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## THE SYNTHESIS AND SOME REACTIONS OF RHODIUM(I) COMPLEXES OF BIS(3-DIMETHYLARSINOPROPYL)PHENYLARSINE AND 1,2-BIS(METHYLPHENYLARSINO)ETHANE

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### Summary

The tridentate ligand  $\text{PhAs}(\text{CH}_2\text{CH}_2\text{CH}_2\text{AsMe}_2)_2$  (tasp) reacts with  $[\text{RhCl}(\text{PPh}_3)_3]$ ,  $[\text{Rh}(\text{cod})\text{Cl}]_2$  (cod = 1,5-cyclooctadiene), or  $[\text{Rh}(\text{C}_2\text{H}_4)_2\text{Cl}]_2$  to give the square-planar complex  $[\text{RhCl}(\text{tasp})]$ . Under similar conditions the bidentate ligand,  $\text{PhMeAsCH}_2\text{CH}_2\text{AsMePh}$  (dase) affords the five coordinate compound  $[\text{RhCl}(\text{dase})_2]$  on reaction with  $[\text{RhCl}(\text{PPh}_3)_3]$ . In solution  $[\text{RhCl}(\text{tasp})]$  forms the stable adducts  $[\text{RhCl}(\text{O}_2)(\text{tasp})]$  and  $[\text{RhCl}(\text{SO}_2)(\text{tasp})]$  with  $\text{O}_2$  and  $\text{SO}_2$  respectively, and reacts with CO to give  $[\text{RhCl}(\text{CO})(\text{tasp})]$  which partially dissociates to  $[\text{Rh}(\text{CO})(\text{tasp})]\text{Cl}$  in methanol forming  $[\text{Rh}(\text{CO})(\text{tasp})]\text{BPh}_4$  on reaction with  $\text{NaBPh}_4$ . The oxygen adduct reacts with  $\text{SO}_2$  to give the sulphato complex  $[\text{RhCl}(\text{SO}_4)(\text{tasp})]$ , and with CO to produce the carbonato complex  $[\text{RhCl}(\text{CO}_3)(\text{tasp})]$ . Both  $[\text{RhCl}(\text{tasp})]$  and  $[\text{RhCl}(\text{dase})_2]$  react with the esters  $\text{MeO}_3\text{SF}$  and  $\text{RO}_3\text{SCF}_3$  to give the compounds  $[\text{RhClR}(\text{tasp})]\text{X}$  (R = Me, X =  $\text{O}_3\text{SF}$ ; R = Me, Et, X =  $\text{O}_3\text{SCF}_3$ ) and  $[\text{RhClMe}(\text{dase})]\text{O}_3\text{SCF}_3$ , which are readily converted to the corresponding tetraphenylborate derivatives.

