Journal of Organometallic Chemistry, 231 (1982) 255—264
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

RHODIUM COMPLEXES CONTAINING THE TRI-3-BUTENYLARSINE LIGAND

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(Received December 11th, 1981)

Summary

The potential tetradentate ligand tri-3-butenylarsine (tba) reacts with $[Rh(cod)Cl]_2$ (cod = cycloocta-1,5-diene) and $[Rh(C_2H_4)_2Cl]_2$ to give either $[Rh(tba)Cl]_2$ or [Rh(tba)Cl] depending on the reaction conditions. The complex $[Rh(tba)Cl]_2$ undergoes bridge-cleavage reactions with phosphines and carbon monoxide to give the compounds [Rh(tba)LCl] [L = PPh_3, $PMePh_2$, PBu^n_3, $Ph_2P(CH_2)_4PPh_2$, and CO]; the compound where L = PPh_3 has also been obtained from reaction between tba and $[RhCl(PPh_3)_3]$. The square-planar complex [Rh(tba)Cl] forms the corresponding bromo- and iodo-derivatives by metathetical halogen exchange; reacts with $NaBPh_4$ to give $[Rh(tba)(\eta^2\text{-}C_6H_5BPh_3)]$; and with CO affords [Rh(tba)(CO)Cl]. Pyridine displaces the CO ligand in this last compound to give [Rh(tba)pyCl], and both [Rh(tba)(CO)Cl] and the triphenylphosphine analogue ionise in polar solvents, and yield $[Rh(tba)L]BPh_4$ (L = CO or PPh_3) with $NaBPh_4$. Reaction between tba and $[Rh(CO)_2Cl]_2$ is complex, giving $[(tba)Rh(\mu\text{-}Cl)_2Rh(CO)_2]$ as the major product with a 1 : 1 molar ratio of reactants, but *cis*- and *trans*-$[(tba)(CO)Rh(\mu\text{-}Cl)_2\text{-}Rh(CO)(tba)]$ with a 2 : 1 molar ratio, and [Rh(tba)(CO)Cl] with a 4 : 1 excess of tba at room temperature.

The structures of these various compounds are discussed in the light of IR and variable temperature ^1H NMR spectroscopic evidence.

Introduction

Reactions of multidentate tertiary phosphine and arsine ligands with rhodium(I) and iridium(I) complexes have attracted considerable interest in recent years [1]. The ability of phosphines to stabilise a variety of oxidation states and the variation in stereochemistry with multidentate chelate ligands is of particular interest. Ligands such as $Ph_2P(CH_2CH_2CH{=}CH_2)$ [2], $PhP(CH_2CH_2CH{=}CH_2)_2$

