Cis–trans isomerism in $[M(CO)_2I_4]^-$ (M = Rh, Ir): Kinetic, mechanistic and spectroscopic studies [1]

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Abstract

Infrared spectroscopic studies show that the *cis–trans* isomerisation of $[Rh(CO)_2I_4]^-$ (**1**) reaches an equilibrium in solution favouring the *trans* isomer ($K_{eq} \approx 10$ in CH_2Cl_2 at 25°C). The approach to equilibrium obeys a first order rate law with a half life of ca. 40 min at 25°C. Activation parameters for the isomerisation are $\Delta H^{\ddagger}$ 103 (± 3) kJ mol^{-1}, $\Delta S^{\ddagger}$ + 32 (± 9) J mol^{-1} K^{-1} in CH_2Cl_2 and $\Delta H^{\ddagger}$ 99 (± 2) kJ mol^{-1}, $\Delta S^{\ddagger}$ + 25 (± 4) J mol^{-1} K^{-1} in THF. In polar coordinating solvents, formation of monocarbonyl complexes $[Rh(CO)I_4(sol)]^-$ occurs in competition with *cis–trans* isomerisation, and in the presence of added iodide salt, $[Rh(CO)I_5]^{2-}$ is formed. Isotopic labelling experiments show that added ^{12}CO is incorporated into *trans*-**1** on isomerisation of *cis*-$[Rh(^{13}CO)_2I_4]^-$. Addition of CO to the monocarbonyls, $[Rh(CO)I_4(sol)]^-$ and $[\{Rh(CO)I_4\}_2]^{2-}$ gives predominantly *trans*-$[Rh(CO)_2I_4]^-$. A mechanism is proposed for *cis–trans* isomerisation involving dissociation of a CO ligand. Elemental and infrared spectroscopic analysis of crystals obtained from the residues of carbonylation experiments on $[Ir(CO)_2I_3(Me)]^-$ are consistent with a new *trans* isomer of $[Ir(CO)_2I_4]^-$. The same species is formed in the reaction of $[\{Ir(CO)I_4\}_2]^{2-}$ with CO. Isomerisation to *cis*-$[Ir(CO)_2I_4]^-$ only occurs in the presence of added CO. The $\nu(CO)$ frequencies for isotopomers of *cis*- and *trans*-$[M(CO)_2I_4]^-$ (M = Rh, Ir) are analysed using C–O factored force-fields. The force constants obtained indicate stronger metal–CO back-donation for the *cis* relative to the *trans* isomers and also for iridium relative to rhodium. © 1998 Elsevier Science S.A.

Keywords: Rhodium; Iridium; Carbonylation; Kinetics; Mechanism

1. Introduction

Rhodium and iridium carbonyl iodide complexes are of key importance as catalysts for the industrial carbonylation of methanol to acetic acid. In the well known Monsanto process, now operated by BP Chemicals, the active catalytic species is a square planar Rh(I) complex, $[Rh(CO)_2I_2]^-$. The main catalytic cycle for carbonylation has been the subject of numerous studies, and is now well understood [1–3]. The key steps are oxidative addition of methyl iodide, migratory CO insertion and reductive elimination (or solvolysis) of a rhodium acetyl complex. Although highly selective, the process generates small amounts of some by-products, including propionic acid (via homologation) methane,

CO_2 and H_2. The latter pair result from the water gas shift (WGS) reaction (Eq. (1)).

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad (1)$$

The mechanism by which the WGS reaction proceeds is thought to involve Rh(III) carbonyl iodide intermediates, as shown in Scheme 1 [4]. Thus, oxidation of $[Rh(CO)_2I_2]^-$ by HI gives $[Rh(CO)_2I_4]^-$ (**1**), releasing H_2 and subsequent reduction back to Rh(I) by CO and H_2O results in formation of CO_2. The Rh(III) tetra-iodide complex, **1**, can also be made by the facile reaction of $[Rh(CO)_2I_2]^-$ with I_2 which gives initially, *cis*-**1** resulting from formal *trans* addition of I_2 [5]. A subsequent rather slow isomerisation results in the formation of the thermodynamically favoured *trans*-**1** (Scheme 2). This *trans* isomer can be isolated and has been the subject of two X-ray crystallographic studies [6,7]. The isomers of **1** have also been studied using ^{13}C NMR spectroscopy [8]. In this paper we report the

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[1] Dedicated to Professor Peter Maitlis on the occasion of his 65th birthday.
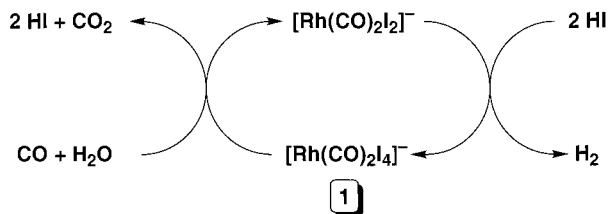
Scheme 1. Proposed mechanism for the WGS reaction catalysed by rhodium carbonyl iodide complexes.

results of a kinetic study of the *cis–trans* isomerisation of **1**. We present evidence that the reaction proceeds via a dissociative mechanism involving loss of a carbonyl ligand.

An iridium catalysed methanol carbonylation process (*Cativa*) has recently been commercialised by BP Chemicals and shows significant improvements in rate, selectivity and catalyst stability compared to the conventional rhodium process [8]. The organometallic chemistry underlying the two systems is quite similar, although there are substantial differences in relative reaction rates for individual steps in the catalytic cycles [9–11]. During our studies of the mechanisms operating in the iridium system, we have also found evidence, which we report in this paper, for the previously unknown *trans* isomer of $[Ir(CO)_2I_4]^-$ (*trans*-**2**).