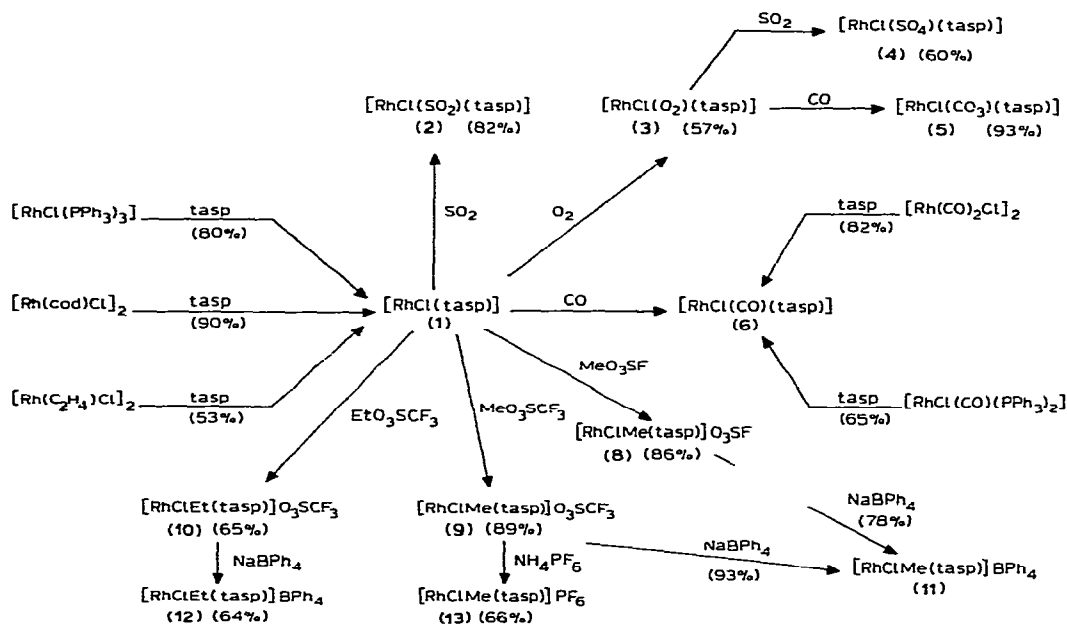
### Introduction

There has been a considerable interest in the synthesis, characterisation, and reactions of complexes of rhodium(I) with multidentate phosphine ligands [1]. Several of these compounds have been shown to form adducts with small molecules such as  $\text{H}_2$ ,  $\text{O}_2$ , CO,  $\text{CO}_2$ , and  $\text{SO}_2$  [1–3]. The chemistry of rhodium(I) complexes containing multidentate arsine ligands have not been explored in any detail. This present paper reports the synthesis of rhodium(I) complexes of the tridentate arsine ligand,  $\text{PhAs}(\text{CH}_2\text{CH}_2\text{CH}_2\text{AsMe}_2)_2$  (tasp), and the bidentate arsine ligand  $\text{PhMeAsCH}_2\text{CH}_2\text{AsMePh}$  (dase), and their reaction with CO,  $\text{O}_2$ ,  $\text{SO}_2$  and alkylating reagents.

## Results and discussion

Provided air is rigorously excluded the rhodium(I) complexes  $[\text{RhCl}(\text{PPh}_3)_3]$ ,  $[\text{Rh}(\text{cod})\text{Cl}]_2$ , and  $[\text{Rh}(\text{C}_2\text{H}_4)_2\text{Cl}]_2$  react readily with an excess of *tasp* in boiling benzene to give good yields of  $[\text{RhCl}(\text{tasp})]$  (1) (Scheme 1). This com-

SCHEME 1



plex is monomeric in solution, and all four methyl groups of the *tasp* ligand appear as a broad signal in the  $^1\text{H}$  NMR spectrum at  $\delta$  1.70 ppm indicative of coordination of the arsenic atoms to rhodium; the methyl groups of the free ligand have a chemical shift of  $\delta$  0.86 ppm. This is consistent with a four-coordinate, square planar structure. As found for the related phosphorus compound  $[\text{RhCl}\{\text{PhP}(\text{CH}_2\text{CH}_2\text{CH}_2\text{PPh}_2)_2\}]$  [2] complex 1 is quite a powerful Lewis base and forms a bright yellow adduct  $[\text{RhCl}(\text{SO}_2)_2(\text{tasp})]$  (2) with sulphur dioxide. This has characteristic IR bands at 1150 ( $\nu_{\text{asym}}(\text{S}-\text{O})$ ) and 1031 ( $\nu_{\text{sym}}(\text{S}-\text{O})$ )  $\text{cm}^{-1}$  for an S-bonded "bent"  $\text{SO}_2$  ligand [2,4] and is presumed to have a square pyramidal structure with the  $\text{SO}_2$  ligand in the apical position as suggested for related rhodium(I) and iridium(I) adducts [2–6]. The  $\text{SO}_2$  group in this complex was not labile and did not react with oxygen at room temperature. A solution of compound 1 in dichloromethane combines rapidly with dioxygen in the air to form the stable adduct  $[\text{RhCl}(\text{O}_2)(\text{tasp})]$  (3); in the solid state 1 remains unchanged in air over several weeks. The best yields of 3 are obtained when dry dioxygen is bubbled through a solution of 1 in dichloromethane. The isolated crystals invariably contain between 0.5 and 1.0 mol of dichloromethane of crystallisation which can not be removed by warming under vacuum. A similar problem has been reported previously for  $[\text{RhCl}(\text{O}_2)(\text{PPh}_3)_3]$  [7,8] and has been shown to be caused by strong hydrogen bonding between