TABLE 1

ANALYTICAL (%), MELTING POINT, AND MOLECULAR WEIGHT DATA FOR THE RHODIUM(I) COMPLEXES

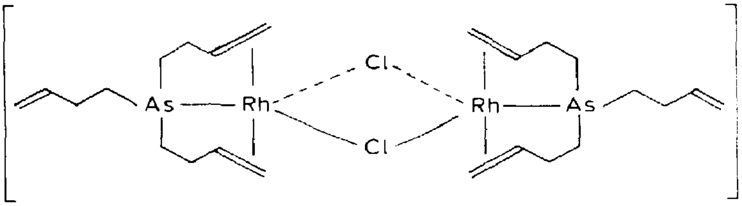
Complex		M.p. (°C) [b]	Analysis [a]				M
			C	H	halogen	Rh	
$[Rh(tba)Cl]_2$	(1)	138	38.1 (38.1)	5.5 (5.6)	9.1 (9.4)	26.5 (27.2)	—
$[RhCl(tba)(PPh_3)]$	(2)	155	56.0 (56.2)	5.8 (5.7)	5.6 (5.5)	15.9 (16.1)	585 (600)
$[RhCl(tba)(PPh_2Me)]$	(3)	160	52.2 (51.9)	5.8 (5.9)	6.0 (6.1)	—	—
$[RhCl(tba)(PBu^n_3)]$	(4)	168–170	50.6 (50.9)	6.0 (6.1)	6.2 (6.3)	—	—
$[RhCl(tba)(dpb)]$	(5)	164–166	59.4 (59.7)	5.8 (6.1)	4.3 (4.4)	—	815 (804)
$[Rh(tba)(PPh_3)]BPh_4$	(6)	182–184	70.3 (70.2)	6.3 (6.1)	—	—	—
$[RhCl(tba)(CO)]$	(7)	126	38.5 (38.4)	5.2 (5.2)	8.7 (8.7)	25.2 (25.4)	400 (407)
$[RhCl(tba)py]$	(8)	148	43.9 (44.6)	6.0 (5.7)	7.9 (7.8)	—	480 (458) [c]
$[Rh(tba)(CO)]BPh_4$	(9)	146	64.3 (64.4)	5.8 (6.0)	—	—	—
$[RhCl(tba)]$	(10)	110	37.8 (38.1)	5.3 (5.6)	9.3 (9.4)	27.2 (27.2)	480 (478)
$[RhBr(tba)]$	(11)	116	33.9 (34.1)	5.0 (5.0)	17.9 (18.9)	24.0 (24.3)	550 (523)
$[RhI(tba)] \cdot 0.5$ MeOH	(12)	96–98	30.1 (30.9)	4.6 (4.8)	24.9 (26.1)	—	—
$[Rh(tba)(\eta^2\text{-}C_6H_5BPh_3)]$	(13)	198	65.7 (65.3)	6.1 (6.2)	—	—	—
$[Rh_2(tba)(CO)_2Cl_2]$	(14)	134	29.3 (29.3)	3.8 (3.7)	12.4 (12.4)	—	600 (573)

[a] Calculated values are given in parentheses. [b] With decomposition. [c] Nitrogen 3.0 (3.1).

[3], and $P(CH_2CH_2CH{=}CH_2)_3$ [4] can behave as bidentate, tridentate, and tetradentate ligands, respectively, on reaction with $[Rh(CO)_2Cl]_2$ or $[Rh(C_2H_4)_2Cl]_2$. We now report the synthesis and some reactions of rhodium(I) complexes of the arsine ligand, tba, $As(CH_2CH_2CH{=}CH_2)_3$ [5].

Results and discussion

Both $[Rh(cod)Cl]_2$ and $[Rh(C_2H_4)Cl]_2$ (1 mol) react with tba (2 mol) in boiling benzene to give $[Rh(tba)Cl]_2$ (**1**) (Table 1) in 33% and 97% yield respectively. This compound was only slightly soluble in $CHCl_3$ and CH_2Cl_2, and decomposed in ether and ethanol. Its IR spectrum (Table 2) showed both a free olefin stretching vibration (1640 cm^{-1}) and new bands at 1250 [$\nu(C{=}C)$], 892, 880, and 860 cm^{-1} [$\delta_{o.o.p.}(C{-}H)$] indicative [6,7] of coordinated olefin. A laser Raman spectrum could not be obtained as this compound, and all the other compounds isolated in this work, decomposed in the laser beam. In the ^1H NMR spectrum at 32°C (Table 2) the resonances for the olefin ligands are equivalent due to rapid exchange (on the NMR time scale) of the bonded and non-bonded olefins. At −60°C the exchange is so slow that the spectrum resolves into a set of sharp bands at δ5.24 (H^3), 3.80 (H^1) and 3.24 ppm (H^2) and broad resonances at δ 5.80 (H^3) and 4.90 ppm (H^1 and H^2) for free olefinic protons. Integration of the spectrum suggests that two of the olefin groups are coordinated consistent with structure I. At low temperature rapid equilibration between the different possible conformers leading to equivalence of the methylene protons (H^4 and H^5) is stopped and these protons become non-equivalent as noted previously for complexes of $P(CH_2CH_2CH{=}CH_2)_3$ [4].



