

THE PREPARATION OF *cis*- AND *trans*-[RhI(CO)(PAr₃)₂] (Ar = ARYL) AND THEIR READY DISSOCIATION IN SOLUTION

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Summary

Attempts to prepare [RhX(CO)(PAr₃)₂] complexes have shown that when X = I these complexes are far less stable than the well-known [RhCl(CO)(PPh₃)₂]. The bromo complexes [RhBr(CO)(PAr₃)₂] (Ar = C₆H₅, *p*-EtC₆H₄) can be prepared by simple halide exchange from their respective chloro complexes. However a similar attempt to prepare the iodo complexes was frustrated by dissociative equilibria; in the absence of oxygen dimers were formed, whereas in the presence of oxygen polymeric oxygen complexes were formed. The ease of dissociation of phosphine can be attributed to the greater steric crowding in the iodo complexes than in the chloro and bromo complexes. The complex [RhI(CO)(PPh₃)₂] could only be obtained in the presence of excess PPh₃, which inhibits the dissociation. The identification of this monomer was further complicated by the previously unnoticed presence of both *cis* and *trans* isomers in the solid state.

Introduction

Investigation into the oxidative-addition of methyl iodide to *trans*-[RhCl(CO)(PAr₃)₂] (I) where Ar = *p*-alkylaryl, has been found to be more complex [1] than previously indicated in the literature [2]. Attempts to determine the mechanism, which involves halide catalysis, were complicated by the possibility of halide exchange with the rhodium complex I which may lead to the more reactive species [RhX(CO)(PAr₃)₂] (II, X = I). It was considered appropriate therefore, to prepare and characterise complexes of type II where Ar = aryl and X = Br or I in order to study their oxidative-addition with alkyl bromides or iodides respectively, which would obviate any possibility of halide exchange.

Experimental

The *trans*-[RhCl(CO)(PAr₃)₂] (Ar = Ph, *p*-EtC₆H₄ and *p*-PrC₆H₄) and [RhX(CO)(PPh₃)₂] complexes were prepared by literature methods [3–5].

Preparation of trans-[RhBr(CO){P(p-EtC₆H₄)₃}]₂

To *trans*-[RhCl(CO){P(*p*-EtC₆H₄)₃}]₂ (0.1 g, 1.2×10^{-4} mol) was added sodium bromide (0.17 g, 1.7×10^{-3} mol) in acetone (100 ml). After stirring for 2½ h at room temperature, the excess sodium bromide together with the sodium chloride formed in the reaction was filtered off. The solvent was evaporated under reduced pressure and the yellow residue washed with ethanol. This was filtered and dried, yield 0.06 g, 56%, $\nu(\text{CO})$ 1967 cm⁻¹ (Nujol mull), TLC (acetone) gave one spot, *R_f* 0.83 (cf. *trans*-[RhCl(CO){P(*p*-EtC₆H₄)₃}]₂, *R_f* 0.68 under identical conditions). Recrystallisation of the product from benzene/ethanol, gave the product, m.p. 164°C. Found: C, 65.0; H, 6.0. C₄₉H₅₄BrOP₂Rh calcd.: C, 65.3; H, 5.9%.

Preparation of trans-[RhBr(CO)(PPh₃)₂]

trans-[RhBr(CO)(PPh₃)₂] was prepared by the same method as *trans*-[RhBr(CO){P(*p*-EtC₆H₄)₃}]₂, yield 65%, m.p. 173°C, $\nu(\text{CO})$ (Nujol mull) 1969 cm⁻¹ (as literature [12b]) TLC (acetone) gave one spot, *R_f* 0.83.

*Attempted preparation of [RhBr(CO){P(*p*-PrC₆H₄)₃}]₂*

To *trans*-[RhCl(CO){P(*p*-PrC₆H₄)₃}]₂ (0.12 g, 1.27×10^{-4} mol) in acetone (30 ml) was added sodium bromide (0.2 g, 1.9×10^{-3} mol) and the solution stirred for 2½ h at room temperature. The excess sodium halides were filtered off under reduced pressure leaving a yellow solid which was recrystallised from a benzene/ethanol mixture and the orange precipitate filtered and dried, yield 0.06 g, 77%, m.p. 63°C. IR (Nujol mull) indicated no $\nu(\text{CO})$ but absorbances typical of tris(*p*-propylphenyl)phosphine were present. Found: C, 56.8; H, 6.1. [C₂₇H₃₃BrO₂PRh]_x calcd.: C, 56.6; H, 5.8%. TLC (acetone) gave *R_f* 0.58.

