

## Iridium(v) and Rhodium(v) Intermediates in Aromatic Metallation; the Unusual Reactivity of Iodobenzene

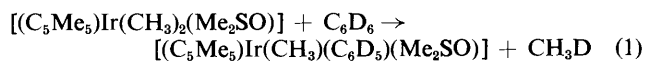
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$[(C_5Me_5)Ir(Me)_2(Me_2SO)]$  reacts with arenes ( $C_6H_5X$ ) to give methane and a mixture of *m*- and *p*-substituted  $[(C_5Me_5)Ir(Me)(C_6H_4X)(Me_2SO)]$ ; the order of reactivity is  $X = I > NO_2 > CF_3 > Br > H > OMe > Cl > F > Me$ ; iridium(v) species are proposed as intermediates.

Most organometallic reactions (especially catalytic ones) of mononuclear rhodium and iridium complexes have so far been interpreted to involve only oxidation states +I and +III. We have recently described a number of stable organometallic complexes of rhodium<sup>1</sup> and of iridium<sup>2,3</sup> where the formal oxidation state of the metal is +V. We here present evidence which indicates that  $Ir^V$  and  $Rh^V$  alkyl-hydrides can be intermediates in aromatic substitution (metallation) reactions.

The recently synthesised complexes  $[(C_5Me_5)M(Me)_2\{(CH_3)_2SO\}]$  (**1a**,  $M = Rh$ ; **1b**,  $M = Ir$ )<sup>4</sup> exchange readily with  $(CD_3)_2SO$  ( $k_{Rh} = 1.6 \times 10^{-1} \text{ mol}^{-1} \text{ s}^{-1}$ ,  $k_{Ir} = 5.4 \times 10^{-2} \text{ mol}^{-1} \text{ s}^{-1}$  at 35 °C). On heating the iridium complex (**1b**) in benzene, methane and the complex  $[(C_5Me_5)Ir(Me)(Ph)(Me_2SO)]$  (**2b**) were obtained. Hexadeuteriobenzene reacted more slowly with (**1b**) ( $k_H/k_D = 2.24$ ) to give the penta-deuteriophenyl analogue of (**2b**) and essentially pure  $CH_3D$  (by mass spectrometry), in agreement with the equation (1).



A second, much slower, substitution also occurred with (**2b**) and benzene to give the diphenyl complex  $[(C_5Me_5)Ir(Ph)_2(Me_2SO)]$ .

We have investigated the relative rates of substitution of some monosubstituted benzenes by the iridium complex (**1b**). Toluene, anisole, chloro- and fluoro-benzene reacted more slowly than benzene, but very much faster rates were observed for other halogenobenzenes, trifluoromethylbenzene, and nitrobenzene (Table 1).

Attention is drawn particularly to the unprecedented behaviour of iodobenzene since it reacted the fastest of all and because the attack was at a C-H bond. This is in marked contrast to the reaction of iodobenzene with low-valent metal complexes, when oxidative addition of the C-I bond occurs.<sup>5,6</sup>

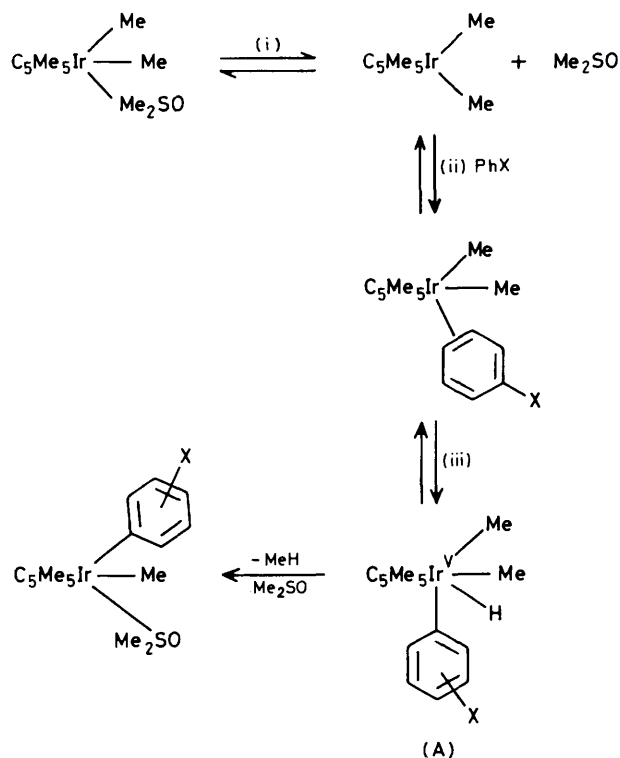
The rapid rate of reaction of (**1b**) with iodobenzene allowed the isolation and characterisation of the bis-iodophenyl as well as the methyl(iodophenyl) complex. Analysis by n.m.r. spectroscopy showed that in both cases a 3:1 mixture of *m*- and *p*-iodophenyl isomers was present: for example,

\* Satisfactory microanalytical and spectroscopic data have been obtained for all new complexes.