(I)

Chlorine-bridge cleavage takes place on reaction of **1** with PPh_3, PPh_2Me, PBu^n_3 and $Ph_2P(CH_2)_4PPh_2$ (bdpb) to give compounds **2**—**5**, respectively (Scheme 1). Compound **2** has also been prepared in 66% yield by reaction of $[RhCl(PPh_3)_3]$ with tba in benzene at room temperature. The IR and ^1H NMR spectra of compounds **2**—**5** (Table 2) are similar to those of compound **1**, and integration of resonances due to coordinated and free olefin ligands in the NMR spectrum of compound **2** at −60°C indicates that they are five coordinate. The solid state structure of $[RhCl\{P(CH_2CH_2CH{=}CH_2)_3\}]$ [8] has been found to be trigonal bipyramid with the chlorine ligand *trans* to phosphorus. A similar structure (II) with the phosphine in the trigonal plane is tentatively proposed for the compounds **2**—**5**. In methanol, compound **2** reacts with $NaBPh_4$ to form the ionic complex $[Rh(tba)(PPh_3)]BPh_4$ (**6**), which showed no IR band at 1640 cm^{-1} for free olefin consistent with structure III; this compound was only slightly soluble in dimethyl sulphoxide-d_6 and insoluble in $CDCl_3$, so that a low temper-