Reaction of trans-[RhCl(CO)(PPh₃)₂] with potassium iodide in the presence of triphenylphosphine and air to give trans-[RhI(CO)(PPh₃)₂]

trans-[RhCl(CO)(PPh₃)₂] (0.12 g, 1.7×10^{-4} mol), triphenylphosphine (0.3 g, 1.2×10^{-3} mol) and potassium iodide (0.4 g, 2.4×10^{-3} mol) were mixed together in acetone (50 ml). The mixture was stirred at room temperature for 25 h and left at room temperature for a further 3 days. A yellow solid was filtered off and dried. The complex was recrystallised from ethanol/benzene in the presence of some triphenylphosphine and washed with ethanol, yield 0.1 g, 75%; m.p. 153–155°C (dec.); $\nu(\text{CO})$ (Nujol) 1985 cm⁻¹; $\nu(\text{CO})$ (CHCl₃) 1980 (vs) and 2025 cm⁻¹ (w). Found C, 56.9; H, 3.8. C₃₇H₃₀IOP₂Rh calcd.: C, 56.9; H, 3.8%. ³¹P NMR in CDCl₃ gave δ 27.3 ppm (d), *J*(Rh–P) 123.05 Hz due to *trans*-[RhI(CO)(PPh₃)₂] and, if air is not rigorously excluded δ 30.97 ppm (d), *J*(Rh–P) 83.98 Hz due to *trans*-[RhI(CO)(O₂)(PPh₃)₂] together with a very weak signal at δ 29.04 ppm (d), *J*(Rh–P) 123.0 Hz.

To the filtrate was added water causing triphenylphosphine to precipitate (yield 0.28 g, 93%). The product was identified by IR spectroscopy and melting point.

Preparation of cis-[RhI(CO)(PPh₃)₂]

cis-[RhI(CO)(PPh₃)₂] was prepared in air by an identical method to that used to prepare *trans*-[RhI(CO)(PPh₃)₂], but here the preparation was carried out at 0°C. The product *cis*-[RhI(CO)(PPh₃)₂], gave $\nu(\text{CO})$ 1969 cm⁻¹ (Nujol mull) and $\nu(\text{CO})$ 1980 (s) and 2025 cm⁻¹ (w) (CHCl₃). When dissolved in CDCl₃ ³¹P NMR gave δ 27.3 ppm (d), *J*(Rh–P) 123.05 Hz due to *trans*-[RhI(CO)(PPh₃)₂] and if air is not

vigorously excluded, δ 30.97 ppm (d), $J(\text{Rh-P})$ 83.98 Hz due to *trans*- $[\text{RhI}(\text{CO})(\text{O}_2)(\text{PPh}_3)_2]$. IR spectroscopy showed the *cis* isomer converted to the *trans* isomer when stored in the solid state at room temperature (25°C) for 1 month.

Reaction of trans-[RhCl(CO)(PPh₃)₂] with potassium iodide under carbon monoxide in the absence of added triphenylphosphine

trans- $[\text{RhCl}(\text{CO})(\text{PPh}_3)_2]$ (0.13 g, 1.9×10^{-4} mol) was dissolved in acetone (40 ml). After 20 minutes at room temperature, under carbon monoxide, potassium iodide was added (0.6 g, 3.6×10^{-3} mol). The solution was stirred for 17 h at room temperature, after which time yellow crystals had precipitated. These were filtered under carbon monoxide, washed with water and dried in vacuo, yield 0.14 g, 94%. IR spectroscopy and microanalysis confirmed that the product was *trans*- $[\text{RhI}(\text{CO})(\text{PPh}_3)_2]$.

