 (*m*-), 199.3 (*p*). [d] Quartets, *J*(F–C) 4 Hz. [e] *C*N 151.2 (*m*-); 151.3 (*p*-).

TABLE 3

^{1}H NMR SPECTRA[a] (δ, ppm)

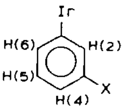
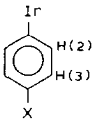
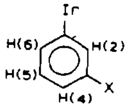
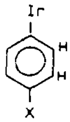
[$C_5Me_5IrR^1R^2(Me_2SO)$]		C_5Me_5	Me(Ir)	Me_2SO		
R^1	R^2					
Me	C_6H_5	1.63	0.24	2.67, 3.30	H(2)	7 32 (d, 8)
					H(3)	6.95 (t, 8)
					H(4)	6.90 (t, 8; t, 1.5)
C_6H_5	C_6H_5	1.61	–	2.81	H(2)	7.5 (d, 8; t, 1.5)
					H(3)	6 95 (m)
					H(4)	6 93 (m)
Me	m-C_6H_4Cl	1.63	0 23	2 70, 3.24	H(2)	7.16 (bd)
					H(4) H(5) H(6)	6.87 (m) 7.31 (m)
Me	p-C_6H_4Cl	1.62	0.21	2.64, 3.34	H(2)	6 93 (d, 8)
					H(3)	7.24 (d, 8)
C_6H_4Cl	m-C_6H_4Cl	1.60	–	2 82	H(2)	7.46 (t, 1.5)
					H(4)	7.37 (d, 8; t, 1.5)
					H(5)	6.88 (t, 8)
					H(6)	6.94 (m)
C_6H_4Cl	p-C_6H_4Cl	1.59	–	2.78	H(2)	7.42 (d, 8)
					H(3)	6 95 (m)
Me	m-C_6H_4Br	1.622	0.222	2.662,	H(2)	7.33
				3 027	H(4)	7.19 (d, 8)
					H(5)	6.71 (t, 8)
					H(6)	6.95 (d, 8; m)
Me	p-C_6H_4Br	1.619	0 205	2.637	H(2)	7.36(d, 8)
				3 001	H(3)	6 93 (d, 8; m)
Me	m-C_6H_4I	1.615	0.208	2 67	H(2)	7.54
				3.02	H(4)	7.39 (d, 8)
					H(5)	6.68 (t, 8)
					H(6)	7.23 (m)
Me	p-C_6H_4I	1.617	0.195	2.64	H(2)	7.23 (m)
				3.03	H(3)	7.09 (d, 8)
C_6H_4I	m-C_6H_4I	1.582	–	2.815	H(2)	7.80 (t, 1.5)
					H(4)	7.44 (d, 8; t, 1.5)
					H(5)	6.73 (t, 8)
					H(6)	7.25 (m)
C_6H_4I	p-C_6H_4I	1.588	–	2.781 2.826	H(2) H(3)	7.25 (m)
Me	m-$C_6H_4CO_2Me$ [b]	1.627	0.296	3.026	H(2)	7 90
				3.041	H(4)	7.67 (d, 8)
					H(5)	7.00 (t, 8)
					H(6)	7.57 (m)
Me	p-$C_6H_4CO_2Me$ [b]	1.619	0.261	2.651 (bd)	H(2)	7.47 (d, 8)
					H(3)	7.58 (d, 8; m)
Me	m-C_6H_4COMe [c]	1.544	0.188	2.565	H(2)	7.79
				2.574	H(4)	7.58 (d, 8)
					H(5)	6.95 (t, 8)
					H(6)	7.43 (m)
Me	p-C_6H_4COMe [c]	1.550	0.212	2.969 (bd)	H(2) H(3)	7 43 (m)

TABLE 3 (continued)