2. Experimental

2.1. Instrumentation

Solution infrared spectra ($2 \ cm^{-1}$ resolution) were recorded on a Perkin Elmer 1640 or a Mattson Genesis FTIR spectrometer, using a liquid cell with CaF_2 windows (0.1–0.5 mm pathlength). Elemental analyses were performed by the Microanalysis Service at the University of Sheffield.

2.2. Purification of reagents

Solvents were thoroughly degassed and distilled under nitrogen before use. Dichloromethane was distilled from calcium hydride. THF was pre-dried over molecular sieve and then distilled from a purple solution of

sodium/benzophenone. Methanol was distilled from magnesium methoxide.

2.3. Synthetic procedures

Unless otherwise indicated, all reactions were carried out under nitrogen or argon using standard Schlenk-line techniques. All the complexes were air sensitive to varying degrees and were stored under nitrogen or carbon monoxide at ca. 5°C. The synthetic methods used to prepare salts of $[RhCO)_2I_2]^-$ and $[Ir(CO)_2I_2]^-$ have been described previously [10,12]. The compounds $(Bu_4N)_2[\{Rh(CO)I_4\}_2]$ and $(Ph_4As)_2[\{Ir(CO)I_4\}_2]$ were prepared using literature procedures [8,13]. Isotopic enrichment of complexes with ^{13}CO was achieved using methods described previously [14].

2.4. Kinetic experiments

In a typical experiment, a solution containing *cis*-**1** was prepared in situ by the addition of a small excess of I_2 (1.6 mg, 6.3 μmol) in CH_2Cl_2 (1 cm^3) to $Bu_4N[Rh(CO)_2I_2]$ (4 mg, 6.1 μmol) under nitrogen. Immediately after mixing, a sample of the reaction solution was transferred by syringe to an infra-red cell (CaF_2 windows, 0.5 mm pathlength) fitted with a thermostatted jacket and placed in the sample compartment of a Mattson Genesis FTIR spectrometer. Spectra were taken at timed intervals under the control of a microcomputer and stored to disk for subsequent analysis. The progress of the isomerisation reaction was followed by monitoring the decay of the high frequency $\nu(CO)$ band of *cis*-**1** at 2120 cm^{-1}. First order rate constants, k_{obs}, were obtained by fitting an exponential curve to the experimental data using a non-linear least-squares regression program. Observed rate constants were reproducible within 5%.

3. Results

3.1. Kinetic studies

Solutions of *cis*-**1** were prepared by the stoichiometric reaction of $Bu_4N[Rh(CO)_2I_2]$ with I_2 in
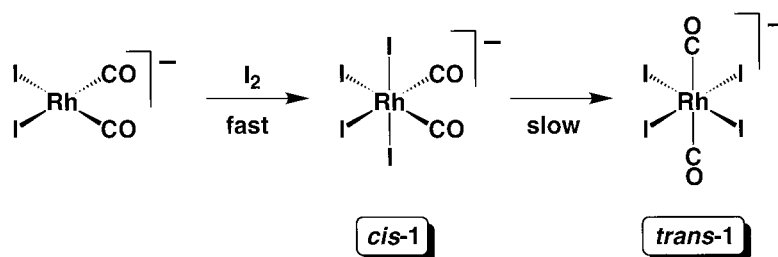
Scheme 2. Preparation and isomerisation of $[Rh(CO)_2I_4]^-$ (**1**).

dichloromethane. The *cis*-dicarbonyl product exhibits infrared absorptions at 2120 and 2089 cm^{-1} due to the symmetric (A$_1$) and antisymmetric (B$_1$) ν(CO) vibrational modes respectively. A series of spectra illustrating the changes that accompany *cis–trans* isomerisation are shown in Fig. 1. The high frequency band of *cis*-**1** decays, whilst the low frequency band appears to grow. The apparent growth is due to the appearance of the single infrared active (A$_{2u}$) ν(CO) mode of *trans*-**1** at 2091 cm^{-1}, almost coincident with the low frequency band of *cis*-**1**. The kinetics of isomerisation are most easily measured by analysis of the decay of the 2120 cm^{-1} absorption of *cis*-**1**. The plot of absorbance vs. time in Fig. 2 shows that this decay curve does not reach zero, but reaches an equilibrium at ca. 10% of the starting absorbance, indicating that the isomerisation does not go to completion under these conditions. An exponential decay of the form $A = (A_o - A_\infty)\exp(-k_{obs}t) + A_\infty$ was fitted to the data to give a value of k_{obs}, the first order rate constant for approach to equilibrium. Rate constants measured at several temperatures in dichloromethane are presented in Table 1. At 25°C, the observed rate constant corresponds to a half life of ca. 40 min. An Eyring plot of the variable temperature data gives a good straight line yielding activation parameters of $\Delta H^\ddagger = 103$ (± 3) kJ mol^{-1} and $\Delta S^\ddagger = +32$ (± 9) J mol^{-1} K^{-1}. Changing the counter-ion from Bu$_4$N$^+$ to Ph$_4$As$^+$ resulted in only a marginal change in k_{obs}.