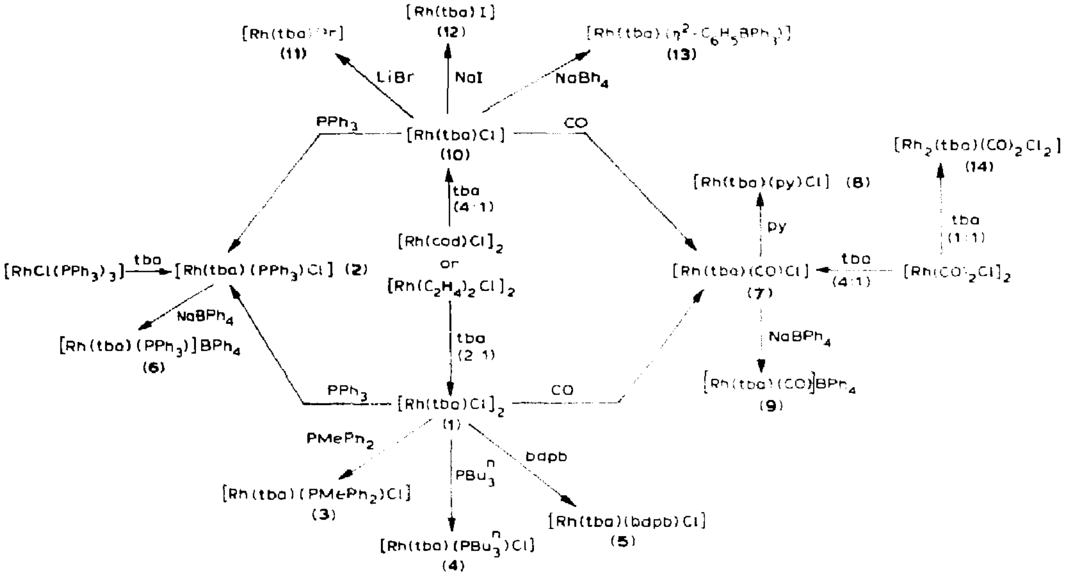
TABLE 2

IR AND ^{1}H NMR DATA FOR THE RHODIUM(I) COMPLEXES OF THE LIGAND $As(CH^5H^{5'}-CH^4H^{4'}-CH^3=CH^1H^2)_3$

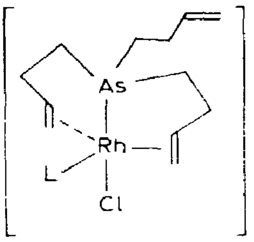
Complex	IR (cm^{-1})			Temp. (°C)	Chemical shifts (s) [a]					Coupling constants (Hz) [b]	
	ν(C=C) free	ν(C=C) bound	ν(Rh—Cl)		H^1	H^2	H^3	H$^{4,4'}$	H$^{5,5'}$	$J_{2,3}$	$J_{1,3}$
tba	1645w	—	—	32	5,00	4,87	5,75	2,10	1,40	9,0	18,0
(1)	1640w	1250w	250w, 289w	32	3,30	3,90	5,40	2,30—	—1,80	8,5	14,0
				—60 [c]	3,24 (4,90)	3,80 (4,90)	5,24 (5,80)	2,30—	—1,70		
(2)	1640w	1250w	240w	32	3,28	3,60	4,94	2,00	1,40	8,0	14,0
				—60 [c]	3,20 (4,95)	3,54 (4,95)	4,92 (5,78)	2,30—	—1,40		
(3)	1640w	1250w	240w	32	3,02	3,54	4,92	2,02	1,50	8,0	14,0
(4)	1640w	1250w	236w	—	—	—	—	—	—	—	—
(5)	1640w	1250w	240w	32	3,42	3,70	4,95	2,30	1,40	9,0	14,0
(6)	—	1262m	—	32 [d]	3,20	3,60	4,95	2,30	1,70	8,0	14,0
(7)	1640w	1256w	226w	32	3,60	4,22	5,20	2,00	1,80	8,0	14,0
				—60 [c]	3,50 (4,95)	4,12 (4,95)	5,10 (5,80)	2,15—	—1,40		
(8)	1640w	1260w	226w	32	3,38	3,60	4,90	2,10	1,40	9,0	14,0
(9)	—	1246m	—								
(10)	1640w	1250w	236w	32	3,7	4,04	4,98	2,30—	—1,60	8,0	12,0
				—60 [c]	3,22 (4,92)	3,74 (4,92)	5,30 (5,80)	2,15—	—1,50		
(11)	1640w	1252w	—	32	3,42	3,80	5,35	2,15	1,50	8,0	14,0
(12)	1640w	1252w	—	32	3,36—	—3,62	5,20	2,15	1,40		
(13)	—	1248w									
(14)	1640w	1256m	270s, 286s	32	3,35	4,20	5,20	1,98	1,75	8,0	13,5
				—60 [c]	3,52 (4,76)	4,15 (4,76)	5,14 (5,76)	2,30—	—1,40		

[a] Except where stated spectra were measured on solutions in $CDCl_3$. [b] The coupling constants $J_{4,5}$ and $J_{3,4}$ could not be determined. [c] The figures in parentheses are for the non-coordinated olefinic ligand. [d] In DMSO-d_6.

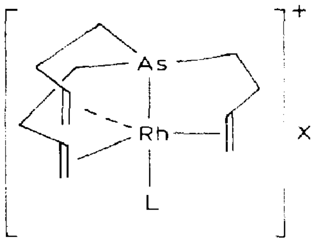
SCHEME 1



ature NMR spectrum could not be obtained. It seems likely that in more polar solvents dissociation of chloride ion from **2** takes place readily to give [Rh(tba)-(PPh_3)]Cl.



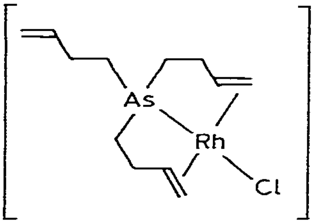
(II)



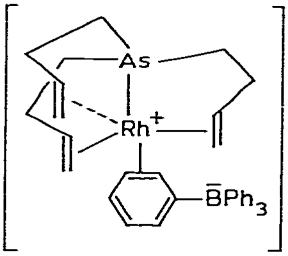
(III)