$[C_5Me_5IrR^1R^2(Me_2SO)]$		C_5Me_5	Me(Ir)	Me_2SO		
R^1	R^2					
Me	$m\text{-}C_6H_4NO_2$	1.630	0.275	2.536	H(2)	8.03
				2.965	H(4)	7.87 (d, 8)
					H(5)	7.07 (t, 8)
					H(6)	7.75 (d, 8; m)
Me	$p\text{-}C_6H_4NO_2$	1.638	0.305	2.529	H(2)	7.58 (d, 8)
				2.972	H(3)	7.76 (d, 8; m)
Me	$m\text{-}C_6H_4CF_3$	1.617	0.265	2.637	H(2)	7.48
				3.042	H(4)	7.63 (d, 8)
					H(5)	7.01 (t, 8)
					H(6)	7.14 (d, 8)
Me	$p\text{-}C_6H_4CF_3$	1.622	0.252	2.630	H(2)	7.14 (d, 8)
				3.048	H(3)	7.47 (d, 8)
Me	$m\text{-}C_6H_4NH_2$	1.632	0.220	2.715	H(4)	6.28 (d, 8)
				3.019	H(2,3,6)	6.7 m
$[C_5Me_5RhMe(Ph)(Me_2SO)]$		1.58	0.11 (d)	2.48	H(2–4)	6.96
			(*J*(Rh)	2.84		7.14 m
			3 Hz)			

[a] In $CDCl_3$ solution. [b] *Me*CO_2 3.855 (*p*-), 3.869 (*m*-). [c] *Me*CO 2.441 (*m*-), 2.476 (*p*-).

DMSO ligands showed two methyl resonances from each DMSO ligand in each isomer; the DMSO methyls are inequivalent since they are diastereotopic. A partial analysis of the aromatic region was possible at 400 MHz (with some decoupling). H(2) of the *m*-isomer generally appeared at lowest field as a broad singlet; occasionally this would show fine structure as a triplet, *J* 1.5 Hz, due to long-range coupling. H(5) of the *m*-isomer almost invariably appeared as a clean triplet (*J* 8 Hz), due to coupling to H(4) and H(6), at the high-field end of the aromatic region. H(4) and H(6) of the *m*-isomer and H(2) and H(3) of the *p*-isomer were less easily assigned but usually appeared as doublets (*J* 8 Hz), often with broadening or fine structure due to long-range coupling. The general pattern showed clear support for the assignments based on the ^{13}C spectra. No bands which could be ascribed to *o*-disubstituted benzenes were ever observed; we estimate that less than 5% of such isomers (if any) are formed. We observed little sign of the existence of rotamers under the conditions of measurement though the broadness of some lines could have been caused by their presence.

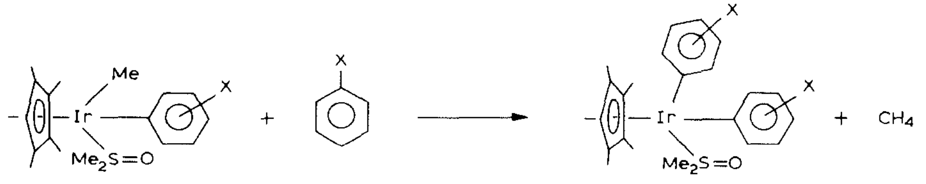
The ratios of *m*- to *p*-aryl isomers formed in the reactions varied with the nature of the substituent. It was ca. 3/1 for the halobenzenes, 2/1 for trifluoromethylbenzene, 3/2 for benzonitrile, and close to 1/1 for nitrobenzene, acetophenone, and methyl benzoate. Another surprising aspect of these reactions is that aniline also reacted with **1b**, albeit slowly but in the same way as the other arenes. In this case, however, only a single isomer, identified as the *m*-substituted aniline, was formed. These results imply a significant electronic influence over the direction of substitution.

