

## Dramatic Acceleration of Migratory Insertion in $[\text{MeIr}(\text{CO})_2\text{I}_3]^-$ by Methanol and by Tin(II) Iodide

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Carbonylation of  $[\text{MeIr}(\text{CO})_2\text{I}_3]^-$  to  $[\text{MeCOIr}(\text{CO})_2\text{I}_3]^-$  requires temperatures  $>80^\circ\text{C}$  in chlorobenzene, but is dramatically accelerated on addition of methanol ( $\times 10^4$  at  $33^\circ\text{C}$ ) or of the Lewis acid  $\text{SnI}_2$  ( $\times 200$  at  $93^\circ\text{C}$ ); the acceleration is proposed to arise from activation of an Ir–I bond.

We have established that the rate-determining step in the overall catalytic cycle for the rhodium and iodide catalysed carbonylation of methanol to acetic acid (BP–Monsanto process) is the oxidative addition of iodomethane to  $[\text{Rh}(\text{CO})_2\text{I}_2]^-$ .<sup>1</sup> The transient  $[\text{MeRh}(\text{CO})_2\text{I}_3]^-$  undergoes rapid methyl migration to give  $[\text{MeCORh}(\text{CO})\text{I}_3]^-$ .

An alternative catalyst, which is also active for methanol carbonylation, is based on iridium and iodide.<sup>2</sup> The iridium system was proposed by Forster to have cycles basically similar to the rhodium-promoted process but with a greater degree of complexity, due to the participation of both neutral and anionic species.<sup>3</sup> The rate-determining step at low  $[\text{I}^-]$  is given by reaction (1).



We recently reported quantitative kinetic studies which showed that migration of methyl onto carbonyl is *ca.*  $10^5$ – $10^6$  faster for  $\text{Rh}^{\text{III}}$  than for  $\text{Ir}^{\text{III}}$  in comparable systems.<sup>4</sup> Thus, to make an iridium-catalysed process competitive with one based on rhodium, it is necessary to promote the migration reaction. We have confirmed Forster's observation that reaction (1) proceeds slowly at  $80^\circ\text{C}$  in chlorobenzene and have found it to be independent of  $p_{\text{CO}}$  above a threshold of *ca.* 50 psi (1 psi  $\approx$  6.9 kPa). We now report that this reaction is dramatically accelerated on addition of small amounts of methanol (*e.g.* 1% v/v); addition of the Lewis acid,  $\text{SnI}_2$ , also causes large rate enhancements.

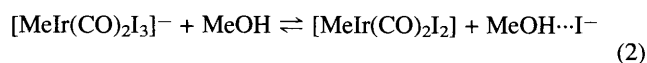
The kinetics of reaction (1) were measured in a cylindrical internal reflectance (CIR) cell<sup>5</sup> by FTIR spectroscopy;† first-order rate constants are given in Table 1. An Eyring plot for the unpromoted reaction over the temperature range  $80$ – $122^\circ\text{C}$ , gave  $\Delta H^\ddagger$   $155 \pm 4$  kJ mol<sup>-1</sup> and  $\Delta S^\ddagger$   $91 \pm 8$  J mol<sup>-1</sup> K<sup>-1</sup>. Addition of  $\text{I}^-$  resulted in a decrease in rate, as previously reported by Forster, consistent with a mechanism involving dissociative substitution of  $\text{I}^-$  by CO (Scheme 1).

Addition of methanol (1–50% v/v) to the reaction in chlorobenzene increased the rate dramatically and it could now