**Table 1.** Second-order rate constants for the reaction between  $[(C_5Me_5)Ir(Me)_2(Me_2SO)]$  and  $ArX$  (at 52 °C).

ArX	$k \times 10^6 / \text{mol}^{-1} \text{s}^{-1} \text{ a}$	ArX	$k \times 10^6 / \text{mol}^{-1} \text{s}^{-1} \text{ a}$
$C_6D_6$	5.2	$C_6H_5Br$	13
$C_6H_5F$	5.6	$C_6H_5CF_3$	37
$C_6H_5Cl$	7.6	$C_6H_5NO_2$	60
$C_6H_5OMe$	8.8	$C_6H_5I$	78
$C_6H_6$	11.7		

<sup>a</sup> Second-order rate constants were determined for the reaction carried out in benzene or the substituted benzene by monitoring the <sup>1</sup>H n.m.r. spectra.

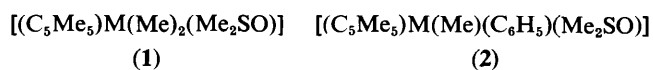


**Scheme 1**

$[(C_5Me_5)Ir(Me)(m\text{-}p\text{-}C_6H_4I)(Me_2SO)]$ , <sup>1</sup>H n.m.r.,  $CDCl_3$  (400 MHz); *m*-isomer:  $\delta$  0.208 (s, Me-Ir), 1.615 (s,  $C_5Me_5$ ), 2.67, 3.02 (2  $\times$  s,  $Me_2SO$ ), 6.68 (t,  $J$  7.5 Hz, *m*-H), 7.37 (d, br.,  $J$  8 Hz, *p*-H), 7.22 (m, *o*-H), and 7.54 (s, br., *o*-H); *p*-isomer:  $\delta$  0.195 (s, Me-Ir), 1.720 (s,  $C_5Me_5$ ), 2.65, 3.03 (2  $\times$  s,  $Me_2SO$ ), 7.07 (d, br.,  $J$  7.5 Hz, *m*-H), and 7.22 (dd,  $J$  8, 1.3 Hz, *o*-H).

The rhodium complex (1a) also reacted with benzene to give  $[(C_5Me_5)Rh(Me)(C_6H_5)(Me_2SO)]$  (2a) but the reaction giving the iridium complex (2b) was ca. 400 times faster.

This type of reactivity seems quite unprecedented though Hey and collaborators did note that the order for free-radical phenylation of substituted benzenes was  $C_6H_5NO_2$  (4) >  $C_6H_5I$  (1.8) >  $C_6H_5F$  (1.4) >  $C_6H_6$  (1).<sup>7</sup> We may rule out any significant contribution of free-radical processes to the reactions described here on three grounds. (i) The reactions are 'clean' and the isolated yields of products are between 75 and 90%. (ii) The rates are unaffected by addition of either free-radical inhibitors (galvanoxyl) or initiators (di-*t*-butyl peroxide). (iii) The absence of scrambling. When (1b) was



a; M = Rh

b; M = Ir

reacted with a mixture of benzene and deuteriobenzene, the proportion of  $CH_3D$  in the methane (by mass spectrometry) was the same as the proportion of  $[(C_5Me_5)Ir(CH_3)(C_6D_5)(Me_2SO)]$  in the product (by n.m.r. spectrometry).

These results are consistent with the mechanism outlined in Scheme 1. Step (i) involves the initial dissociation of  $Me_2SO$  to create a vacant site. In support of this proposal, addition of even small amounts of  $Me_2SO$  to the reaction of (1) and arene slows down the rate very dramatically. Step (ii) involves  $\eta^2$ -co-ordination of the arene and (iii) the oxidative addition giving the  $Ir^V$  intermediate (A). Reductive elimination of methane and re-co-ordination of  $Me_2SO$  complete the process. The lower stability expected for a  $Rh^V$  intermediate analogous to (A) can account for the lower reactivity of (1b) in these reactions.

The reactions described here may be contrasted with the oxidative C-H additions to  $Ir^I$  and  $Rh^I$  recently reported by a number of workers.<sup>8-10</sup> They may also be compared to the reaction undergone by the solution from  $[(C_5Me_5)Ir_2Cl_4]$  and  $Al_2Me_6$  with benzene or toluene to give aryl-iridium complexes which already occurs above  $-60^\circ C$ .<sup>11</sup> We tentatively suggest substitution to occur there by electrophilic attack of species such as  $[(C_5Me_5)IrMe]^+[Al_2Me_6Cl_2]^-$  on the arene. When this reaction cannot occur the alternative process described in this communication can take place at rather higher temperatures. This is then the higher energy path.

We also note that there are similarities between the reactions described here and the H/D exchange reactions of benzenes catalysed by  $[(Me_3P)_2IrH_5]$ .<sup>12</sup>

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