The formation of di-aryl iridium complexes occurred reasonably smoothly when either **1b** or the appropriate methyl mono-aryl complex (**2b**, **4b**, or **7b**) was heated in an excess of arene at the higher temperature of 84 °C (Scheme 2). The corresponding diaryl complexes **3b**, **5b** and **8b** were isolated and fully characterised. Again the presence of *m*- and *p*-isomers in the two last was indicated from analysis of their ^{13}C spectra, as indicated above, by comparison with that of **3b**. Thus, for the bis-iodophenyl complex **8b** the calculated and found (in brackets) chemical shifts are, *p*-isomer, δ 135.8 (136.7), 143.4 (143.9), 135.7 (136.1), 87.7 (88.9), and *m*-isomer, δ 138.6 (142.1), 150.7 (150.0), 92.9 (95.3), 130.5 (131.0), 129.2 (129.1), and 140.6 (140.3) for C(1)–C(4) and C(1)–C(6) respectively. The NMR spectra of the bis-chloro- and the bis-iodo-phenyl complexes showed the presence mainly of two isomers, identified as the *m*-,*m*- and the *m*-,*p*-, together with a small amount of a third, presumably the *p*-,*p'*-. The ratio of *m*- to *p*- was very close to that found in the mono aryl complexes **4b** and **7b**. This again points to the importance of electronic factors in directing the substitution, since the steric factors in the transition states leading to the diaryl complexes **5b** and **8b** are not likely to be similar to those in the transition states leading to **4b** and **7b**.

Relative rate measurements

The relative reactivity of **1b** towards a series of substituted benzenes was measured by monitoring the decrease in the integrals of the **1b** methyl resonances in the ^{1}H NMR spectrum, when a sample of the complex was heated in an NMR tube in the arene as solvent. From these data a series of relative rate constants were obtained. The reactions actually showed pseudo-first order behaviour (first order in complex **1b**, zero in the arene; Table 4 and Fig. 1) at the high arene concentrations used. However, second order behaviour was shown for the reaction of **1b** at lower benzene concentrations. Since there were marked differences in concentrations between one arene and another the second order rate constants were also evaluated to allow better comparisons to be made; in fact the rate constants relative to benzene were similar in both cases. These data show a most unusual and irregular variation; thus toluene and anisole, which are activated towards electrophiles and normally the most reactive in metallation reactions, react rather slowly here. On the whole, benzenes with eletron-withdrawing substituents are activated, thus trifluoromethyl- and nitrobenzene react four and five times faster, respectively, than benzene. However, methyl benzoate and acetophenone are only slightly faster than benzene, and fluorobenzene and chlorobenzene are actually slower. The most surprising result

SCHEME 2



	X
2b	H
4b	Cl
7b	I

	X
3b	H
5b	Cl
8b	I

was that of all the arenes so far investigated, iodobenzene reacted by far the fastest, nearly eight times as fast as benzene. Although disubstituted benzenes were not investigated in any detail, *o*-xylene was very slow indeed and *o*-diiobenzene reacted more slowly than iodobenzene. We may conclude that while electronic factors are very important in the activation, they cannot override the steric effects. The relative rate of the reaction of **2b** with excess benzene to give the diphenyl complex **3b** was ca. 10% of the rate at which **2b** itself was formed.

Addition of even small amounts of DMSO (1–3 equivalents) stopped the reactions of **1b** entirely; this indicates that they occur at the sites previously occupied by the DMSO.

From the reactivity pattern the metallation reaction is clearly not electrophilic in character; one possibility then is that it proceeds by some type of free radical process. For example, Hey and collaborators found the order $PhNO_2$ (4) > PhI (1.8) > PhF (1.4) > PhH (1) for the free-radical phenylation of substituted benzenes [13]. Three comparative reactions between iodobenzene and **1b** were carried out. The first was a control with no additives, the second contained di-t-butyl peroxide as a radical initiator, and the third contained galvinoxyl as a radical trap. There was no significant difference in rates (at 50 °C) between the first two. The third was a little (ca. 20%) slower but we ascribe this to a direct reaction between **1b** and galvinoxyl rather than to an inhibitory effect. Our present evidence therefore argues against significant participation by free radicals in the substitution process. Further, free radical reactions are typically rather random leading to a diversity of products; our reactions usually gave the products in high yields.

