

# Spectroscopic identification and reactivity of $[\text{Ir}(\text{CO})_3\text{I}_2\text{Me}]$ , a key reactive intermediate in iridium catalysed methanol carbonylation

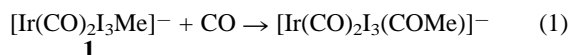
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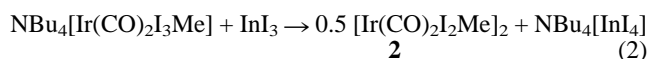
The dimer  $[\text{Ir}(\text{CO})_2\text{I}(\mu\text{-I})\text{Me}]_2$  **2** reacts with CO to give the tricarbonyl  $[\text{Ir}(\text{CO})_3\text{I}_2\text{Me}]$  **3** identified by high pressure IR and NMR spectroscopy and isotopic labelling; kinetic data for the migratory CO insertion reaction of **3** support its role as a key intermediate in iridium catalysed methanol carbonylation.

A new homogeneous catalytic process for the carbonylation of methanol to acetic acid has recently been commercialised by BP Chemicals.<sup>1,2</sup> The *Cativa* process is based on a promoted iridium/iodide catalyst system, and shows enhancements in rate, selectivity and stability compared with the established rhodium-based technology. The catalytic cycles for the two metals are similar, but show some important differences.<sup>3–6</sup> Forster's original kinetic and spectroscopic studies of the iridium system led to the proposal of catalytic cycles involving both anionic and neutral complexes. At moderate iodide concentrations, the resting state of the catalyst is the anionic methyl complex,  $[\text{Ir}(\text{CO})_2\text{I}_3\text{Me}]^-$  **1** and the rate determining step is thought to be carbonylation of this species [eqn. (1)]



Both the catalytic reaction and the carbonylation of **1** were found to be inhibited at high  $[\text{I}^-]$ , suggesting a mechanism involving neutral intermediates formed by iodide dissociation from **1**.<sup>6</sup> We recently reported that the carbonylation of **1** is promoted substantially by protic solvents which can aid the dissociation of an iodide ligand.<sup>7</sup> Here, we report the synthesis and characterisation of  $[\text{Ir}(\text{CO})_2\text{I}(\mu\text{-I})\text{Me}]_2$  and its reaction with carbon monoxide to give  $[\text{Ir}(\text{CO})_3\text{I}_2\text{Me}]$ . This tricarbonyl species, a key intermediate in the proposed carbonylation mechanism, was never detected in Forster's original studies. Its observation has now allowed us to compare the rate of migratory CO insertion in neutral and anionic species.

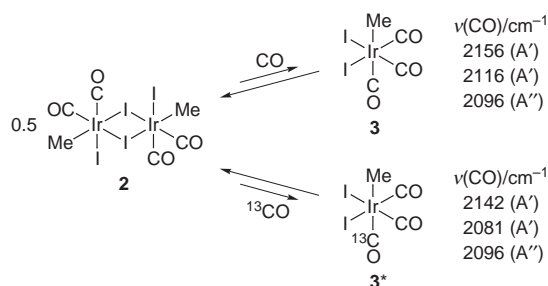
In our initial attempts to synthesise and isolate a neutral iridium methyl complex we used silver salts (*e.g.*  $\text{AgBF}_4$ ) to abstract iodide from the anionic precursor, **1**. Although IR spectroscopy indicated the formation of a product with  $\nu(\text{CO})$  bands (2119 and 2074  $\text{cm}^{-1}$ ) similar to those reported by Forster for  $[\text{Ir}(\text{CO})_2\text{I}_2\text{Me}]_n$ , we were not able to isolate a pure product from these reactions. Treatment of **1** with indium triiodide in  $\text{CH}_2\text{Cl}_2$  gave a species with identical IR absorptions to those found in the reactions with silver salts. In this case the product was isolated in good yield by extraction into hot cyclohexane and characterised as an iodide-bridged dimer,  $[\text{Ir}(\text{CO})_2\text{I}(\mu\text{-I})\text{Me}]_2$  **2** [eqn. (2)], by spectroscopy<sup>‡</sup> and X-ray crystallography.<sup>§</sup> Addition of 2 equiv. of  $\text{I}^-$  to **2** quickly regenerates the anion, **1**, indicating that the iodide bridges are broken quite easily.



Isolation of **2** has allowed us to investigate its reaction with CO. Brief bubbling of CO through a solution of **2** in  $\text{CH}_2\text{Cl}_2$  resulted in the formation of small amounts of a species, **3**, with  $\nu(\text{CO})$  bands at 2156 and 2096  $\text{cm}^{-1}$ . A third absorption, at 2116  $\text{cm}^{-1}$

of similar intensity to the other two, was revealed by computer subtraction of the bands of unreacted **2**. The number and relative intensities of these bands are consistent with a *fac*-tricarbonyl complex [symmetry  $C_s$ ,  $\nu(\text{CO})$  modes  $2A' + A''$ ].<sup>9</sup> Under an inert atmosphere, **3** was found to revert to **2** over several minutes.