Reaction of trans-[RhCl(CO)(PPh₃)₂] with potassium iodide in air in the absence of free triphenylphosphine

To *trans*- $[\text{RhCl}(\text{CO})(\text{PPh}_3)_2]$ (0.19 g, 2.7×10^{-4} mol) was added potassium iodide (0.6 g, 3.6×10^{-3} mol) in acetone (100 ml). After 24 h the colour of the solution had changed to brown. The potassium iodide and potassium chloride were filtered off. The reaction mixture was then evaporated to dryness, dissolved in benzene and again filtered. On evaporation of the filtrate under reduced pressure a brown oil remained. IR spectroscopy showed no absorbances assignable to $\nu(\text{CO})$ or $\nu(\text{M-Cl})$ but gave absorbances corresponding to triphenylphosphine oxide and water. The brown oil crystallized on cooling in liquid nitrogen under petroleum ether (b.p. 40–60°C). This was filtered off and dried, yield 0.09 g, 59.0%. Found: C, 37.2; H, 3.57. $\text{C}_{18}\text{H}_{15}\text{IO}_3\text{PRh} \cdot 2\text{H}_2\text{O}$ calcd.: C, 37.5; H, 3.3%, $[\text{RhCl}(\text{O}_2)(\text{OPPh}_3)_{0.67}]_x$ has previously been reported [6] as the product of photoinduced oxidation of *trans*- $[\text{RhCl}(\text{CO})(\text{PPh}_3)_2]$.

Decarbonylation of trans-[RhI(CO)(PPh₃)₂]

trans- $[\text{RhI}(\text{CO})(\text{PPh}_3)_2]$ (0.05 g, 6.4×10^{-4} mol) was partially dissolved in degassed acetone (12 ml), after stirring for 45 h under nitrogen the solution remained yellow. On evaporating the acetone under reduced pressure at 50°C, the solution started to darken. After complete evaporation to dryness a brown solid remained. The product was dissolved in degassed dichloromethane, and again evaporated to dryness. This was repeated several times to effect complete decarbonylation. The product was isolated from degassed petroleum ether (b.p. 40–60°C). The product was filtered off and dried, yield 0.04 g, 83%. It was identified as $[\text{Rh}_2\text{I}_2(\text{PPh}_3)_4]$ by mixed melting point and IR spectroscopy.

Reaction of trans-[RhCl(CO){P(p-EtC₆H₄)₃}]₂ with potassium iodide

To *trans*- $[\text{RhCl}(\text{CO})\{\text{P}(p\text{-EtC}_6\text{H}_4)_3\}_2]$ (0.16 g, 1.9×10^{-4} mol) was added potassium iodide (0.4 g, 2.4×10^{-3} mol) in acetone (80 ml) and the mixture stirred for 3 h. The potassium halides were filtered off and the acetone evaporated under reduced pressure. The product was re-dissolved in chloroform, and the remaining halide salts were removed by filtration. After a further evaporation to dryness and washing with ethanol, the product was collected and dried, yield 0.1 g, 89%. TLC (20% chloroform/80% ethanol) gave one spot R_f 0.81, $\nu(\text{CO})$ (Nujol) 1976 (s) and 2020 cm^{-1} (w). Found: C, 49.05; H, 5.29. $\text{C}_{25}\text{H}_{27}\text{IOPRh}$ calcd.: C, 49.6; H, 4.5%.

Reaction of $[\text{Rh}_2\text{Cl}_2\{\text{P}(\text{p-EtC}_6\text{H}_4)_3\}_4]$ with lithium iodide

$[\text{Rh}_2\text{Cl}_2\{\text{P}(\text{p-EtC}_6\text{H}_4)_3\}_4]$ (0.4 g, 2.4×10^{-4} mol) was stirred with lithium iodide (2.0 g, 1.5×10^{-2} mol) in ethanol (30 ml) for 3 h at reflux under nitrogen. The ethanol was evaporated off until only a brown solid was left. Water (50 ml) was added and the brown solid extracted in petroleum ether (b.p. 60–80°C). Evaporation of the petroleum ether left a brown solid which was filtered off under nitrogen. This was washed with water and dried in a drying pistol, yield 0.41 g, 90.7%. The product was washed with petroleum ether (b.p. 40–60°C) and dried. Found: C, 60.4; H, 5.7. $\text{C}_{48}\text{H}_{54}\text{IP}_2\text{Rh} \cdot 2\text{H}_2\text{O}$ calcd.: C, 59.8; H, 6.0%.