Reaction of **1b** with hexadeuteriobenzene proceeded much more slowly than with benzene itself ($k_H/k_D = 2.4$). The gas produced was shown by mass-spectrometry to contain only CH_3D. This supports the picture of the reaction proceeding by an

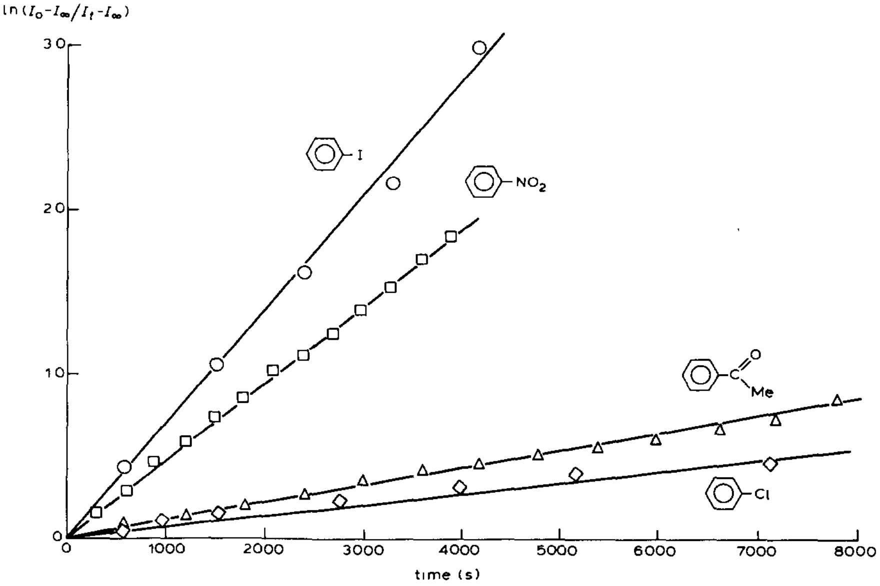


Fig. 1. Pseudo first-order plots for the reaction of $[C_5Me_5IrMe_2(DMSO)]$ with ArH.

TABLE 4

RATE CONSTANTS FOR THE REACTION [$C_5Me_5M(Me)_2DMSO$]+Arene

Arene	$k \times 10^5$ (s^{-1})[a]	$k_2 \times 10^6$ ($mol^{-1}\ l\ s^{-1}$)[b]
M = Ir (at 52 °)		
$C_6D_5CD_3$	2	0.8
$C_6H_5NH_2$	2	1
C_6D_6	4	5
C_6H_5F	7	6
C_6H_5Cl	7	8
C_6H_5OMe	9	9
C_6H_6	10	12
C_6H_5Br	13	13
C_6H_5COMe	12	14
$C_6H_5CO_2Me$	13	15
C_6H_5CN	15	16
$C_6H_5CF_3$	41	37
$C_6H_5NO_2$	48	60
C_6H_5I	77	78
M = Rh (at 84 °C)		
$C_6H_5CF_3$	0.4	0.3
C_6H_6	0.3	0.3
$C_6H_5NO_2$	3	1
C_6H_5I	3	2

[a] Pseudo first-order rate constants. [b] Second-order rate constants.

initial slow oxidative addition of aryl–H(D) to give a transition state from which CH_3–H(D) is then reductively eliminated. The formation of methane in these reactions also excludes the possibility that the reaction involves an initial (bimolecular) reductive elimination to give a lower oxidation state complex which then oxidatively adds the Ar-H in a subsequent step. Such a process would demand the formation of ethane, which was not observed.