Attempts to study the kinetics of isomerisation in more polar and/or coordinating solvents met with two problems, namely (1) poor solubility of **1**, leading to weak infrared bands and inaccurate kinetic measure-
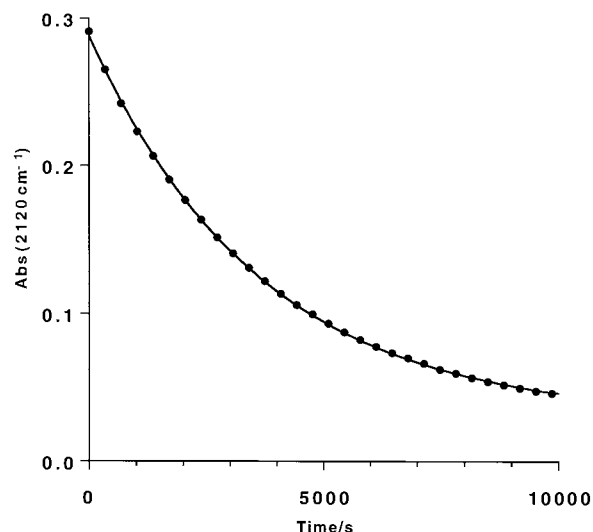
Fig. 2. A plot of absorbance vs. time showing the decay of the high frequency ν(CO) band of *cis*-**1** during its isomerisation to give *trans*-**1** (CH$_2$Cl$_2$, 25°C). The experimental data points are fitted to an exponential decay curve. The decay approaches an equilibrium value, indicating the isomerisation does not go to completion.

ments and (2) lability of **1** leading to formation of monocarbonyl solvate complexes (Eq. (2)).

$$\left[Rh(CO)_2I_4 \right]^- + sol \rightarrow \left[Rh(CO)I_4(sol) \right]^- + CO \quad (2)$$
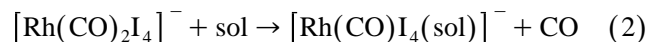
The monocarbonyls were identified by their single ν(CO) band at 2068 (MeOH), 2064 (THF), 2074 (MeCN) and 2076 cm^{-1} (MeNO$_2$). The substitution reactions occurred over a similar timescale to the *cis–trans* isomerisation, making it difficult to analyse the kinetics of the two processes separately. Formation of
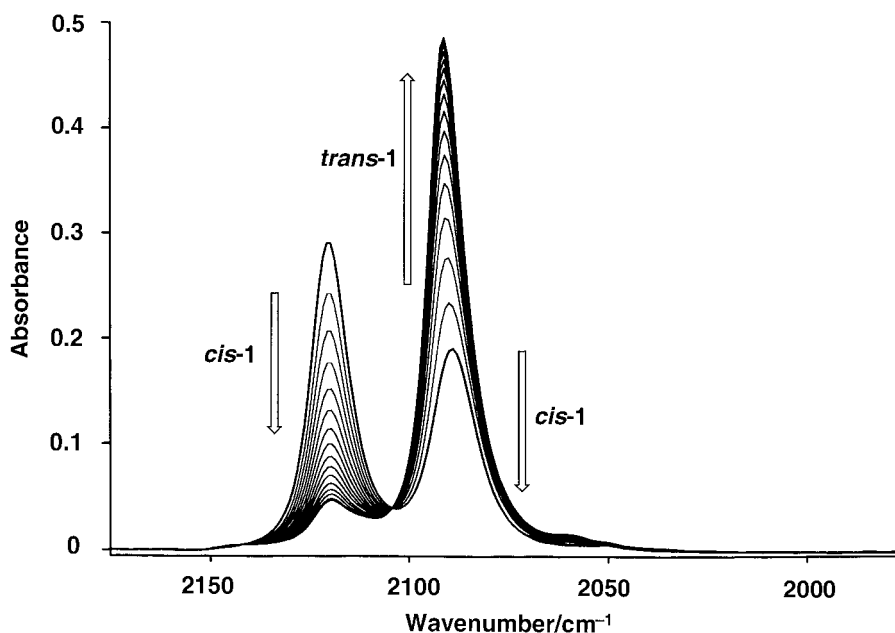
Fig. 1. A series of infrared spectra recorded during the *cis–trans* isomerisation of [Rh(CO)$_2$I$_4$]$^-$ (**1**) in CH$_2$Cl$_2$ at 25°C. Note that the band due to the product, *trans*-**1**, is almost coincident with the low frequency band of the starting complex, *cis*-**1**.

Table 1
Observed first order rate constants for *cis–trans* isomerisation of $[Rh(CO)_2I_2]^-$ (**1**) in CH_2Cl_2 and in THF

| Temperature (°C)	$10^4 k_{obs}$ (s^{-1})	
	CH_2Cl_2	THF
10	0.28	
15	0.74	
20	1.37	
25	2.90	4.7
25	3.0[a]	
30	6.17	9.2
35	10.80	17.4
40		34.0

[a] Using Ph_4As^+ counter-ion.

the monocarbonyl was least problematic in THF, and kinetic data measured for the isomerisation in this solvent are given in Table 1. Activation parameters derived from an Eyring plot of these data are $\Delta H^{\ddagger} = 99$ (± 2) kJ mol^{-1} and $\Delta S^{\ddagger} = +25$ (± 4) J mol^{-1} K^{-1}. Single kinetic runs were also performed in methyl-substituted THF derivatives to investigate the influence of steric effects in a coordinating solvent. At 30°C, the values of k_{obs} obtained were 8.2×10^{-4} s^{-1} (2-methyl THF) and 9.1×10^{-4} s^{-1} (2,5-dimethyl THF), showing no marked difference from the rate observed in unsubstituted THF.