Passage of carbon monoxide through a suspension of compound **1** in dichloromethane at 0°C gives initially an orange solution which shows two strong terminal metal—carbonyl bands at 2068 and 1990 cm^{-1}, and a weak band at 1640 cm^{-1} for a non-coordinated olefin ligand. When this solution is allowed to warm to room temperature it produces the yellow complex [Rh(tba)(CO)Cl] (**7**) [ν(CO) 2004 cm^{-1}] shown by IR and NMR spectroscopy to have both free and coordinated olefinic groups consistent with structure II (L = CO). A similar pyridine derivative [Rh(tba)(py)Cl] (**8**) is formed on treatment of the orange solution with pyridine at room temperature, while addition of NaBPh$_4$ to this solution affords [Rh(tba)(CO)]BPh$_4$ (**9**), which has all three olefinic ligands coordinated to the rhodium atom (structure III; L = CO). We have been unable to isolate a pure complex from the orange solution, but an orange solution having the same two metal—carbonyl absorptions in the IR spectrum is produced when carbon monoxide is passed through [Rh(tba)Cl] (**10**) in dichloromethane at 0°C; compound **7** is unaffected under these conditions. This suggests that the orange intermediate may be [Rh(tba)$(CO)_2$]Cl, or possibly [RhCl(tba)$(CO)_2$], although it is difficult to understand why, if it has the last structure, it cannot be obtained by carbonylation of **7**. In separate experiments it has been shown that **7** is non-conducting in dichloromethane or chloroform solution, and this may account for the absence of reaction with CO (vide infra). In methanol solution, however, conductivity measurements indicate that **7** is almost completely dissociated into [Rh(tba)(CO)]Cl, and reacts with pyridine to give **8** and with $NaBPh_4$ to give **9**.

Use of a 4 : 1 molar excess of tba in the reaction with either $[Rh(cod)Cl]_2$ or $[Rh(C_2H_4)_2Cl]_2$ gave the monomer **10** as the major product. This, unlike the dimer **1**, was soluble in most of the common organic solvents, and undergoes metathetical halogen exchange reactions with LiBr and NaI in methanol at room temperature to give [Rh(tba)Br] (**11**) and [Rh(tba)I] (**12**). These compounds show the characteristic IR band at 1640 cm^{-1} for a free olefinic group, and from a ^1H NMR spectroscopic study of a solution of compound **10** in $CDCl_3$ over the temperature range of 32 to —60°C there is clear evidence for both coordinated and free olefin ligands at the lower temperature. Thus, these arsine complexes probably have a square planar structure IV both in the solid state and in solution, rather than the trigonal bipyramid arrangement found for the phosphorus analogue $[RhX\{P(CH_2CH_2CH{=}CH_2)_3\}]$ (X = Cl or Br) [4]. The iodo complex $[RhI\{P(CH_2CH_2CH{=}CH_2)_3\}]$ is reported to exist as an iodo-bridged dimer in the solid state [4] but there was no evidence for similar behaviour with compound **12**. In benzene solution compound **10** reacts with PPh_3 to give the five-coordinate complex **2**, and in dichloromethane or methanol solution it appears to dissociate into [Rh(tba)]Cl or [Rh(tba)S]Cl (where S = CH_2Cl_2 or CH_3OH). A similar dissociation is believed to occur on reaction of [Rh(ttp)Cl] [ttp = $PhP(CH_2CH_2CH_2PPh_2)_2$] with carbon monoxide [8]. Support for such a dissociation comes from the reaction of compound **10** with $NaBPh_4$ in methanol to give [Rh(tba)(η^2-$C_6H_5BPh_3$)] (**13**). This compound, which is insoluble in all common solvents, shows no evidence for a free olefin ligand in the IR spectrum, but has strong bands at 1392 and 1452 cm^{-1} characteristic of the η-bonded phenyl group of a BPh_4 ligand [2,9,10,11]. On this basis compound **13** is assigned the structure V, and appears to be the first example of a compound in which the tetraphenylborate ligand acts as a two-electron, rather than a six-electron, donor ligand.