When a solution of **1b** in a mixture of benzene and hexadeuteriobenzene was heated the methane given off was composed of 61 ± 1% CH_4 and 39 ± 1% CH_3D. ^1H NMR analysis (at 400 MHz) of the complex **2b** formed showed it to have 60 ± 5% [$C_5Me_5IrMe(C_6H_5)(DMSO)$] and 40 ± 5% [$C_5Me_5IrMe(C_6D_5)(DMSO)$]; no significant scrambling of the deuterium elsewhere in the molecule had occurred. This result indicates that there is a direct relation between the gas given off and the product formed and implies that they are formed in the same concerted process.

Benzene and substituted benzenes also reacted with the rhodium complex **1a** but very much more slowly (by a factor of ca. 400) than with the iridium analogue **1b** and required a higher temperature to get useful rates. Again, iodo- and nitro-benzene reacted much faster than benzene. It is interesting that although the rhodium complex **1a** exchanges DMSO faster than the iridium complex **1b** the rates of reaction with the arenes go the other way. These results point to a number of factors being of importance in the overall reaction.

Mechanism of the reactions

The data cited above may be summarised. (i) Benzene and monosubstituted benzenes are readily metallated by Ir, more slowly by Rh. Diarylation is slower than mono-arylation. (ii) Reaction occurs initially at the site occupied by the DMSO. (iii) The metallation goes *m*-, *p*-; *m*-substitution usually predominates and electronic factors strongly influence the chosen site. (iv) Deuteriation experiments suggest that the aryl–H(D) bond is broken in the rate-determining step and show that one CH_3D is formed for every deuteriophenyl in the complex.

While we cannot definitively exclude all odd-electron species, the data appear to effectively rule out substantial participation by free radicals in the reactions. Accordingly the mechanism shown in Scheme 3 is proposed; all the data that we have at the moment are in good agreement with it.

The first stage in the mechanism is proposed to be the replacement of coordinated DMSO by arene. This may be part of the rate-determining step since although DMSO exchanges fast in **1**, the presence of even a small excess of DMSO stops the metallation process entirely.

Since the faster reactions involve arenes bearing hetero-substituents (-I, -CN, -COOMe, $-NO_2$, etc), it is possible that the hetero-atom may coordinate first. This is the conventional mode by which oxidative addition of, say, alkyl halides is believed to occur [14]. The high rate of reaction shown by iodobenzene here might also be thought to be related to the recently reported isolation of a stable complex in which *o*-diiodobenzene is chelated to iridium [15]. However, we believe that interactions between the metal and the aryl hetero-atom are incidental to the reactions described here. For example, in none of our reactions have we seen attack either at the hetero-substituent or *ortho*- to it. *Meta*-attack predominates, which would not be anticipated. Further, in our reactions *o*-diiodobenzene is significantly slower than iodobenzene.