the oxygen ligand and a hydrogen atom of dichloromethane. No dissociation of oxygen from compound **3** occurs up to 80°C at 0.1 mmHg from the solid adduct. The IR spectrum is virtually identical to that of compound **1**, but with an additional band of medium intensity at 852 cm<sup>-1</sup> assigned to the RhO<sub>2</sub> mode [9]. When sulphur dioxide is bubbled through a solution of **3** in dichloromethane at 0°C it forms the yellow sulphato complex [RhCl(SO<sub>4</sub>)(tasp)] (**4**). This exhibits IR bands at 1255, 1140 and 640 cm<sup>-1</sup> characteristic of the bidentate sulphate group, [10,11] while the band at 852 cm<sup>-1</sup> is absent. A related oxidation occurs when carbon monoxide is bubbled through a solution of **3** at room temperature giving a product which is thought to be [RhCl(CO<sub>3</sub>)(tasp)] (**5**). The solid state IR spectrum of this compound exhibits strong ν(C=O) bands at 1650 and 1620 cm<sup>-1</sup> indicative of bidentate coordination of the carbonate ligand [2,12]; the possibility that this may be an η<sup>2</sup>-bonded carbon dioxide complex [13] cannot be entirely excluded on the available spectroscopic and analytical evidence, but it is considered less likely.

When carbon monoxide is bubbled through a solution of **1** in dichloromethane at room temperature [RhCl(CO)(tasp)] (**6**) is obtained as an orange solid. The same compound has also been synthesised from [Rh(CO)<sub>2</sub>Cl]<sub>2</sub> and [RhCl(CO)(PPh<sub>3</sub>)<sub>2</sub>] by reaction with *tasp* in boiling dichloromethane. This compound is monomeric and non-ionic in dichloromethane solution, and a carbonyl stretching vibration of 1925 cm<sup>-1</sup> in the IR spectrum of a dichloromethane solution supports a non-ionic structure. The four methyl groups of the *tasp* ligand which appear as a broad singlet at δ 1.70 ppm in the <sup>1</sup>H NMR spectrum indicate a five-coordinate complex presumably having a trigonal bipyramid structure. In methanol the IR spectrum shows a metal carbonyl stretching vibration of medium intensity at 1980 cm<sup>-1</sup> in addition to the band at 1925 cm<sup>-1</sup> indicating partial dissociation to [Rh(CO)(tasp)]Cl. Addition of NaBPh<sub>4</sub> to a methanolic solution of **6** at room temperature affords a white precipitate of [Rh(CO)(tasp)]BPh<sub>4</sub> (**7**). This probably has a square-planar structure as proposed for the analogous iridium complex [14].

The nucleophilic properties of compound **1** are illustrated by the reactions with the esters MeO<sub>3</sub>SF and RO<sub>3</sub>SCF<sub>3</sub> to give the complexes [RhClR(tasp)]X (**8**, R = Me, X = O<sub>3</sub>SF; **9**, R = Me, X = O<sub>3</sub>SCF<sub>3</sub>; **10**, R = Et, X = O<sub>3</sub>SCF<sub>3</sub>) isolated as yellow-orange solids. The observed order of reactivity MeO<sub>3</sub>SF > MeO<sub>3</sub>SF<sub>3</sub> > EtO<sub>3</sub>SCF<sub>3</sub> is consistent with an S<sub>N</sub>2-type mechanism at room temperature in dichloromethane solution, but this is purely speculative in the absence of a proper kinetic and stereochemical analysis. The compounds **8–10** are insoluble in non-polar and chlorinated solvents as anticipated for ionic compounds. Their IR spectra (Nujol mulls) showed no evidence of bands attributable to covalently bound O<sub>3</sub>SF (1350–1398s, 1130–1170s, 1070–1090s) [15,16] or O<sub>3</sub>SCF<sub>3</sub> (1340s and 1220s cm<sup>-1</sup>) [17] ligands, but bands at 1280s and 1065 ± 5s cm<sup>-1</sup> (FSO<sub>3</sub><sup>-</sup>) [15,17] and 1280vs, 1260s, 1160s, 1030s and 640 cm<sup>-1</sup> (CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>) [17,18] were prominent. Molar conductivity measurements in acetone clearly indicate an ionic structure, and treatment of methanolic solutions of these compounds with NaBPh<sub>4</sub> afford [RhClR(tasp)]BPh<sub>4</sub> (**11**, R = Me; **12**, R = Et), and with NH<sub>4</sub>PF<sub>6</sub> compound **9** gives [RhClMe(tasp)]PF<sub>6</sub> (**13**). Accurate analyses could not be obtained for the compounds **8–10** and compound **13** as the presence of fluorine, a polyarsine ligand, sulphur and rhodium in these complexes causes the