The reaction stereochemistry was probed by using isotopic labelling. The IR spectrum of the product obtained from the reaction of **2** with  $^{13}\text{CO}$  (1 atm) in  $\text{CH}_2\text{Cl}_2$  displayed three  $\nu(\text{CO})$  bands, one of which (2096  $\text{cm}^{-1}$ ) was at identical frequency to a band of unlabelled **3**, whereas the other two absorptions (2142 and 2081  $\text{cm}^{-1}$ ) were shifted to low frequency. This behaviour is exactly as expected if the incoming  $^{13}\text{CO}$  ligand coordinates *trans* to the methyl group to give **3\*** (Scheme 1), which retains  $C_s$  symmetry. The two  $A'$   $\nu(\text{CO})$  modes of **3\*** involve vibration of all three carbonyl ligands, explaining the observed shift of two of the  $\nu(\text{CO})$  bands. The  $A''$  mode involves only the two equivalent carbonyls, and is unaffected by labelling of the CO *trans* to methyl. All the observed  $\nu(\text{CO})$  frequencies for **3** and **3\*** can be modelled accurately by a CO factored force field.<sup>¶</sup> When the  $^{13}\text{CO}$  atmosphere was removed, **3\*** was found to revert cleanly to **2**, with no detectable retention of isotopic label. The reversible reaction of **2** with CO is therefore stereospecific, with the ligand entering and leaving from the site *trans* to methyl. The C–O stretching force constant for the carbonyl ligand *trans* to methyl is calculated to be *ca.* 30  $\text{N m}^{-1}$  larger than that for the two carbonyls *trans* to iodides. The unique carbonyl therefore experiences less  $\pi$  back donation from the iridium centre, consistent with the higher lability at this site.



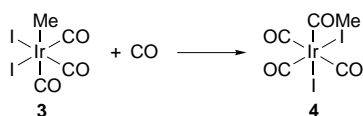
Scheme 1

Less than 10% conversion of **2** into **3** was achieved using CO at atmospheric pressure. Larger quantities of **3** were observed using a high pressure infrared cell to monitor the reaction *in situ*.<sup>5</sup> At 400 psi, essentially complete conversion of **2** into **3** was achieved, using  $\text{CH}_2\text{Cl}_2$  or chlorobenzene as solvent. By contrast, in acetonitrile formation of **3** was suppressed even at high CO pressures, presumably due to cleavage of the dimer and occupation of the vacant site by a solvent molecule. This was confirmed by the observation of  $\nu(\text{CN})$  for  $[\text{Ir}(\text{CO})_2(\text{NCMe})\text{I}_2\text{Me}]$  at 2341  $\text{cm}^{-1}$  and osmometry measurements (observed molecular weight 538) for solutions of **2** in MeCN.

Evidence for **3** was also obtained by high pressure NMR spectroscopy using a sample of **2** isotopically enriched with  $^{13}\text{C}$

in both methyl (>99%) and carbonyl (70–80%) positions. When a solution of this sample in CD<sub>2</sub>Cl<sub>2</sub> was placed under 415 psi <sup>13</sup>C (>99% enriched), new doublets were observed in the <sup>13</sup>C NMR spectrum at δ –21.7 and 148.7 (<sup>2</sup>J<sub>CC</sub> 27 Hz) which are assigned to mutually *trans* methyl and carbonyl ligands in **3**. The carbonyls *trans* to iodide gave a singlet at δ 146.1 with no coupling to the *cis* ligands resolved. The methyl group of **3** was also detected by <sup>1</sup>H NMR spectroscopy at δ 2.14 (d, J<sub>CH</sub> 139 Hz).

It has been proposed previously by Forster<sup>6</sup> and ourselves<sup>7</sup> that **3** is a reactive intermediate in the carbonylation of **1**, and that the tricarbonyl is activated towards migratory CO insertion compared with the anionic precursor. We have therefore studied the reaction of **3** with CO to investigate the validity of this proposal. Below 40 °C, complex **3** was found to be stable indefinitely in chlorobenzene under 400 psi CO. Above this temperature, a reaction was observed in which the ν(CO) bands of **3** were replaced by new absorptions at 2176w, 2115s and 1708m cm<sup>-1</sup>. These bands correspond well with those assigned by Forster<sup>6</sup> to a neutral acetyl complex, [Ir(CO)<sub>3</sub>I<sub>2</sub>(COMe)], the relative intensities suggesting a *mer*-tricarbonyl configuration, **4** (Scheme 2). An iridium acetyl species was also observed in the high-pressure NMR experiment after heating to 70 °C [<sup>13</sup>C, δ 52.4 (CH<sub>3</sub>CO), 186.4 (CH<sub>3</sub>CO), <sup>1</sup>J<sub>CC</sub> 35 Hz; <sup>1</sup>H, δ 3.04, <sup>1</sup>J<sub>CH</sub> 131, <sup>2</sup>J<sub>CH</sub> 5.5 Hz].