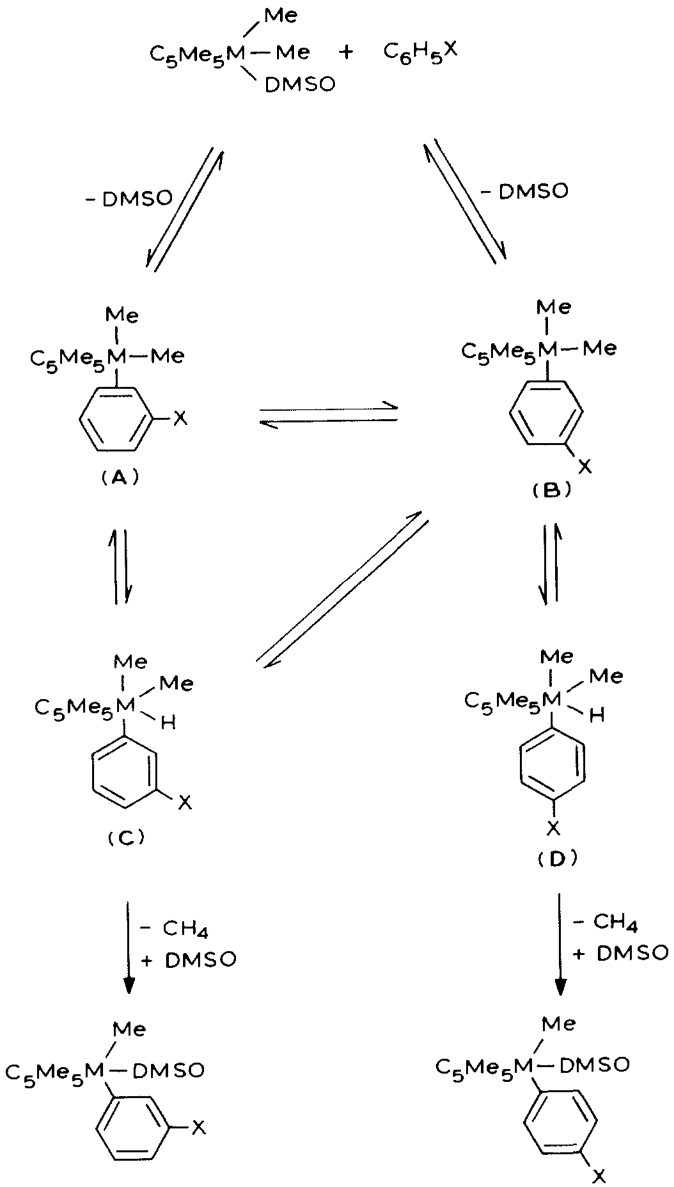
Indeed, for iodobenzene itself attack *meta* to the iodine is wholly unexpected; low valent metal ions invariably oxidatively add to it by cleaving the Ph–I bond [16]. We presume that this form of attack does not occur here since the product, $[C_5Me_5IrMe_2(Ph)I]$, would have iodide bonded to Ir formally in the +5 oxidation state. This would not be anticipated to be very favourable since iodide is so easily oxidised; indeed our attempts to prepare higher oxidation state complexes with iodide as ligand have been unsuccessful [17].

We presume that the arene is η^2-coordinated in the first step as this retains the 18-electron configuration for the metal. η^2-Coordination of arenes to $C_5Me_5Rh^I$ and to $CpRe^I$ has recently been demonstrated [8,18] and was shown to be an important step in the aromatic metallation by these centres.

Three η^2-orientations are possible for a monosubstituted benzene; the metal may coordinate to the 1,2-, the 2,3-, or the 3,4-bonds (substituent at 1-). The first is the least likely on steric grounds since the bulk of the 1-substituent may be expected to interfere very strongly with coordination. Since none of the *o*-isomer is detected in the metallation products, this also argues against the metal binding to the 1,2-bond. We presume however that equilibria exist between isomers **A** and **B** of Scheme 3 in which the 2,3- and the 3,4- bonds are coordinated. Jones and Graham and their coworkers [8,18] noted that complexes of the type LL′M(tolyl)H readily isomerised (*m*-$\rightleftharpoons$*p*-) and were in equilibrium with η^2-toluene complexes.

However, whereas in the Graham system the predominant isomer was the *m*- for trifluoromethylphenyl but *p*- for tolyl [18], in our work the *m*-isomer predominated in all cases except for nitrobenzene, acetophenone and methyl benzoate where *m*-

SCHEME 3



and p- were equal. One possible reason for this difference between the two systems is that the site where the η^2-arene coordinates is more open in the iridium than in the rhenium system, thus disfavouring the m-site in favour of the p- for rhenium.

An alternative explanation is that the C_5Me_5Ir is acting more like a negative centre (i.e. more nucleophile-like, owing to the electron-releasing properties of the C_5Me_5 ring [19]) and that the benzenoid substituents are directing largely by inductive effects. In that case attack by Ir should occur preferentially o- to strongly electron-withdrawing $(-I)$ substituents. If this is inhibited for steric reasons then the next most likely position of attack is *m*-. One would also expect that substituents where the mesomeric $(-M)$ effect is important, such as COOMe, COMe, or NO_2, will direct attack *p*- in addition.