The influence of added iodide salts was also investigated. When the reaction was performed in the presence of excess Bu_4NI, an extra carbonyl band was observed in the infrared spectrum at lower frequency than those of *cis* and *trans* **1**. The additional $\nu(CO)$ absorption, at 2047 cm^{-1}, corresponds to that of the known dianion,

$[Rh(CO)I_5]^{2-}$ which results from substitution of a CO ligand in **1** by iodide (Eq. (3)) [5].

$$[Rh(CO)_2I_4]^- + I^- \rightarrow [Rh(CO)I_5]^{2-} + CO \qquad (3)$$
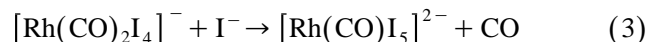
The intensity of the 2047 cm^{-1} band due to $[Rh(CO)I_5]^{2-}$ grew quickly at the start of the reaction and then changed more slowly whilst the *cis–trans* isomerisation of remaining **1** proceeded. Larger amounts of the dianion were formed at higher concentrations of iodide salt. The occurrence of this side-reaction again presented difficulty in analysing kinetic data for the isomerisation process. Addition of a large excess of the weakly coordinating salt, Bu_4NBF_4 (0.1 M) had no significant effect on the isomerisation rate ($k_{obs} = 2.7 \times 10^{-4}$ s^{-1}, CH_2Cl_2, 25°C). The presence of an atmosphere of carbon monoxide was also found to have negligible effect on the observed rate constant.

3.2. Isomerisation in the solid-state

Samples of *cis*-**1** in the solid state were obtained by removing the solvent immediately after oxidative addition of I_2 to $[Rh(CO)_2I_2]^-$. The solid was kept in a flask at room temperature under carbon monoxide. At intervals samples were withdrawn and redissolved in CH_2Cl_2 for analysis by infrared spectroscopy. The spectra showed that *cis–trans* isomerisation proceeded over a period of several days in the solid state at room temperature.

3.3. Isotopic labelling studies

Isotopic labelling of the carbonyl ligands of $[Rh(CO)_2I_2]^-$ is easily achieved by stirring a solution of the anion in CH_2Cl_2 under an atmosphere of ^{13}CO.

Table 2
Infrared spectroscopic data for isotopomers of *cis*- and *trans*-$[M(CO)_2I_4]^-$ (**1**, M = Rh; **2**, M = Ir). The suffixes * and ** denote complexes which are, respectively, singly and doubly labelled with ^{13}CO. Calculated $\nu(CO)$ frequencies are based on the C–O stretching and interaction force constants k and i given in the last two columns

Complex	$\nu(CO)$ (cm^{-1})[a]		$\nu(CO)$ (cm^{-1})[b]		k (N m^{-1})	i (N m^{-1})
	Observed	Calculated	Observed	Calculated		
cis-**1**	2120	2119.5	2089	2089.0		
cis-**1***	2108	2108.6	[d]	2051.9	1788.2	25.9
cis-**1****	2071	2071.1	2042	2041.3		
trans-**1**	[c]	2143.6	2091	2091.7		
trans-**1***	2129	2128.8	2059	2058.4	1811.2	44.4
trans-**1****	[c]	2095.0	2044	2044.2		
cis-**2**	2112	2111.2	2067	2067.0		
cis-**2***	2097	2097.6	2033	2033.1	1762.6	37.3
cis-**2****	2063	2063.3	2020	2020.0		
trans-**2**	[c]	2141.4	2070	2069.4		
trans-**2***	2124	2124.3	2038	2038.6	1790.6	61.2
trans-**2****	[c]	2092.8	[d]	2022.4		

[a] High frequency band, symmetry A_1 for *cis*-$[M(CO)_2I_4]^-$ and A_{1g} for *trans*-$[M(CO)_2I_4]^-$.
[b] Low frequency band, symmetry B_1 for *cis*-$[M(CO)_2I_4]^-$ and A_{2u} for *trans*-$[M(CO)_2I_4]^-$.
[c] Infrared inactive.
[d] Not observed.

Levels of ^{13}CO enrichment of ca. 90% were achieved by this method. Addition of I_2 to $[Rh(^{13}CO)_2I_2]^-$ gave cis-$[Rh(^{13}CO)_2I_4]^-$, (cis-**1****) identified by $\nu(CO)$ absorptions in the infrared spectrum at 2071 and 2042 cm^{-1}. These bands are shifted to low frequency by the expected amount compared to those of unlabelled cis-**1** [17]. Small amounts of the singly labelled species, cis-$[Rh(CO)(^{13}CO)I_4]^-$ (cis-**1***, $\nu(CO)$ 2108 cm^{-1}) [2] were also present due to incomplete labelling of the carbonyl ligands. When a solution of the isotopically labelled cis isomer in CH_2Cl_2 was left to stand under an inert atmosphere, the expected isomerisation occurred to give $trans$-**1****, ($\nu(CO)$ 2044 cm^{-1}). Weaker bands observed at 2129 and 2059 cm^{-1} are assigned to singly labelled $trans$-**1*** which is expected to exhibit two infrared active $\nu(CO)$ modes due to reduction of symmetry from D_{4h} to C_{4v}. All the observed $\nu(CO)$ frequencies for isotopomers of cis-**1** and $trans$-**1** can be fitted well using C–O factored force-fields [15]. Observed and calculated frequencies are given in Table 2, together with the values of the C–O stretching force constant (k) and the CO–CO interaction force constant (i) which give the best fits.

When cis-**1**** was allowed to isomerise under an atmosphere of unlabelled CO rather than N_2, the infrared spectra indicated that very little doubly labelled $trans$-**1**** was formed. Instead, the principal features were absorptions due to singly labelled $trans$-**1*** and unlabelled $trans$-**1**. Thus, ^{13}CO ligands are lost during the isomerisation process under these conditions. The spectra for this experiment did not indicate significant incorporation of unlabelled CO into cis-**1** prior to isomerisation.