Reaction of $[\text{Rh}_2\text{I}_2(\text{PPh}_3)_4]$ with carbon monoxide [7]

$[\text{Rh}_2\text{I}_2(\text{PPh}_3)_4]$ (0.04 g, 2.7×10^{-5} mol) was dissolved in acetone (50 ml) and carbon monoxide was passed through the solution for 2 h. The solution turned yellow and on addition of water gave a yellow precipitate which was filtered off and dried, yield 0.03 g, 72%, $\nu(\text{CO})$ (Nujol) 1985 cm^{-1} . The IR spectrum was identical to that of *trans*- $[\text{RhI}(\text{CO})(\text{PPh}_3)_2]$.

Attempted preparation of $[\text{RhI}(\text{CO})\{\text{P}(\text{p-EtC}_6\text{H}_4)_3\}_2]$ from the reaction of carbon monoxide with $[\text{Rh}_2\text{I}_2\{\text{P}(\text{p-EtC}_6\text{H}_4)_3\}_4] \cdot 2\text{H}_2\text{O}$

$[\text{Rh}_2\text{I}_2\{\text{P}(\text{p-EtC}_6\text{H}_4)_3\}_4] \cdot 2\text{H}_2\text{O}$ (0.16 g, 8.4×10^{-5} mol) was dissolved in degassed acetone (80 ml), through which carbon monoxide was passed. After 4 h degassed water was added causing a brown product to precipitate which was filtered off and dried. IR spectroscopy confirmed the presence of some $[\text{Rh}_2\text{I}_2(\text{CO})_2\{\text{P}(\text{p-EtC}_6\text{H}_4)_3\}_2]$, but following dissolution in degassed ethanol and evaporation to dryness, the brown product was shown by IR spectroscopy to have no $\nu(\text{CO})$ and be identical to the starting material, yield 0.12 g, 75%.

Preparation of $[\text{RhI}(\text{PPh}_3)_3]$ [7]

To triphenylphosphine (6.0 g, 2.3×10^{-2} mol) in hot ethanol (200 ml) was added $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ (1.0 g, 3.8×10^{-3} mol) in ethanol (60 ml) and the mixture brought to the boil. When lightening of the colour occurred and orange crystals deposited (5–10 min), a solution of LiI (4.0 g, 2.9×10^{-2} mol) in hot ethanol (80 ml) was added and the solution stirred under reflux for 3–4 h and brown crystals collected from the warm solution. These were filtered off and dried, yield 3.85 g, 99.7%. The solid was recrystallised from ethanol/benzene containing some triphenylphosphine. Found: C, 67.2; H, 4.9. $\text{C}_{54}\text{H}_{45}\text{IP}_3\text{Rh}$ calcd.: C, 67.8; H, 4.7%.

Preparation of $[\text{Rh}_2\text{I}_2(\text{PPh}_3)_4]$

To $[\text{RhI}(\text{PPh}_3)_3]$ (1.0 g, 9.8×10^{-4} mol) under nitrogen was added degassed isobutyl methyl ketone and the mixture refluxed for 2 h; addition of lithium iodide (1.0 g, 7.5×10^{-3} mol) and stirring under reflux for another hour gave darkening of the solution. The solution was cooled and then filtered under nitrogen. The red precipitate was dried in vacuo and was recrystallised twice from dichloromethane/petroleum ether (b.p. 40–60°C) under nitrogen, yield 0.7 g, 95%. Found: C, 57.3; H, 4.0. $\text{C}_{36}\text{H}_{30}\text{IP}_2\text{Rh}$ calcd.: C, 57.3, H, 4.0%.

Spectroscopic and TLC measurements

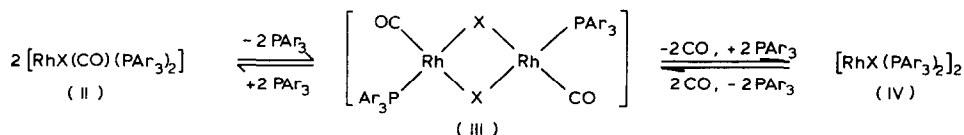
Infrared spectra were recorded on a Perkin–Elmer 577 spectrophotometer. Solids

were run as Nujol mulls using potassium bromide plates for the range 4000–400 cm^{-1} and cesium iodide plates 400–200 cm^{-1} . Solution infrared spectra were run in potassium bromide cells. ^{31}P NMR spectra were recorded on a JEOL PS/PFT Fourier-transform NMR spectrometer with phosphoric acid external reference. TLC was performed using Merck plastic sheets precoated with Silica Gel 60 F_{254} .