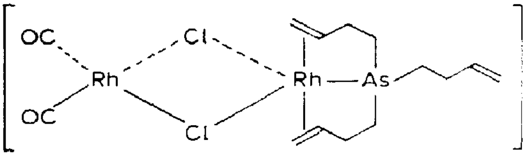


(IV)

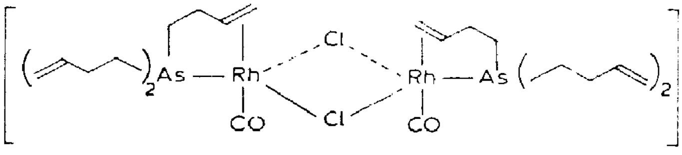


(V)

When tba is caused to react with $[Rh(CO)_2Cl]_2$ (1 : 1 molar ratio) in diethyl ether at room temperature the major product is $[Rh_2(tba)(CO)_2Cl_2]$ (**14**). The IR spectrum of this compound shows two strong metal carbonyl bands at 2090 and 2010 cm^{-1} for *cis*-carbonyl ligands [12,13], a weak band at 1640 cm^{-1} for free olefinic ligand, and strong bands at 286 and 270 cm^{-1} assigned to bridging chlorine ligands. A variable temperature NMR study has confirmed that one of the olefin groups is not bonded to the rhodium atom, and hence, this compound probably has structure VI. The use of a 2 : 1 molar excess of tba in this reaction leads to the formation of an orange oil having three strong metal carbonyl bands in its IR spectrum at 2080, 2028 and 1960 cm^{-1}. This oil, which could not be obtained in a pure state, is converted in boiling diethyl ether into compound 7 as the only product, and is assumed to be a mixture of the *cis*[ν(CO) 2080 and 2028 cm^{-1}] and *trans*[ν(CO) 1960 cm^{-1}] isomers of $[Rh(CO)(tba)Cl]_2$ (structure VII). Related compounds having similar metal carbonyl absorptions have been isolated previously from the reactions of donor ligands with $[Rh(CO)_2Cl]_2$ [10,14,15]. When the ratio of tba to rhodium complex is increased to 4 : 1 at room temperature the monomeric complex 7 is the only product.



(VI)



(VII) and the *trans* isomer

Experimental

IR spectra were recorded both as mulls in Nujol and in solution using a Perkin-Elmer model 621 spectrophotometer, and ^1H NMR spectra were recorded either on a Varian HA 100 instrument or a Perkin-Elmer R32 instrument. Conductivities were measured in nitromethane or 1,2-dichloroethane at 20°C on a Cambridge Instruments Ltd conductivity bridge, and molecular weights were determined on chloroform solutions using the isopiestic method on a Perkin-Elmer model 115 apparatus. The starting materials $[Rh(C_2H_4)_2Cl]_2$ [16], $[Rh(cod)Cl]_2$ [17], $[Rh(CO)_2Cl]_2$ [18], $[RhCl(PPh_3)_3]$ [19], and tba [5], were prepared and purified by standard procedures. Except where stated all reactions were carried out under dry nitrogen, and all solvents were purified, dried, and de-aerated.

Reactions of tri(3-butenyl)arsine

(a) With $[Rh(CO)_2Cl]_2$ in a 1 : 1 molar ratio. When an ethereal solution of tba (0.48 g, 2.0 mmol) was added dropwise with stirring to a solution of the rhodium complex (0.78 g, 2.00 mmol) in the same solvent there was some effervescence and the light yellow colour of the solution deepened. After heating under reflux for 2 h golden-yellow crystals of 14 (0.42 g, 0.73 mmol, 37%) precipitated, and these were filtered, washed with ether, and dried in vacuo.

(b) With $[Rh(CO)_2Cl]_2$ in a 2 : 1 molar ratio. Under similar conditions addi-

tion of tba (0.96 g, 4.0 mmol) to the rhodium complex (0.78 g, 2.0 mmol) gave immediate effervescence and the solution turned deep orange [IR: ν(CO) 2080s, 2028s and 1960m cm^{-1}]. Removal of the solvent gave an intractable orange oil, which on dissolving in fresh diethyl ether and heating at reflux for 2 h gave a precipitate of deep yellow crystals of **7** (1.0 g, 2.46 mmol, 62%) [IR (CH_2Cl_2): ν(CO) 1970s cm^{-1}.] A methanol solution of this compound ionised to [Rh(CO)(tba)]Cl [IR (MeOH): ν(CO) 2004vs cm^{-1}; Λ_M in 10^{-3} *M* methanol = 95 ohm^{-1} cm^2 mol^{-1}].