conveniently be monitored between  $30$  and  $52^\circ\text{C}$  ( $p_{\text{CO}}$  80 psi; Table 1). For example, addition of only 1% MeOH (v/v) resulted in a  $t_{\frac{1}{2}}$  of 13 h at  $33^\circ\text{C}$ ; by contrast, from the above activation parameters,  $t_{\frac{1}{2}}$  is predicted to be *ca.* 17 years in neat chlorobenzene at  $33^\circ\text{C}$ . Thus, 1% MeOH results in a 10 000-fold rate enhancement. Higher methanol concentrations give approximately linear rate increases. Smaller rate enhancements were found for the higher alkyl alcohols, the relative rates  $[\text{MeOH} (100) > \text{EtOH} (36) \approx \text{ethylene glycol} (35) > \text{PrOH} (12) > \text{Pr}^i\text{OH} (9) > \text{BuOH} (\text{ca. } 0.1)]$  being in agreement with their Taft  $\alpha$  values of hydrogen bond donor ability.<sup>6</sup> Other protic compounds (phenol,  $\text{CF}_3\text{CH}_2\text{OH}$ , or acetic acid), were less effective, and aprotic donor solvents (THF, MeCN) had little effect. Addition of water to a PhCl:MeOH (3:1) solvent system resulted in a further modest acceleration of reaction (1).

Kinetic measurements in a PhCl:MeOH (3:1) solvent system gave quite different activation parameters from those in neat chlorobenzene, with a much lower  $\Delta H^\ddagger$  ( $33 \pm 6$  kJ mol<sup>-1</sup>) and a large negative  $\Delta S^\ddagger$  ( $-197 \pm 11$  J mol<sup>-1</sup> K<sup>-1</sup>). This suggests a change in the nature of the rate-determining step of reaction (1) from dissociative in neat chlorobenzene ( $\Delta S^\ddagger$   $+91$  J mol<sup>-1</sup> K<sup>-1</sup>) to associative ( $\Delta S^\ddagger$   $-197$  J mol<sup>-1</sup> K<sup>-1</sup>) in chlorobenzene–methanol.

Since the rate of migration in the presence of methanol was again strongly retarded by added  $\text{I}^-$  we suggest that a reversible dissociation of  $\text{I}^-$  is the key step which is promoted by methanol, by virtue of H-bonding interactions [eqn. (2)]. The proposed five-coordinate intermediate,  $[\text{MeIr}(\text{CO})_2\text{I}_2]$ , may also be stabilised by methanol solvation.

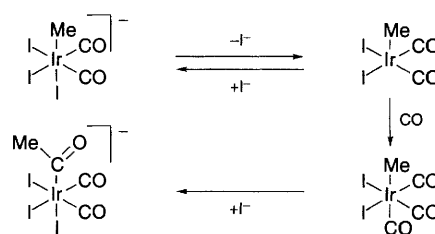


Donor solvents have frequently been found to give large rate enhancements in migratory CO insertion reactions, but those effects are generally explained in terms of solvent stabilisation of an unsaturated intermediate generated after the alkyl migration step. In this iridium system, however, the acceptor properties of the solvent play a more prominent role, aiding the dissociation of an anionic ligand prior to alkyl migration. Alcohols have also been found to accelerate alkyl isomerisation by facilitating dissociation of  $\text{I}^-$  in the iridium complexes,  $[\text{R}^i\text{Ir}(\text{CO})(\text{L})_2(\text{Y})\text{I}]^-$ .<sup>7</sup>

Rate data for the iridium-catalysed carbonylation of methanol (in acetophenone;  $125$ – $173^\circ\text{C}$ ; independent of  $p_{\text{CO}}$  above a

**Table 1** First-order rate constants for carbonylation of  $\text{Ph}_4\text{As}[\text{MeIr}(\text{CO})_2\text{I}_3]$  ( $[\text{Ir}] = 3.65 \times 10^{-2}$  mol dm<sup>-3</sup>,  $p_{\text{CO}} = 80$  psi)

$T/^\circ\text{C}$	Solvent	Additive (% v/v or mol equiv./Ir)	$k_{\text{obs}}/10^{-5} \text{ s}^{-1}$
80	PhCl	—	0.41
93	PhCl	—	3.65
108	PhCl	—	20
122	PhCl	—	140
93	THF	—	3.0
93	THF	$\text{SnI}_2$ (2 equiv.)	700
33	PhCl	MeOH (1%)	1.47
33	PhCl	MeOH (25%)	65.6
33	PhCl	MeOH (50%)	137
30	PhCl	MeOH (25%)	62.6
39	PhCl	MeOH (25%)	93.3
44	PhCl	MeOH (25%)	123
47	PhCl	MeOH (25%)	128
52	PhCl	MeOH (25%)	155