Results and discussion

The chloro complexes, *trans*- $[\text{RhCl}(\text{CO})(\text{PAr}_3)_2]$, where $\text{Ar} = \text{Ph}$ and *p*- EtC_6H_4 were prepared by the reaction of the phosphine with $[\text{Rh}_2\text{Cl}_2(\text{CO})_4]$ [3] and by carbonylation of $[\text{RhCl}(\text{PAr}_3)_3]$ by aqueous formaldehyde [4]. Metathesis of these complexes with sodium bromide in acetone solution in the presence of air gave the bromo-derivatives *trans*- $[\text{RhBr}(\text{CO})(\text{PAr}_3)_2]$, where $\text{Ar} = \text{Ph}$ and *p*- EtC_6H_4 , in good yield at room temperature. They were readily purified by recrystallisation from benzene/ethanol mixtures.

Attempts to prepare *trans*- $[\text{RhI}(\text{CO})(\text{PPh}_3)_2]$ by the same method yielded a brown solid which did not show a carbonyl absorption in the infrared region. *trans*- $[\text{RhI}(\text{CO})(\text{PPh}_3)_2]$ could only be isolated without decomposition by metathesis and recrystallisation in the presence of excess triphenylphosphine under an atmosphere of either air or nitrogen. The lack of stability of *trans*- $[\text{RhI}(\text{CO})(\text{PPh}_3)_2]$ in solution has previously been noted in the literature [8] and recently attempts to prepare II ($\text{X} = \text{Br}$ and I) have failed to give any pure products [9]. We have now established that the decomposition is the result of a series of dissociative equilibria which are absent in the chloro complex and only present in the bromo complex when more bulky arylphosphines are coordinated to the rhodium. If the absence of air, decomposition is via the dissociative equilibria shown in Scheme 1. Thus, when



SCHEME 1

II is dissolved in acetone, phosphine is released to give an equilibrium amount of $[\text{Rh}_2\text{X}_2(\text{CO})_2(\text{PAr}_3)_2]$ (III). Decarbonylation by repeated evaporation of the solvent to dryness under vacuum yields $[\text{Rh}_2\text{X}_2(\text{PAr}_3)_4]$ (IV, $\text{X} = \text{I}$, $\text{Ar} = \text{Ph}$). The product was identified by comparison with an authentic sample prepared from $[\text{RhI}(\text{PPh}_3)_3]$ [7]. The reverse of the above reactions was also shown to occur, II being obtained from $[\text{Rh}_2\text{I}_2(\text{PPh}_3)_4]$ (IV) and carbon monoxide. Treatment of IV ($\text{X} = \text{I}$, $\text{Ar} = p\text{-EtC}_6\text{H}_4$) with carbon monoxide yielded III ($\text{X} = \text{I}$, $\text{Ar} = p\text{-EtC}_6\text{H}_4$) and phosphine. The positions of the equilibria shown in Scheme 1 are strongly dependent on both the phosphine and the halide. Thus when $\text{Ar} = p\text{-EtC}_6\text{H}_4$, the equilibria lie in favour of structure IV so that attempts to prepare $[\text{RhI}(\text{CO})(\text{P}(p\text{-EtC}_6\text{H}_4)_3)_2]$ by treatment of I ($\text{Ar} = p\text{-EtC}_6\text{H}_4$) with KI yielded III ($\text{X} = \text{I}$, $\text{Ar} = p\text{-EtC}_6\text{H}_4$), only traces of II ($\text{X} = \text{I}$, $\text{Ar} = p\text{-EtC}_6\text{H}_4$) being obtained in solution at 0°C and in the presence of a very large excess of the phosphine. When $\text{X} = \text{Cl}$ and Br , and $\text{Ar} = \text{Ph}$ and *p*- EtC_6H_4 , the equilibria shown in Scheme 1 lie in favour of structure II.

trans- $[\text{RhI}(\text{CO})(\text{PPh}_3)_2]$ has $\nu(\text{CO})$ 1980 cm^{-1} (CHCl_3 solution). This is the