3.4. Reactions of monocarbonyl Rh complexes with CO

The data presented above indicate that the carbonyl ligands in this system are relatively labile, implicating the participation of monocarbonyl intermediates. We therefore tested the reactivity of the monocarbonyl rhodium complexes, $[\{Rh(CO)I_4\}_2]^{2-}$, and $[Rh(CO)I_4(sol)]^-$ with CO. Bubbling CO through a CH_2Cl_2 solution of the dimer, $[\{Rh(CO)I_4\}_2]^{2-}$, resulted in a rapid reaction (even at 0°C) giving predominantly $trans$-**1** with a small amount of cis-**1**. The monomeric methanol complex, $[Rh(CO)I_4(MeOH)]^-$, generated by dissolving $[\{Rh(CO)I_4\}_2]^{2-}$ in methanol, was unreactive towards CO (1 atm). However, in a 20% (v/v) MeOH–CH_2Cl_2 solvent mixture, the methanol adduct reacted slowly with CO to give $trans$-**1** as the major product. Very similar behaviour was observed for the analogous acetonitrile complex,
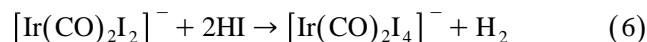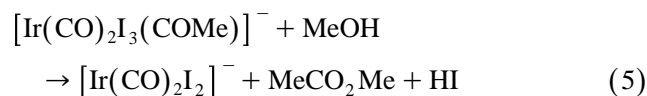
$[Rh(CO)I_4(NCMe)]^-$. These results suggest that coordinating solvents can compete quite effectively with CO for '$[Rh(CO)I_4]^-$'.

3.5. Serendipitous discovery of $trans$-$[Ir(CO)_2I_4]^-$

Oxidative addition of I_2 to $[Ir(CO)_2I_2]^-$ is known to give cis-$[Ir(CO)_2I_4]^-$ (cis-**2**) which, in contrast to the rhodium analogue, shows no tendency to isomerise to the $trans$ geometry. During our studies of the carbonylation of an iridium methyl complex, $[Ir(CO)_2I_3(Me)]^-$, we have found evidence for the formation of the previously unknown $trans$ isomer of the tetraiodide. Kinetic studies of the reaction of $[Ir(CO)_2I_3(Me)]^-$ with CO (Eq. (4)) were carried out using a high pressure infrared cell which has been described previously [3,11].

$$\left[Ir(CO)_2I_3(Me)\right]^- + CO \rightarrow \left[Ir(CO)_2I_3(COMe)\right]^- \tag{4}$$
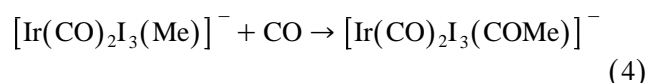
The previously characterised cis isomer of $[Ir(CO)_2I_4]^-$ ($\nu(CO)$ 2112, 2067 cm^{-1}) is sometimes formed as a by-product in these reactions, probably by the sequence of reactions shown below (Eqs. (5) and (6)).

$$\left[Ir(CO)_2I_3(COMe)\right]^- + MeOH$$
$$\rightarrow \left[Ir(CO)_2I_2\right]^- + MeCO_2Me + HI \tag{5}$$

$$\left[Ir(CO)_2I_2\right]^- + 2HI \rightarrow \left[Ir(CO)_2I_4\right]^- + H_2 \tag{6}$$

Reaction mixtures recovered from these experiments were routinely stored in the refrigerator (5°C). It was noticed that, after several months, some of the samples contained large red cuboidal crystals for which elemental analysis was consistent with formulation as $Ph_4As[Ir(CO)_2I_4]$. [3] However, an infrared spectrum of one of the crystals dissolved in CH_2Cl_2 showed only a single strong $\nu(CO)$ band at 2070 cm^{-1}, which is inconsistent with the normal cis dicarbonyl geometry of **2**. The proximity of this infrared band to the low frequency absorption of cis-**2** (2067 cm^{-1}) is very reminiscent of the spectroscopic data for the cis and $trans$ isomers of the rhodium analogue, **1** (Table 2). After standing for several hours under an atmosphere of CO, the 2070 cm^{-1} absorption was replaced by the familiar $\nu(CO)$ bands of cis-**2** at 2112 and 2067 cm^{-1}. These observations suggested that the crystals obtained from the residues of our carbonylation reactions contained a new species, $trans$-$[Ir(CO)_2I_4]^-$ ($trans$-**2**). Unfortunately, the crystals were of insufficient quality for an X-ray diffraction study.

In order to test this hypothesis, we attempted to prepare the $trans$ isomer by an independent route. By

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[2] The low frequency $\nu(CO)$ band of cis-**1***, is hidden by the low frequency band of cis-**1****.

[3] $Ph_4As[Ir(CO)_2I_4]$ Analysis Found: C, 27.7; H, 1.8; I, 44.4. Calculated for $C_{26}H_{20}AsI_4IrO_2$: C, 27.4; H, 1.8; I, 44.6.
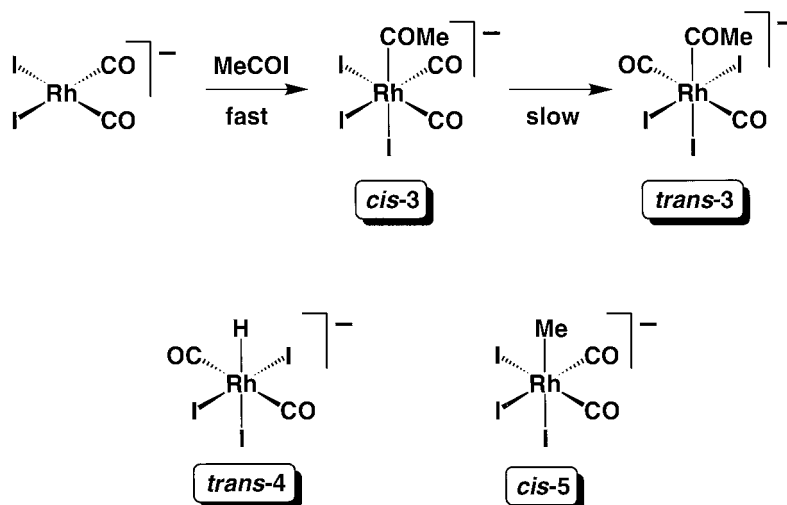
Scheme 3. Isomerism in the complexes $[Rh(CO)_2I_3(R)]^-$ (R = H, methyl, acetyl).