**Scheme 1**

threshold of 200 psi) have been reported,<sup>8</sup> from which the activation parameters can be evaluated ( $\Delta H^\ddagger$  34 kJ mol<sup>-1</sup> and  $\Delta S^\ddagger$  -246 J mol<sup>-1</sup> K<sup>-1</sup>). These data are very similar to those for our model migration reactions in chlorobenzene containing methanol and indicate that the same factors are common to both.

In view of the dramatic accelerations induced by Lewis acids that have been reported by Shriver and his collaborators,<sup>9</sup> we also tested a range of metal iodides, including AlI<sub>3</sub>, ZnI<sub>2</sub>, SnI<sub>2</sub> and SnI<sub>4</sub>. Significant acceleration of the migratory insertion was only found for SnI<sub>2</sub>. Rate data for this reaction were measured in THF solution for solubility reasons (Table 1). Addition of 2 equiv. of SnI<sub>2</sub> gave a rate enhancement of ca. 200, at 93 °C and 80 psi CO. Extrapolation of data for the methanol-promoted reaction in chlorobenzene indicates a very similar rate enhancement at 93 °C, making the two promoters comparable. Lewis acids have been found to effect a wide range of accelerations of migration processes for neutral complexes, but this appears to be the first example of an acceleration for an anionic complex.

Spectroscopic evidence suggests that [MeIr(CO)<sub>2</sub>I<sub>3</sub>]<sup>-</sup> is activated by reaction with SnI<sub>2</sub> even in the absence of CO. The <sup>1</sup>H NMR spectrum of a THF solution of [MeIr(CO)<sub>2</sub>I<sub>3</sub>]<sup>-</sup> immediately after adding 3 equiv. of SnI<sub>2</sub> showed a new resonance with satellites due to H-Sn coupling [ $\delta$  2.20; <sup>3</sup>J<sub>117Sn-1H</sub> 57 Hz; <sup>3</sup>J<sub>119Sn-1H</sub> 59 Hz]; integration of the satellite intensities relative to the central peak was consistent with the presence of one Sn per Ir-Me moiety. Thus, we propose that the species initially formed is [MeIr(CO)<sub>2</sub>I<sub>2</sub>(SnI<sub>3</sub>)]<sup>-</sup> resulting from formal insertion of SnI<sub>2</sub> into an Ir-I bond. Consistent with this proposal, IR spectroscopy showed an immediate change in  $\nu(\text{CO})/\text{cm}^{-1}$  to higher frequency (from 2089, 2036 to 2094, 2047) on addition of SnI<sub>2</sub>, a change of the magnitude and in the direction expected for the replacement of an iodide by the much stronger  $\pi$ -acceptor ligand, SnI<sub>3</sub>. We suggest that the SnI<sub>3</sub> ligand activates the complex towards migratory insertion due either to its strong *trans*-effect or to its high lability.<sup>10</sup>

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### Footnote

† Standard carbonylation conditions for kinetic experiments monitored by CIR-FTIR spectroscopy (silicon rod): [Ir] = 3.65 × 10<sup>-2</sup> mol dm<sup>-3</sup>; 8 cm<sup>3</sup> solvent, *p*<sub>CO</sub> 80 psi. The reactions were monitored by following the replacement of the  $\nu(\text{CO})/\text{cm}^{-1}$  bands in the IR at 2095, 2043 due to [MeIr(CO)<sub>2</sub>I<sub>3</sub>]<sup>-</sup> by those at 2106, 2058 and 1670 (*b*) due to [MeCOIr(CO)<sub>2</sub>I<sub>3</sub>]<sup>-</sup>. For the unpromoted reaction at higher temperatures, weak absorptions were also observed at 2043 and 1965 cm<sup>-1</sup> due to formation of small amounts of [Ir(CO)<sub>2</sub>I<sub>2</sub>]<sup>-</sup>.

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