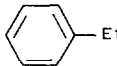
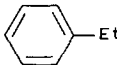
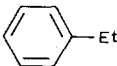
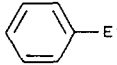
major isomer formed in solution by the dissociation of $[\text{RhI}(\text{CO})(\text{PPh}_3)_2]$, although IR spectroscopy (Table I) shows that *cis*- $[\text{RhI}(\text{CO})(\text{PPh}_3)_2]_2$ ($\nu(\text{CO})$ 2025 cm^{-1} in CHCl_3 solution) is also present. IR spectroscopy show III ($\text{X} = \text{I}$, $\text{Ar} = p\text{-EtC}_6\text{H}_4$) to exist as both *cis* and *trans* isomers. *cis*- $[\text{RhI}(\text{CO})(\text{P}(p\text{-EtC}_6\text{H}_4)_3)_2]$ has $\nu(\text{CO})$ 2020 cm^{-1} (Nujol mull); *trans*- $[\text{RhI}(\text{CO})(\text{P}(p\text{-EtC}_6\text{H}_4)_3)_2]$ has $\nu(\text{CO})$ 1980 cm^{-1} (Nujol mull).

^{31}P NMR has shown the existence of $[\text{RhIO}_2(\text{CO})(\text{PPh}_3)_2]$ in solution at 20°C, when both *cis*- and *trans*- $[\text{RhI}(\text{CO})(\text{PPh}_3)_2]$ are dissolved in CDCl_3 under an atmosphere of air. Although the presence of $[\text{RhIO}_2(\text{CO})(\text{PPh}_3)_2]$ can only arise from the dissociative equilibria shown in Scheme 2, the presence of Rh-P spin-spin coupling indicates that phosphine ligand dissociation is slow on the ^{31}P NMR time scale at 20°C.

Attempts to prepare *trans*- $[\text{RhI}(\text{CO})(\text{PPh}_3)_2]$ by metathesis from *trans*- $[\text{RhCl}(\text{CO})(\text{PPh}_3)_2]$ in the absence of free phosphine, in air and light, yielded a brown oil which crystallised on freezing in liquid nitrogen. Microanalysis and infrared spectra were consistent with the formula $[\text{RhI}(\text{O}_2)(\text{OPPh}_3) \cdot 2\text{H}_2\text{O}]_x$. The

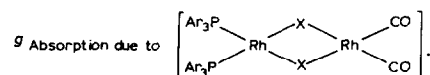
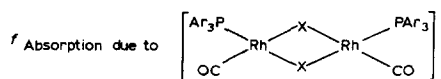
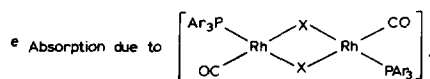
TABLE I

INFRARED STRETCHING FREQUENCIES OF $[\text{RhX}(\text{CO})(\text{PAR}_3)_2]$ (II) AND $[\text{Rh}_2\text{X}_2(\text{CO})_2(\text{PAR}_3)_2]$ (III)

Complex	X	Ar	$\nu(\text{CO}) (\text{cm}^{-1})$ Nujol mull ^a	$\nu(\text{CO}) (\text{cm}^{-1})$ solution ^{a,b}
II	Cl	Ph	1965	1980
	Br	Ph	1969	1980
	I	Ph	1969 ^c	
			1985	1980(s) ^d , 2025(w) ^f
	Cl		1963	1976
	Br		1967	1980
	I		1985	1980 ^d , 2032 ^f
III	Cl	Ph	1980(s) ^e , 2023(w) ^f , 2090(w) ^g	1980 ^{e,h} , 2023 ^{f,h}
	I	Ph	1974 ^e	1980 ^e
	I		1976 ^e , 2020 ^f	

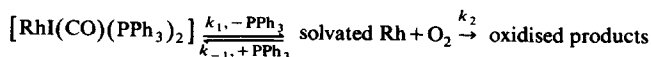
^a *trans* Isomers except where stated. ^b Chloroform except where otherwise indicated. ^c *cis* Isomer.

^d Absorption due to both monomeric II and *trans*-dimeric III (footnote e) dimer formation.



^h Solvent benzene.