Scheme 2

Pseudo-first order rate constants,  $k_{\text{obs}}$ , for this reaction were obtained by monitoring the exponential decay of the high frequency ν(CO) band of **3** at 2156 cm<sup>-1</sup>. Values of  $k_{\text{obs}}$  measured in chlorobenzene over the temperature range 44–85 °C are shown in Table 1. An Eyring plot of these data yields activation parameters ΔH<sup>‡</sup> 89±3 kJ mol<sup>-1</sup> and ΔS<sup>‡</sup> –36 ±8 J mol<sup>-1</sup> K<sup>-1</sup>. Carbonylation of complex **3** is more than 800 times faster than for the anion, **1** at 85 °C in chlorobenzene,<sup>7</sup> representing a lowering of the observed ΔG<sup>‡</sup> by 20 kJ mol<sup>-1</sup> on replacing an iodide ligand by CO. Extrapolation to higher temperatures reduces the difference in rates, but even at 180 °C, the neutral complex is predicted to react *ca.* 9 times faster than the anion. These new kinetic data validate the proposal that migratory insertion occurs in a neutral complex after dissociation of iodide from **1**. Addition of small amounts of methanol was found to accelerate the carbonylation of **3** (see Table 1) but not to the dramatic extent found previously for **1**.<sup>7</sup> Activation parameters calculated for the reaction in 1% methanol–chlorobenzene are ΔH<sup>‡</sup> 73±2 kJ mol<sup>-1</sup> and ΔS<sup>‡</sup> –79±6 J mol<sup>-1</sup> K<sup>-1</sup>.

An explanation for the acceleration of migratory insertion in **3** relative to **1** may reside in the increased competition for π-backbonding in the tricarbonyl complex, **3**. Theoretical calculations on similar systems have suggested that increasing the number of π acceptor ligands lowers the energy of the LUMO (an out of phase combination of π\*<sub>CO</sub> with d<sub>π</sub>) and facilitates methyl migration.<sup>10</sup> Acceleration of migratory CO insertion by coordination of a π acceptor ligand has also been reported for [Ir(CO)(PPh<sub>3</sub>)<sub>2</sub>Cl(Me)]<sup>+</sup>.<sup>11</sup>

**Table 1** First order rate constants for the carbonylation of **3** in chlorobenzene and in chlorobenzene containing 1% (v/v) methanol ( $p_{\text{CO}} = 400$  psi).

$T/^\circ\text{C}$	$10^4 k_{\text{obs}}/\text{s}^{-1}$ (PhCl)	$T/^\circ\text{C}$	$10^4 k_{\text{obs}}/\text{s}^{-1}$ (PhCl–1% MeOH)
44	1.64	44	5.10
		47	6.75
52	3.73	52	10.6
59	9.47	59	17.6
67	19.7	68	39.5
76	41.1		
85	87.6		

To summarise we have confirmed Forster's original suggestion that neutral intermediates play a key role in the migratory insertion step for the iridium catalysed carbonylation of methanol. We have obtained spectroscopic evidence for the previously undetected species, [Ir(CO)<sub>3</sub>I<sub>2</sub>Me] **3** which undergoes CO insertion at a rate substantially faster than its anionic precursor, **1**.

We thank BP Chemicals, The Royal Society, and the University of Sheffield for supporting this research. We thank Cambridge Isotope Laboratories for an award of <sup>13</sup>C labelled carbon monoxide, Dr Mike Taylor (BP, Sunbury, UK) for carrying out high pressure NMR experiments and Dr George Morris for helpful discussions.

## Notes and References

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‡ Analytical and spectroscopic data for [Ir(CO)<sub>2</sub>I(μ-I)Me]<sub>2</sub> **2**. Analysis. Found: C, 7.0; H, 0.4; I, 49.1. Calc for C<sub>6</sub>H<sub>6</sub>Ir<sub>2</sub>I<sub>4</sub>O<sub>4</sub>: C, 7.0; H, 0.6; I, 49.1%. *M* (PhCl). Found: 1001. Calc. 1034; IR (CH<sub>2</sub>Cl<sub>2</sub>), ν(CO)/cm<sup>-1</sup>: 2119, 2074. NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ<sub>H</sub> 1.94, 1.88; δ<sub>C</sub> 152.4, 150.3 (CO), –5.30, –8.76 (CH<sub>3</sub>). The NMR data suggest the existence of isomeric forms of the dimer in solution.

§ An X-ray crystal structure of **2** shows it be a centrosymmetric dimer, very similar to the chloride analogue.<sup>8</sup> Of particular note is the asymmetry in the Ir–(μ-I)–Ir bridges with a significantly longer Ir–(μ-I) bond *trans* to methyl [2.799(2) Å] than *trans* to CO [2.716(2) Å], attributable to the high *trans* influence of the methyl ligand. Full details of the structure will be reported in a full paper.

¶ The stretching ( $k$ ) and interaction ( $i$ ) force constants used to fit the observed ν(CO) frequencies of **3** and **3**<sup>\*</sup> were:  $k_1 = 1810$  N m<sup>-1</sup>,  $k_2 = 1840$  N m<sup>-1</sup>,  $i_{11} = 35.5$  N m<sup>-1</sup>,  $i_{12} = 24.6$  N m<sup>-1</sup> where CO<sub>(1)</sub> is *trans* to I and CO<sub>(2)</sub> is *trans* to Me.

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