(c) With [Rh(cod)Cl]$_2$ in a 2 : 1 molar ratio. When a solution of tba (0.48 g, 2.0 mmol) in benzene (5 cm^3) was added dropwise to a stirred solution of [Rh(cod)Cl]$_2$ (0.49 g, 1.0 mmol) in refluxing benzene (20 cm^3) the colour changed from pale yellow to orange, and after 5 h at this temperature a deep orange solid had precipitated. This was washed in hot benzene, and dried in vacuo to give green-brown crystals of **1** (0.25 g, 0.33 mmol, 33%).

(d) With [Rh(cod)Cl]$_2$ in a 4 : 1 molar ratio. Using a similar procedure reaction between tba (0.96 g, 4.0 mmol) and the rhodium complex (0.49 g, 1.0 mmol) in benzene over 1.5 h gave an orange oil, which was recrystallised from a mixture of benzene and cyclohexane to give **10** (0.48 g, 1.27 mmol, 64%) as orange crystals.

(e) With [Rh(C_2H_4)$_2$Cl]$_2$ in a 2 : 1 molar ratio. Reaction between tba (2.40 g, 10.0 mmol) and [Rh(C_2H_4)$_2$Cl]$_2$ (1.96 g, 5.0 mmol) at the reflux temperature of benzene over 12 h gave **1** (3.70 g, 4.90 mmol, 97%).

(f) With [RhCl(PPh$_3$)$_3$]. Addition of tba (0.96 g, 4.0 mmol) in benzene (5 cm^3) to a rapidly stirred solution of [RhCl(PPh$_3$)$_3$] (1.85 g, 2.0 mmol) in the same solvent at room temperature caused a colour change from deep red to yellow, and after 2 h yellow crystals of **2** (1.10 g, 1.72 mmol, 86%) precipitated. These were washed with diethyl ether, recrystallised from benzene, and dried in vacuo.

Reactions of [Rh(tba)Cl]$_2$

(a) With triphenylphosphine. Dropwise addition of a solution of triphenylphosphine (0.52 g, 2.0 mmol) in benzene to a rapidly stirred suspension of the rhodium complex (0.7 g, 1.0 mmol) in the same solvent gave a yellow solution over 30 min. The excess of rhodium starting material was removed by filtration and the filtrate was kept at $<0°$C for 12 h whereupon compound **2** (1.05 g, 1.6 mmol, 81%) precipitated.

(b) With diphenylmethylphosphine. Following a similar procedure, reaction between diphenylmethylphosphine (0.40 g, 2.0 mmol) and the rhodium complex (0.76 g, 1.0 mmol) gave orange crystals of **3** (0.81 g, 1.4 mmol, 70%) which were recrystallised from benzene.

(c) With tri-n-butylphosphine. Reaction between tri-n-butylphosphine (0.40 g, 2.0 mmol) and the rhodium complex (0.76 g, 1.0 mmol) in benzene gave **4** (0.72 g, 1.27 mmol, 64%) as an orange solid recrystallised from benzene.

(d) With bis(diphenylphosphino)butane (bdpb). Under similar conditions bis(diphenylphosphino)butane (0.86 g, 2.0 mmol) and the rhodium complex (0.76 g, 1.0 mmol) in benzene after 12 h at $<0°$C gave **5** (1.0 g, 1.24 mmol, 62%) as a yellow solid recrystallised from benzene.

(e) Reaction with carbon monoxide. Passage of a steady stream of carbon

monoxide for 30 min through a stirred suspension of the rhodium complex (0.76 g, 1.0 mmol) at 0°C gave a light orange solution which showed strong IR bands at 2068 and 1990 cm^{-1} in the metal carbonyl region, and a weak band at 1640 cm^{-1} [ν(C=C)]. Filtration of this solution to remove unchanged rhodium starting material followed by bubbling of carbon monoxide through the filtrate for a further 2 h gave a yellow solution [ν(CO) 1964vs cm^{-1}], which on concentration gave [Rh(tba)(CO)Cl] (0.10 g, 0.25 mmol, 25%).