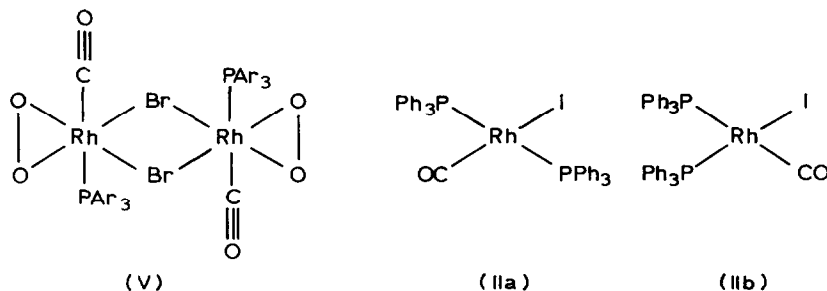
photoproduct $[\text{RhCl}(\text{O}_2)(\text{OPPh}_3)_{0.67}]_x$ has previously been isolated [6] from UV irradiation of $\text{trans-}[\text{RhCl}(\text{CO})(\text{PPh}_3)_2]$. In the presence of phosphine, $\text{trans-}[\text{RhI}(\text{CO})(\text{PPh}_3)_2]$ is not photo-oxidised, indicating that this reaction proceeds along a dissociative mechanism (Scheme 2). The added phosphine was isolated at the end



SCHEME 2

of the reaction, and this also had not been oxidised. The sensitivity to oxygen of $\text{trans-}[\text{RhX}(\text{CO})(\text{PAR}_3)_2]$ is dependent on both phosphine and halide. The complexes with $\text{X} = \text{Cl}$ are more stable to oxidation than those with $\text{X} = \text{Br}$ or I . When $\text{X} = \text{Br}$, the ease of oxidation is dependent on the phosphine in the order: $\text{Ar} = p\text{-PrC}_6\text{H}_4 > p\text{-EtC}_6\text{H}_4 \sim \text{Ph}$. Attempts to prepare II ($\text{X} = \text{Br}$, $\text{Ar} = p\text{-PrC}_6\text{H}_4$) by metathesis from the chloride yielded an oil showing no carbonyl absorption in the infrared spectrum. In this case the product was found to crystallise from benzene/ethanol and gave microanalysis and IR spectra consistent with the formula $[\text{RhBr}(\text{O}_2)\text{P}(p\text{-PrC}_6\text{H}_4)_3]_x$. The decarbonylation may occur via a photo-oxidation to carbon dioxide [6] or via loss of carbon monoxide from an oxidised rhodium(III) species such as V. Decarbonylations are known to occur easily from six-coordinate rhodium(III) complexes [10].

Identification of $[\text{RhI}(\text{CO})(\text{PPh}_3)_2]$ was complicated by the existence of two isomers in the solid state. Similar isomerism of $[\text{RhCl}(\text{CO})(\text{PPh}_3)_2]$ has previously been reported in the literature [11]. Both the thermodynamically more stable *trans*-isomer, Ia, and a less stable *cis*-isomer, Ib, can be obtained in pure form and may be distinguished by their infrared absorptions in the carbonyl region, where the *trans*-isomer absorbs at 1965 cm^{-1} and the *cis*-isomer at 1978 cm^{-1} (both in Nujol



mulls). The two isomers of $[\text{RhI}(\text{CO})(\text{PPh}_3)_2]$ have been separately reported in the literature previously but not recognised as isomers; IIa was reported as having $\nu(\text{CO})$ at 1985 cm^{-1} (Nujol mull) [12] and IIb was reported [2] as having $\nu(\text{CO})$ at 1968 cm^{-1} , in chloroform solution $\nu(\text{CO})$ has been reported as being at 1981 cm^{-1} [13]. Halide exchange of $\text{trans-}[\text{RhCl}(\text{CO})(\text{PPh}_3)_2]$ at room temperature was found to give isomer IIa, which has a carbonyl absorption at 1985 cm^{-1} (Nujol mull), whilst an otherwise identical reaction carried out at 0°C yielded IIb which has a carbonyl absorption at 1969 cm^{-1} (Nujol mull). Over a period of one month at room temperature in the solid state, the thermodynamically less stable *cis* isomer, IIb, converts to IIa; at room temperature in chloroform solution this occurs within the time required for dissolution.

The dissociative equilibria discussed in this paper complicate the study of the oxidative addition of alkyl halides to II, where $X = I$ and Br , when bulky aryl phosphines are coordinated to the rhodium.

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