analogy with our observations in the rhodium system, we suspected that reaction of CO with a monocarbonyl iridium complex, might lead to the desired *trans* isomer. The monocarbonyl dimer $[\{Ir(CO)I_4\}_2]^{2-}$, is easily obtained by decarbonylation of $[Ir(CO)_2I_4]^-$ [13]. Bubbling CO through a solution of $[\{Ir(CO)I_4\}_2]^{2-}$ in CH_2Cl_2 for 5 min resulted in the disappearance of its single $\nu(CO)$ band at 2047 cm^{-1} and the growth of a new absorption at 2070 cm^{-1}, exactly the same frequency assigned above to *trans*-**2**.

Confirmation that the new species is a dicarbonyl was obtained by infrared spectroscopy of an isotopically labelled sample, since the lower symmetry of a singly labelled isotopomer, *trans*-**2***, should result in two infrared active $\nu(CO)$ bands. Stirring a CH_2Cl_2 solution of $[\{Ir(CO)I_4\}_2]^{2-}$ under ^{13}CO (ca. 90% enriched) for 5 min resulted in formation of a major product with infrared absorptions at 2124 and 2038 cm^{-1}. These frequencies can be fitted well to *trans*-**2*** using force constants given in Table 2.

We have already noted that when a solution containing *trans*-**2** was stored under an atmosphere of CO at room temperature, isomerisation to *cis*-**2** occurred over several hours. However, when left to stand under a nitrogen atmosphere, no conversion to the *cis* isomer was detected. It appears, therefore, that the *cis* isomer of $[Ir(CO)_2I_4]^-$ is preferred thermodynamically, but that isomerisation from the *trans* geometry occurs only in the presence of excess CO.

4. Discussion

Our infrared spectroscopic studies of the isomerisation of *cis*-**1** to *trans*-**1** in CH_2Cl_2 show that the reaction does not reach completion, but attains an equilibrium at which ca. 10% of the initial concentration of *cis*-**1** remains. An equilibrium constant of ca. 10 corresponds to a free energy change for the isomerisation process (Scheme 2) of $\Delta G_{298} \approx -5$ kJ mol^{-1}. Thus the *trans* isomer is only marginally preferred, thermodynamically. The easy isolation of crystals containing the *trans* isomer, reported previously [6,7], can be explained by the lower solubility of salts of this complex, which would tend to drive the equilibrium to the right. It has been suggested that the nature of the counter-ion can influence the preference for *cis* or *trans* geometry in this system [7]. We have not pursued this point further, but note that ion pairing interactions, particularly in weakly polar solvents, may be sufficient to perturb the isomerisation equilibrium. Ab initio calculations performed in Sheffield on the two isomers of **1** are in broad agreement with the experimental observations. Depending on the theoretical method and basis set employed, the predicted energy change for the *cis–trans* isomerisation was found to vary between -60 and $+6$ kJ mol^{-1}.[4]

There are several closely related Rh(III) carbonyl iodides with the general formula $[Rh(CO)_2I_3(R)]^-$ with which our system can be compared. The acetyl complex, $[Rh(CO)_2I_3(COMe)]^-$, is formed as the *mer–trans* isomer (*trans*-**3**) on carbonylation of $[\{Rh(CO)I_3(COMe)\}_2]^{2-}$ [16]. However, it has recently been shown by workers at Du Pont that oxidative addition of acetyl iodide to $[Rh(CO)_2I_2]^-$ gives, at low temperature, the *fac–cis* isomer (*cis*-**3**) which isomerises to the more stable *trans*-**3** on warming (Scheme 3) [17]. The same group has also reported that addition of HI to $[Rh(CO)_2I_2]^-$ at low temperature gives a

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[4] Ab initio molecular orbital calculations on $[Rh(CO)_2I_4]^-$ were carried out by Dr. D.B. Cook and Dr. T.R. Griffin at the University of Sheffield. Calculations were carried out at several levels of theory (Hartree–Fock, MP2, MP4 and DFT). Full details of these studies will be published elsewhere.

species with a single $\nu(CO)$ band, assigned as *mer–trans*-[Rh(CO)$_2$I$_3$(H)]$^-$ (*trans*-**4**) [18]. By contrast, only the *fac–cis* isomer of [Rh(CO)$_2$I$_3$(Me)]$^-$ (*cis*-**5**) has been observed, although rapid migratory CO insertion for this species makes it uncertain whether the observed isomer is preferred thermodynamically [14]. The analogous Ir(III) carbonyl iodides, [Ir(CO)$_2$I$_3$(R)]$^-$ (R = H, alkyl, acetyl) are generally stable in the *fac–cis* geometry [19]. For example, an X-ray crystal structure for the complex where R = *n*-hexyl has been reported by the Sheffield group [12]. Our serendipitous discovery of an unstable *trans* isomer of [Ir(CO)$_2$I$_4$]$^-$ fits into this pattern. A delicate balance of steric and electronic effects is probably responsible for the preferred *cis* dicarbonyl arrangement for iridium as opposed to the *trans* configuration for rhodium. We note that replacing iodide ligands in the rhodium system by bromide or chloride, lowers the preference for a *trans* geometry [5,6,8]. Similar isomerism has been reported for an anionic ruthenium carbonyl iodide complex, [Ru(CO)$_3$I$_3$]$^-$ [20]. The thermodynamically favoured *fac* isomer is obtained by addition of an iodide salt to the neutral dimer, [{Ru(CO)$_3$I$_2$}$_2$]. However, the *mer* isomer can be obtained by carbonylation of the anionic dimer, [{Ru(CO)$_2$I$_3$}$_2$]$^{2-}$ and *mer–fac* isomerisation can be effected thermally under CO.