carbon and hydrogen figures to be lower than expected; similar difficulties have been experienced by other workers [2,12]. It is probable that these ionic complexes have a square pyramidal structure with the alkyl ligand in the apical position as confirmed for the compound  $[\text{RhClMe}\{\text{PhP}(\text{CH}_2\text{CH}_2\text{CH}_2\text{PPh}_2)_2\}]\text{-O}_3\text{SF}$  [19].

The bidentate ligand *dase* reacts with  $[\text{RhCl}(\text{PPh}_3)_3]$  in boiling benzene to give  $[\text{Rh}(\text{dase})_2\text{Cl}]$  (14), which is monomeric and non-ionic in dichloromethane. The  $^1\text{H}$  NMR spectrum showed no evidence for a non-coordinated *AsMePh* ligand at  $\delta$  1.10 ppm indicating a five-coordinate structure. As each coordinated arsenic atom is chiral the spectrum was complex and both the methyl and methylene protons of the *dase* ligands appeared as a non-resolvable multiplet between  $\delta$  1.60–2.00 ppm. Like the *tasp* derivative 1, compound 14 reacts rapidly with  $\text{MeO}_3\text{SF}$  in dichloromethane solution to give  $[\text{RhClMe}(\text{dase})_2]\text{-O}_3\text{SF}_3$  (15), which formed the derivative  $[\text{RhClMe}(\text{dase})_2]\text{BPh}_4$  on reaction with  $\text{NaBPh}_4$  in methanol. The IR spectra of these compounds are consistent with an ionic structure both in the solid state and in solution. A complex multiplet between  $\delta$  1.60–2.00 ppm in the  $^1\text{H}$  NMR spectra ( $\text{DMSO}-d_6$ ) indicates that all four arsenic atoms are coordinated to the rhodium atom.

These rhodium(I) complexes of tridentate and bidentate arsine ligands have been shown to activate a number of small molecules. Unfortunately, none of the complexes isolated in this work show any activity as catalysts for the hydrogenation of cyclohexene and diethyl maleate at ambient temperatures and atmospheric pressure.

## Experimental

The ligands *tasp* [20] and *dase* [21] were prepared by reported procedures. IR spectra were recorded as mulls in Nujol on a Perkin–Elmer model 621 spectrophotometer, and NMR spectra were recorded on a Perkin–Elmer R32 instrument at 90 MHz ( $^1\text{H}$ ) and 56.54 MHz ( $^{19}\text{F}$ ); the  $^{19}\text{F}$  chemical shifts are relative to trifluoroacetic acid external reference and negative value are to low field of the reference. Conductivities were measured on a Cambridge Instruments Ltd. conductivity bridge. All reactions, except where stated, were carried out under dry, de-oxygenated nitrogen.

The analytical and physical data of compounds 1–16 are gathered together in Table 1.

### Reactions of bis(3-dimethylarsinopropyl)phenylarsine (*tasp*)

(a) *With*  $[\text{RhCl}(\text{PPh}_3)_3]$ . A solution of *tasp* (1.78 g, 4.0 mmol) in benzene (10  $\text{cm}^3$ ) was added dropwise to a refluxing solution of the rhodium complex (2.80 g, 3.0 mmol) in benzene (20  $\text{cm}^3$ ), and after 2 h the red solution had turned deep orange. Concentration of the solution to 5  $\text{cm}^3$  gave an orange oil, which was taken up in fresh benzene and cyclohexane was added. Over 12 h at 0°C orange-yellow crystals of 1 (1.40 g, 2.39 mmol, 80%) precipitated from solution and were recrystallised from dichloromethane.