Reactions of [Rh(tba)(CO)Cl]

(a) With pyridine. To a rapidly stirred solution of the rhodium carbonyl complex prepared as in (e) above, was added pyridine (0.16 g, 2.0 mmol), which caused immediate evolution of carbon monoxide. Concentration of the solution gave orange crystals of **8** (0.36 g, 0.80 mmol, 80%) which were washed with diethyl ether and dried in vacuo.

(b) With sodium tetraphenylborate. When a methanolic solution of sodium tetraphenylborate (0.68 g, 2.0 mmol) was added dropwise to a rapidly stirred solution of the carbonyl complex (0.41 g, 1.0 mmol) there was almost immediate formation of **9** (0.60 g, 0.87 mmol, 87%) as a white precipitate [IR (Me_2CO): ν(CO) 2010vs cm^{-1}], which was recrystallised from a mixture of methanol and dichloromethane.

Reactions of [Rh(tba)Cl]

(a) With lithium bromide. Dropwise addition of a solution of lithium bromide (0.24 g, 2.75 mmol) in the minimum amount of methanol to a stirred solution of [Rh(tba)Cl] (0.19 g, 0.5 mmol) in the same solvent at room temperature gave a yellow-orange precipitate of **11** (0.15 g, 0.4 mmol, 80%), which was recrystallised from a mixture of dichloromethane and methanol.

(b) With sodium iodide. Under similar conditions, reaction between sodium iodide (0.27 g, 1.98 mmol) and [Rh(tba)Cl] (0.19 g, 0.50 mmol) gave an orange precipitate of **12** (0.14 g, 0.30 mmol, 60%). The methanol of crystallisation could be removed by recrystallisation from benzene.

(c) With triphenylphosphine. Triphenylphosphine (0.26 g, 1.0 mmol) in a minimum amount of benzene was added dropwise to a stirred solution of [Rh(tba)Cl] (0.38 g, 1.0 mmol) in benzene (5 cm^3) at room temperature to precipitate yellow crystals of **2** (0.40 g, 0.62 mmol, 62%).

(d) With carbon monoxide. Passage of carbon monoxide through a solution of [Rh(tba)Cl] (0.19 g, 0.5 mmol) in dichloromethane (15 cm^3) at 0°C for 30 min gave a light orange solution having IR bands at 2068s and 1990s [ν(CO)], and 1640w cm^{-1} [ν(C=C)]. After passing carbon monoxide through the solution for a further 2 h at room temperature the colour changed to pale yellow, and evaporation of the solvent gave **1** (1.50 g, 0.40 mmol, 80%). No further reaction with CO occurred on extending the reaction time to 4 h.

(e) With sodium tetraphenylborate. A white precipitate of **13** (0.32 g, 0.48 mmol, 24%) was formed when a solution of sodium tetraphenylborate (0.68 g, 2.0 mmol) in methanol (5 cm^3) was added to a solution of [Rh(tba)Cl] (0.76 g, 2.0 mmol) in methanol at 0°C.

Reactions of [Rh(tba)(PPh$_3$)Cl] with sodium tetraphenylborate

Dropwise addition of a methanolic solution of sodium tetraphenylborate (0.68 g, 2.0 mmol) to a rapidly stirred solution of [Rh(tba)(PPh$_3$)Cl] (0.64 g, 1.0 mmol) in methanol gave an orange precipitate of **6** (0.40 g, 0.43 mmol, 43%) [Λ_M in 10^{-3} *M* acetone = 130 ohm^{-1} cm^2 mol^{-1}] which was washed with dichloromethane and methanol.

Acknowledgement

Thanks are due to the S.E.R.C. for a maintenance grant to one of us (G.L.S.).

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