4.1. Isomerisation mechanism

The kinetic and isotopic labelling studies that we have carried out on the *cis–trans* isomerisation of [Rh(CO)$_2$I$_4$]$^-$ are consistent with a mechanism involving loss of CO. The reaction occurs with a first order rate law and has a positive activation entropy, suggesting a dissociative mechanism. The activation enthalpy is quite large, consistent with significant bond breaking in the transition state. Other evidence points to the same mechanistic conclusion. In coordinating solvents, substantial quantities of a solvated monocarbonyl complex, [Rh(CO)I$_4$(sol)]$^-$, are formed as the isomerisation progresses, demonstrating the lability of the carbonyl ligands. Similarly, in the presence of excess iodide salt, the monocarbonyl dianion, [Rh(CO)I$_5$]$^{2-}$ is observed. Further evidence for a CO dissociation pathway is provided by the observation that ^{12}CO is incorporated into the product when the isomerisation of ^{13}CO labelled *cis*-**1**** is carried out under an atmosphere of unlabelled carbon monoxide. A mechanism consistent with these observations is shown in Scheme 4.

Loss of a carbonyl ligand from *cis*-**1** would generate a square pyramidal 16 e intermediate with a vacant coordination site *cis* to the remaining carbonyl ligand. Microscopic reversibility would suggest that if this is the stable geometry for [Rh(CO)I$_4$]$^-$, an incoming CO ligand would coordinate at this site to regenerate the *cis* dicarbonyl. However, our isotopic labelling experiments showed that added ^{12}CO is not significantly incorporated into *cis*-**1**** prior to isomerisation. Rearrangement of the initial square pyramidal intermediate could give (1) an isomeric square pyramid with the carbonyl axial or (2) a trigonal bipyramid (in which the π-acceptor carbonyl ligand will favour an equatorial position).
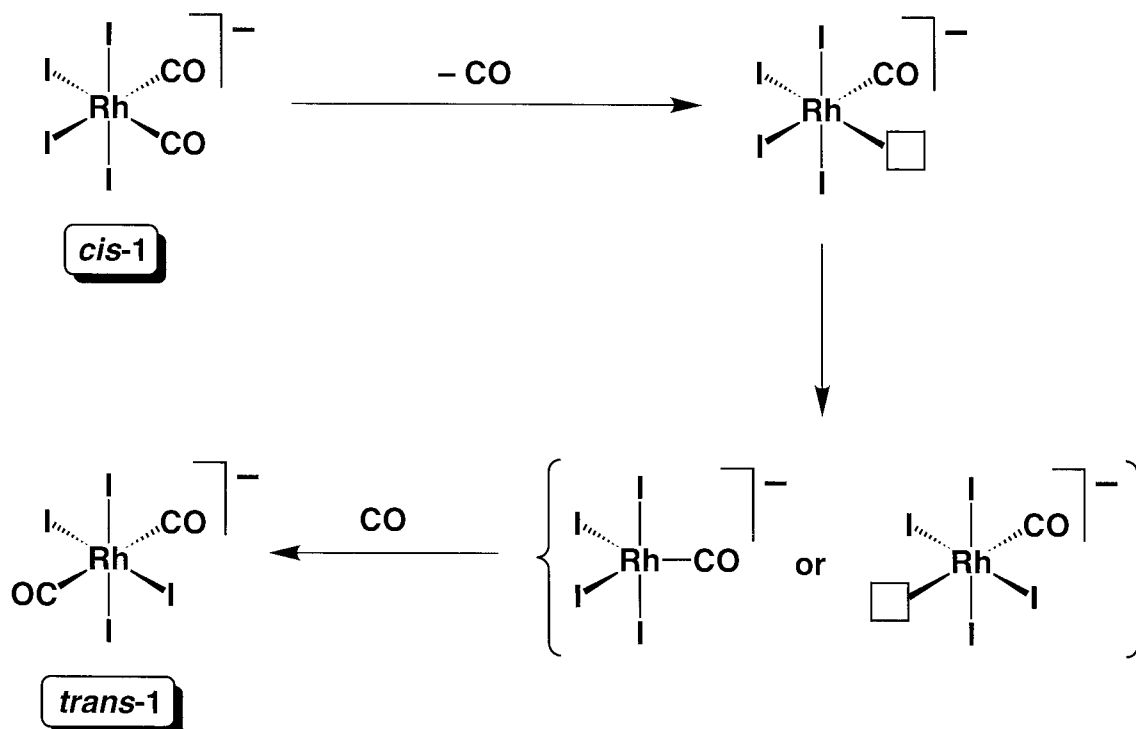
Scheme 4. Proposed mechanism for *cis–trans* isomerisation in [Rh(CO)$_2$I$_4$]$^-$ (**1**).