(b) *With*  $[\text{Rh}(\text{cod})\text{Cl}]_2$ . Using a similar procedure, reaction between *tasp* (1.0 g, 2.24 mmol) and  $[\text{Rh}(\text{cod})\text{Cl}]_2$  (0.49 g, 1.0 mmol) in dichloromethane gave 1 (0.80, 1.79 mmol, 90%).

TABLE 1

ANALYTICAL, MELTING POINT, AND MOLECULAR WEIGHT DATA FOR THE RHODIUM COMPLEXES

Compound	M.p. <sup>a</sup> (°C)	Analysis (Found (calcd.) (%))			
		C	H	Cl	M
[RhCl(tasp)] (1)	94–95	33.1 (32.9)	5.0 (5.0)	6.2 (6.1) <sup>b</sup>	525 (585)
[RhCl(SO <sub>2</sub> )(tasp)] (2)	100–110	30.6 (29.6)	4.6 (4.5)	5.3 (5.5) <sup>c</sup>	
[RhCl(O <sub>2</sub> )(tasp)]0.5 CH <sub>2</sub> Cl <sub>2</sub> (3)	200	29.8 (30.1)	4.5 (4.6)	11.0 (10.8)	
[RhCl(tasp)(SO <sub>4</sub> )] (4)	>250	29.6 (28.2)	4.2 (4.3)	5.0 (5.2) <sup>d</sup>	
[RhCl(tasp)(CO <sub>3</sub> )] (5)	>250	32.0 (31.7)	4.4 (4.5)	5.9 (5.5)	
[RhCl(CO)(tasp)] (6)	110	33.4 (33.3)	4.4 (4.8)	5.9 (5.8)	590 (613)
[Rh(CO)(tasp)]BPh <sub>4</sub> (7)	165	55.0 (54.9)	5.2 (5.5)		
[RhClMe(tasp)]O <sub>3</sub> SF (8)	95	30.0 (29.2)	4.3 (4.6)	5.0 (5.1)	
[RhClMe(tasp)]O <sub>3</sub> SCF <sub>3</sub> (9)	180	27.6 (28.9)	4.1 (4.3)	4.5 (4.7)	
[RhClEt(tasp)]O <sub>3</sub> SCF <sub>3</sub> (10)	160	28.9 (29.9)	4.1 (4.5)	4.6 (4.7)	
[RhClMe(tasp)]BPh <sub>4</sub> (11)	168–170	53.5 (53.6)	5.7 (5.7)	3.9 (3.9)	
[RhClEt(tasp)]BPh <sub>4</sub> (12)	130–132	54.1 (54.1)	5.9 (5.8)	3.8 (3.8)	
[RhClMe(tasp)]PF <sub>6</sub> (13)	180–182	25.9 (27.4)	4.2 (4.3)	5.0 (4.8)	
[Rh(dase) <sub>2</sub> Cl] (14)	78–80	44.1 (44.6)	4.9 (4.7)	4.3 (4.1) <sup>e</sup>	765 (863)
[RhClMe(dase) <sub>2</sub> ]O <sub>3</sub> SCF <sub>3</sub> (15)	172	39.0 (39.8)	4.0 (4.2)	3.7 (3.5)	
[RhClMe(dase) <sub>2</sub> ]BPh <sub>4</sub> (16)	115–119	57.2 (57.2)	5.4 (5.3)	3.0 (2.9)	

<sup>a</sup> With decomposition. <sup>b</sup> Rh, 17.3 (17.6). <sup>c</sup> S, 4.5 (4.9). <sup>d</sup> S, 5.0 (4.7). <sup>e</sup> Rh, 11.6 (11.9).

(c) With  $[Rh(C_2H_4)_2Cl]_2$ . Under similar conditions *tasp* (0.50 g, 1.12 mmol) reacted with  $[Rh(C_2H_4)_2Cl]_2$  (0.19 g, 0.5 mmol) in dichloromethane to give **1** (0.31 g, 0.53 mmol, 53%).