"Arene activation", in which the aryl–H bond is oxidatively added to the metal, occurs in this step. This produces **C** or **D** (Scheme 3), in which the metal is formally now in the +5 oxidation state; the 18-electron configuration is retained if the aryl becomes σ-bonded.

We have recently shown that the C_5Me_5 ligand will stabilise very effectively a substantial number of complexes of rhodium and iridium in both the +4 and the +5 states. Particularly relevant in this context are the complexes $[C_5Me_5M(H)_2(SiEt_3)_2]$ (M = Rh and Ir) [20,21] and $[C_5Me_5IrMe_4]$ [22] which are all surprisingly stable, and rather unreactive except in the presence of electrophiles. These complexes indicate that species such as **C** and **D** are not likely to be so high in energy as to preclude their participation as reaction intermediates.

We have also noted that the predominant mode of decomposition of $[C_5Me_5Rh(H)_2(SiEt_3)_2]$ is by loss of Et_3Si–H. The bond energy of the C–H bond (416 kJ mol^{-1}) is much higher than that for the Si–H bond (326 kJ mol^{-1}) [23] and therefore it may be expected that the reductive elimination will be even more strongly favoured for **C** and **D**. Elimination of aryl–H yields **A** or **B** and is thus non-productive; elimination of Me–H followed by recoordination of DMSO gives the observed products. Other studies have also indicated that reductive elimination of Me–H is strongly favoured [24].

The proposal is also consistent with rhodium reacting more sluggishly than iridium. If the rate-determining step is indeed the oxidative addition of aryl–H in a complex where the formal oxidation state of the metal changes from +3 to +5, then the 5*d* metal would be expected to undergo this more easily than the 4*d* metal since in general the 5*d* metals form more stable high oxidation state complexes.

Attempts to apply Hammett σ or Taft σ^+ parameters [25] to the relative rate data gave very bad scatter and there was no obvious linear relation. We interpret this to mean that different factors in the above scheme are of different significance for each arene. At least three such factors can be distinguished, the rates at which η^2 complexation occur, the equilibria between the various η^2 complexes formed, and the relative rates of oxidative addition.

It is also of interest to mention two related papers. Aoyama et al. have recently reported aromatic metallation by a rhodium centre in a porphyrin complex [26]. The order of reactivity they observe for C_6H_5X, OMe > Me > H > Cl, is typical for electrophilic attack and quite different from our data. They also find that attack is exclusively *p*- on the arene; this is presumably a consequence of the bulk of the porphyrin ligand.

Klabunde and Parshall have reported H/D exchange on four benzenes catalysed by $[Ir(PMe_3)_2H_5]$ [27]. In this case benzene was more activated than anisole or toluene but was less active than fluorobenzene, but their mechanism seems to imply that the active aryl-hydride intermediates are not Ir^V species. Despite this, a family resemblance to our reactions is not surprising.

Coupling to substituted toluenes or biphenyl

Over the last few years we have been interested in electrophile- (1 electron oxidant-) promoted coupling reactions [28–30]. We therefore also examined the reactions of **1a**, **3b**, and a variety of aryl-methyl-iridium complexes with various electrophiles and oxidisers.

The dimethyl complex **1a** reacted with acids (sulphuric, tetrafluoroboric, etc.) and with Ce^{IV} to give largely methane together with a little ethane (1–5%). However with silver tetrafluoroborate the amount of coupling (ethane) increased to 60% while with hexachloroiridate(IV) ethane was the major product (98%) and only a small amount of methane (2%) was formed [29].

Reaction of the aryl-methyl-iridium complexes **4b**, **6b**, **7b**, and **11b** with silver tetrafluoroborate gave predominantly the arene by cleavage of the aryl–Ir bond. A small amount (ca. 1–10%) of the coupled toluene (MeC_6H_4X) was also formed. The substituted toluene was however, the main product when the complexes were reacted with hexachloroiridate(IV), when the proportion of coupled to cleaved product was typically 60–100%.