The most stable geometry of $[Rh(CO)I_4]^-$ might well be intermediate between the square pyramidal and trigonal bipyramidal ideals. Whichever is the case, the greater *trans* directing power of the CO ligand relative to iodide will encourage coordination of CO to give *trans*-**1**. This mechanism is strongly supported by our observation that the monocarbonyl complexes, $[Rh(CO)I_4(sol)]^-$ and $[\{Rh(CO)I_4\}_2]^{2-}$ react with CO to give predominantly *trans*-**1**. It is unclear whether the same mechanism operates for the observed solid state isomerisation process.

We have not carried out detailed mechanistic studies of the *trans–cis* isomerisation of $[Ir(CO)_2I_4]^-$. However, we did observe that the process only occurs at a detectable rate in the presence of carbon monoxide. One mechanism which might account for this is shown in Scheme 5, where isomerisation occurs via loss of an iodide rather than a CO ligand. The coordinatively unsaturated intermediate formed in this way could bind a further CO ligand to give either a *mer*- or *fac*-tricarbonyl species. In either case substitution of a carbonyl by the returning iodide can generates the stable *cis*-$[Ir(CO)_2I_4]^-$. Whilst this mechanism is rather speculative, and a number of related schemes would give the same result, the participation of a tricarbonyl intermediate would explain the necessity for added CO. Forster has reported infrared spectroscopic data for a complex of formula $[Ir(CO)_3I_3]$, although the stereochemistry was not assigned [21]. Mechanisms involving halide dissociation have been proposed to explain the kinetics of carbonylation of $[Ir(CO)_2I_3(Me)]^-$ [11] as well as other reactions of Ir(III) complexes [22,23].

4.2. Vibrational analysis of infrared spectroscopic data

Our analysis of the infrared spectroscopic data for isotopomers of *cis* and *trans*-$[M(CO)_2I_4]^-$ yields some interesting comparisons. The CO stretching force constants, k, are larger for the *trans* isomers by 23 N m^{-1} (Rh) or 28 N m^{-1} (Ir), reflecting the increased competition for π-backbonding and consequent stronger C–O bonds with carbonyls mutually *trans*. The interaction constants (i) are also appreciably larger for the *trans* isomers. This is normally explained by the fact that *trans* carbonyls share π-back-donation from the same pair of metal $d(\pi)$ orbitals, whereas *cis* carbonyls share only one of these orbitals. This relationship led to the well-known Cotton–Kraihanzel approximation [24], which proposed that the ratio of interaction force constants $i_{trans}/i_{cis} \approx 2$. Our calculated force constants for the $[M(CO)_2I_4]^-$ system give values of $i_{trans}/i_{cis} = 1.7$ (M = Rh) and 1.65 (M = Ir). For each isomer, the C–O stretching force constant is larger for Rh than for the corresponding Ir species, whereas the interaction force constant is larger for Ir than for Rh. Both of these observations are consistent with enhanced π-back-donation for the $5d$ metal relative to the $4d$ metal. Theoretical calculations have suggested that this effect is predominantly due to relativistic destabilisation of third row metal d orbitals [25].

5. Conclusions

Isomerisation of *cis*-$[Rh(CO)_2I_4]^-$ results in an equilibrium favouring the *trans* dicarbonyl isomer by a factor of ca. 10. The attainment of equilibrium follows first order kinetics, and activation parameters suggest a dissociative mechanism. The lability of the CO ligands in coordinating solvents and in the presence of excess iodide indicates a mechanism for isomerisation involving CO dissociation. This proposal is supported by isotopic labelling experiments. Isolation of the previ-
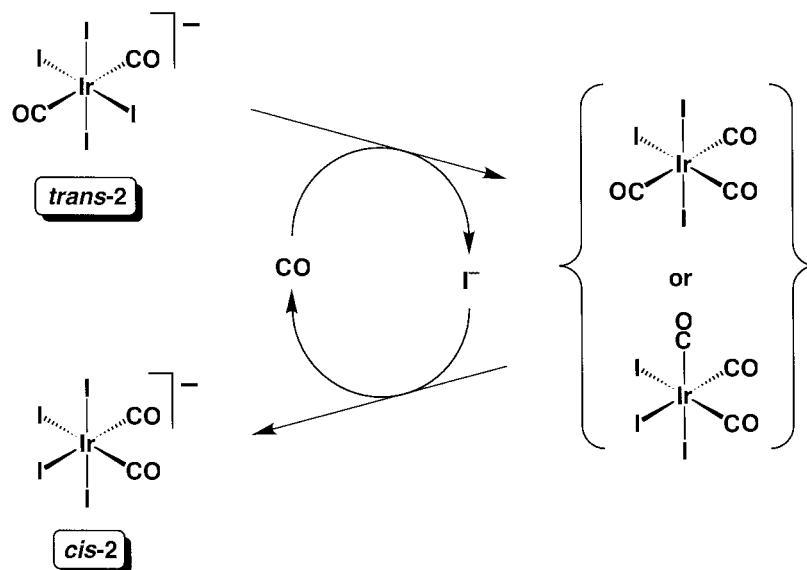
Scheme 5. Proposed mechanism for *trans–cis* isomerisation in $[Ir(CO)_2I_4]^-$ (**2**) promoted by carbon monoxide.

ously unknown *trans* isomer of $[Ir(CO)_2I_4]^-$ has been achieved, both serendipitously from carbonylation experiments on $[Ir(CO)_2I_3(Me)]^-$, and from the reaction of $[\{Ir(CO)I_4\}_2]^{2-}$ with CO. Isomerisation to the *cis* isomer occurs in the presence of CO, showing a thermodynamic preference in the iridium system opposite to that for rhodium. Analysis of the infrared spectroscopic data suggests enhanced π back-donation for iridium relative to rhodium, and for the *cis* isomers relative to the *trans* isomers of $[M(CO)_2I_4]^-$.

Acknowledgements

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