(d) With  $[RhCl(CO)(PPh_3)_2]$ . Addition of a dichloromethane solution of *tasp* (0.50 g, 1.10 mmol) to a solution of the rhodium complex (0.69 g, 1.0 mmol) in the same solvent followed by heating under gentle reflux with stirring for 30 min gave an orange solution. When the solvent was evaporated slowly orange crystals of **6** (0.40 g, 0.65 mmol, 65%) (IR (CH<sub>2</sub>Cl<sub>2</sub>)  $\nu$ (CO) 1925 vs cm<sup>-1</sup>), precipitated, and were washed in n-hexane and dried in vacuo.

(e) With  $[Rh(CO)_2Cl]_2$ . Using a similar procedure reaction between *tasp* (1.0 g, 2.2 mmol) and  $[Rh(CO)_2Cl]_2$  (0.39 g, 1.0 mmol) in dichloromethane gave **6** (1.0 g, 1.63 mmol, 82%).

Reactions of  $[RhCl(tasp)]$ . (a) With dioxygen. When a solution of the rhodium complex (1.20 g, 2.0 mmol) in dichloromethane (10 cm<sup>3</sup>) was stirred

under an atmosphere of dioxygen for 2–3 h at room temperature yellow crystals of **3** (0.75 g, 1.13 mmol, 57%) precipitated and were recrystallised from dichloromethane.

(b) *With sulphur dioxide.* A slow stream of sulphur dioxide was passed for 2–3 h through a benzene solution of [RhCl(tasp)] (0.20 g, 0.34 mmol) at room temperature to give a bright yellow solution. The solution was concentrated and kept at 0°C for 12 h to give bright yellow microcrystals of **2** (0.18 g, 0.28 mmol, 82%), which were washed with diethyl ether and dried in vacuo.

(c) *With carbon monoxide.* A steady stream of carbon monoxide was passed for 30 min through a solution of [RhCl(tasp)] (0.30 g, 0.5 mmol) in dichloromethane to give an orange solution. Concentration of the solution gave orange crystals of **6** (0.20 g, 0.33 mmol, 65%) ( $\Lambda_M$  in  $10^{-3}$  M dichloromethane  $< 2$  ohm $^{-1}$  cm $^2$  mol $^{-1}$ ).

(d) *With methyl fluorosulphonate.* A solution of methyl fluorosulphonate (0.13 g, 1.1 mmol) in dichloromethane (5 cm $^3$ ) was added dropwise to the rhodium complex (0.59 g, 1.0 mmol) in dichloromethane (10 cm $^3$ ) at room temperature and gave an insoluble orange oil, which on titration with fresh dichloromethane gave a solid. On recrystallisation from ethanol this gave orange crystals of **8** (0.60 g, 0.86 mmol, 86%) ( $\Lambda_M$  in  $10^{-3}$  M acetone 124 ohm $^{-1}$  cm $^2$  mol $^{-1}$ ).

When this compound (0.10 g, 0.14 mmol) in methanol was treated with a methanolic solution of sodium tetraphenylborate (0.2 g, 0.59 mmol) in methanol at room temperature it gave **11** (0.12 g, 0.13 mmol, 93%) as a cream solid, ( $\Lambda_M$  in  $10^{-3}$  M acetone 120 ohm $^{-1}$  cm $^2$  mol $^{-1}$ ) which was recrystallised from a mixture of methanol and dichloromethane.

(e) *With methyl trifluoromethanesulphonate.* Dropwise addition of methyl trifluoromethanesulphonate (0.36 g, 2.2 mmol) in dichloromethane to a stirred solution of the rhodium complex (1.17 g, 2.0 mmol) followed by heating under gentle reflux for 2 h gave a yellow oil. This was titrated with fresh dichloromethane and recrystallised from ethanol to give yellow crystals of **9** (1.33 g, 1.78 mmol, 89%) ( $\Lambda_M$  in  $10^{-3}$  M acetone 120 ohm $^{-1}$  cm $^2$  mol $^{-1}$ ).

A methanolic solution of this compound (0.75 g, 1.0 mmol) treated with sodium tetraphenylborate (0.40 g, 1.17 mmol) in methanol gave **11** (0.72 g, 0.78 mmol, 78%).