The diphenyl complex **3b** also reacted with hexachloroiridate to give, as expected, biphenyl.

Although these last reactions have not been optimised or thoroughly explored they provide a good indication of the feasibility of coupling. They make it possible, at least in principle, to carry out the reaction sequence,

$$C_6H_5X + C_6H_5Y \rightarrow XC_6H_4\text{–}C_6H_4Y$$

in a very controlled way.

Experimental

All reactions were carried out under a protective blanket of nitrogen or argon; the complexes **1a** and **1b** were prepared as described [11]. Solvents and liquid (aromatic) reagents were dried and distilled under nitrogen prior to use. Details of typical reactions are given below. Yields and microanalytical data (by the University of Sheffield Microanalytical Service) are collected in Table 1, and $^{13}C\ \{^1H\}$ NMR spectra (measured on a JEOL PFT-100 spectrometer at 25 MHz) and ^1H NMR spectra (measured on a Bruker WH-400 at 400 MHz) of isolated complexes are given in Tables 2 and 3 respectively. Mass spectra were determined on a Kratos MS 25 mass spectrometer; gas samples were introduced through a Carlo Erba gas chromatograph (Poropak Q column).

*(Dimethyl sulphoxide)(methyl)(iodophenyl)(pentamethylcyclopentadienyl)iridium (**7b**)*

A solution of $[C_5Me_5IrMe_2(DMSO)]$ (**1b**) (0.100 g, 0.23 mmol) in iodobenzene (0.5 cm^3; 4.5 mmol) was heated under argon in an NMR tube (52 °C/1.5 h). After this time the ^1H NMR spectrum showed that essentially complete conversion into **7b** had occurred. The excess iodobenzene was removed in vacuo, and the residue exctracted with pentane (2 × 12 cm^3). The pentane extracts were combined, filtered and concentrated; yellow crystals of **7b** (80%) were obtained after standing at 0 °C for 24 h.

*(Dimethyl sulphoxide)bis-iodophenyl(pentamethylcyclopentadienyl)iridium (**8b**)*

A solution of complex **1b** (81 mg, 0.186 mmol) dissolved in iodobenzene (0.5 cm^3, 4.5 mmol) was heated under argon in an NMR tube (24 h/84 °C). After this time the ^1H NMR spectrum showed that no **1b** or **7b** remained. The solvent was removed in vacuo and the residue extracted with pentane (2×10 cm^3). Concentration of the pentane extracts gave yellow crystals of **8b** (80%) on standing at 0 °C.

Kinetic measurements

A solution of complex **1b** (typically 0.05–0.1 mmol) in the arene (0.5 cm^3; 50–100 molar excess), was sealed in an NMR tube under argon. The ^{1}H NMR spectrum was run (at 60 MHz, Perkin–Elmer R-12B spectrometer) and the methyl signals of the Ir–Me, the C_5Me_5 and the DMSO were carefully integrated. The NMR tube was then placed in a constant temperature bath (at 52 or 84 °C, depending on the speed of the reaction) and the NMR spectrum was monitored periodically, careful integrals being measured of the same three resonances. Both the pseudo-first order and the second order rate constants were evaluated by standard methods [31] using a least squares plot (Fig. 1).

Coupling reaction

The nitrophenyl complex **11b** (9 μmol; isomer mix, *metal/para* = 1/1) and sodium hexachloroiridate (45 μmol) were placed in a 5 cm^3 flask fited with a rubber septum. The flask was evacuated and then filled with dry nitrogen. Acetonitrile (0.5 cm^3) was added by syringe and the resulting dark green solution stirred and warmed. GC-MS analysis (OV101 column at 145 °C isothermally) showed the presence of nitrobenzene and nitrotoluene (*m-/p-* = 1/1, no *ortho-*) in the ratio of 1/2.

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