Addition of a methanolic solution of ammonium hexafluorophosphate (0.10 g, 0.61 mmol) to [RhClMe(tasp)]O $_3$ SCF $_3$  (0.30 g, 0.4 mmol) in methanol and stirring the mixture for 3 h at room temperature gave **13** (0.15 g, 0.2 mmol, 66%) as a cream solid ( $\Lambda_M$  in  $10^{-3}$  M acetone 110 ohm $^{-1}$  cm $^2$  mol $^{-1}$ ) which was washed with dichloromethane and diethyl ether before drying in vacuo.

(f) *With ethyl trifluoromethanesulphonate.* A mixture of ethyl trifluoromethanesulphonate (0.40 g, 2.25 mmol) and [RhCl(tasp)] (1.17 g, 2.0 mmol) in dichloromethane was heated under reflux for 24 h to give a yellow oil. This was titrated with dichloromethane and recrystallised from ethanol to give yellow crystals of **10** (1.30 g, 1.70 mmol, 65%) ( $\Lambda_M$  in  $10^{-3}$  M acetone 101 ohm $^{-1}$  cm $^2$  mol $^{-1}$ ).

Treatment of this ionic rhodium complex (0.76 g, 1.0 mmol) in methanol (20 cm $^3$ ) with a methanolic solution of sodium tetraphenylborate (0.40 g, 1.17

mmol) gave a cream precipitate of 12 (0.60 g, 0.64 mmol, 64%) ( $\Lambda_M$  in  $10^{-3} M$  acetone  $115 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ ), which was recrystallised from a mixture of methanol and dichloromethane.

*Reactions of [RhCl(O<sub>2</sub>)(tasp)].* (a) *With carbon monoxide.* When a solution of the rhodium complex (0.62 g, 1.0 mmol) in dichloromethane was stirred under an atmosphere of oxygen for 2 h at room temperature 5 (0.60 g, 0.93 mmol, 93%) precipitated as yellow-orange crystals, which were recrystallised from dichloromethane.

(b) *With sulphur dioxide.* A steady stream of sulphur dioxide was passed for 2 h through a dichloromethane solution of [RhCl(O<sub>2</sub>)(tasp)] (0.30 g, 0.49 mmol) at 0°C to give a yellow oil which was recrystallised from benzene as yellow crystals of 4 (0.20 g, 0.29 mmol, 60%).

*Preparation of [RhCl(dase)<sub>2</sub>].* Addition of a benzene solution of dase (1.0 g, 3.0 mmol) to a stirred solution of [RhCl(PPh<sub>3</sub>)<sub>3</sub>] (0.93 g, 1.0 mmol) in refluxing benzene (20 cm<sup>3</sup>) gave, after 2 h, a deep orange solution. Concentration of this solution gave an orange-yellow oil, which was taken up in fresh benzene and cyclohexane was added before leaving the solution to stand for 12 h at 0°C, whereupon yellow-orange 14 (0.57 g, 0.66 mmol, 66%) ( $\Lambda_M$  in  $10^{-3} M$  dichloromethane  $2 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ ) precipitated and was recrystallised from dichloromethane.

#### *Reaction of [RhCl(dase)<sub>2</sub>] with methyl trifluoromethanesulphonate*

A solution of methyl trifluoromethanesulphonate (0.18 g, 1.10 mmol) and the rhodium complex (0.86 g, 1.0 mmol) in dichloromethane was heated under gentle reflux for 2 h to give a yellow oil. This was titrated with fresh dichloromethane and recrystallised from ethanol to give yellow crystals of 15 (0.60 g, 0.58 mmol, 58%) ( $\Lambda_M$  in  $10^{-3} M$  acetone  $135 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ ).

A solution of this complex (0.20 g, 0.19 mmol) in methanol (10 cm<sup>3</sup>) when treated with a solution of sodium tetraphenylborate (0.10 g, 0.29 mmol) in methanol (5 cm<sup>3</sup>) at room temperature gave 16 (0.15 g, 0.13 mmol, 68%) as a cream powder ( $\Lambda_M$  in  $10^{-3} M$  acetone  $110 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ ) which could be recrystallised from a mixture of methanol and dichloromethane.

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