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## CARBONYL COMPLEXES OF RHODIUM(I) AND RHODIUM(III) WITH 2,2'-BIQUINOLINE

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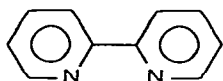
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### Summary

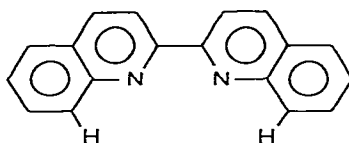
Novel carbonyl complexes of rhodium(I) and rhodium(III) containing the bidentate nitrogen donor ligand 2,2'-biquinoline (biq) have been prepared; they are of the types  $\text{RhX}(\text{CO})_2 \text{biq}$  and  $\text{RhX}(\text{CO})\text{biq}$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ). Cationic carbonyl and substituted carbonyl complexes of the types  $[\text{Rh}(\text{CO})_2\text{biq}]\text{ClO}_4$  and  $[\text{Rh}(\text{CO})\text{biqL}_2]\text{ClO}_4$ , where L is a tertiary phosphine or arsine have also been isolated. In spite of considerable steric crowding around the nitrogen atoms, 2,2'-biquinoline behaves much like 2,2'-bipyridine in forming carbonyl complexes of rhodium.

### Introduction

Cationic complexes of rhodium(I) of the types  $[\text{Rh}(\text{CO})_2(\text{N}-\text{N})]^+$  and  $[\text{Rh}(\text{CO})(\text{N}-\text{N})\text{L}_2]^+$  where  $\text{N}-\text{N} = 2,2'$ -bipyridyl (bipy) or 1,10-phenanthroline (phen) and  $\text{L} =$  tertiary phosphine or arsine, were first synthesised in these laboratories [1,2]. Considerable interest has been shown in these and related complexes [15–17]. 2,2'-Biquinoline (biq) is a bidentate nitrogen donor ligand closely related to bipy, but it has been suggested [3] that the steric crowding caused by the hydrogen atoms in the benzo rings would markedly change the metal chelating properties of biq compared with those of bipy. It was therefore of interest to prepare and study the properties of carbonyl complexes of rhodium containing biq.



(bipy)



(biq)

Except for the isolation of a few complexes of the first transition series and

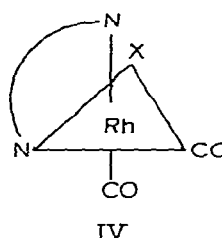
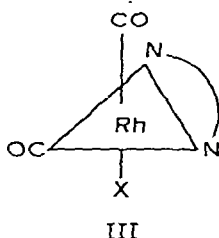
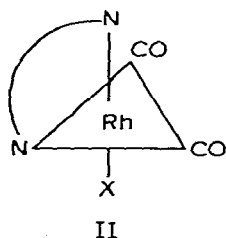
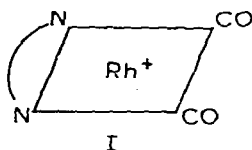
those of the zinc triad [4–10], investigations on the complexing property of biq with transition metals (particularly platinum group metals) has received little attention. Biquinoline has, however, been used for a long time as an analytical reagent in the estimation of copper [4,11]. Ruthenium and osmium complexes of the type  $[M(\text{biq})_3](\text{ClO}_4)_2$  ( $M = \text{Ru}, \text{Os}$ ) have been isolated by Klassen [12]. Tripathi and coworkers [13] have prepared a carbonyl complex of molybdenum containing biq,  $\text{Mo}(\text{CO})_3\text{biq}$ . We recently reported some simple complexes of rhodium of the type  $[\text{Rh}(\text{biq})_2\text{X}_2]\text{X}$  [14], and the syntheses and characterisation of a series of carbonyl complexes of rhodium(I) and rhodium(III) containing biq, are reported below.

## Results and discussion

Rhodium(III) perchlorate reacts with carbon monoxide and biq in a warm alcohol to give orange crystals of the four-coordinate cationic complex  $[\text{Rh}(\text{CO})_2\text{biq}]^+$ . This compound behaves as a 1/1 electrolyte in nitrobenzene and shows two carbonyl stretching bands at 2040 and 2100  $\text{cm}^{-1}$  in the infrared due to the presence of two *cis* carbonyl groups in the cation (configuration I). The reaction of  $\text{RhX}_3 \cdot n\text{H}_2\text{O}$  ( $X = \text{Cl}, \text{Br}$ ) in a hot alcoholic medium with carbon monoxide and biq, in the presence of an excess of  $\text{NaClO}_4$ , does not yield the above cation, and instead the salt  $\text{biq} \cdot \text{ClO}_4$  separates. However, in the absence of  $\text{NaClO}_4$  and when  $X = \text{Cl}$ , the five-coordinate complex  $\text{RhCl}(\text{CO})_2\text{biq}$  is obtained as shining orange-red crystals. The bromo analogue could not be isolated pure by the above method; the yellow crystalline solid which separates from the reaction mixture  $\text{RhBr}_3 \cdot n\text{H}_2\text{O}$ , carbon monoxide and biq shows three  $\nu(\text{CO})$  peaks at 1967, 2000 and 2063  $\text{cm}^{-1}$ , indicating that it may be a mixture of two or more species. Passage of carbon monoxide through an alcoholic solution containing  $\text{RhCl}_3 \cdot n\text{H}_2\text{O}$ , an excess of lithium iodide, and biq gives a dark crystalline solid, which has been identified as the iodorhodium(III) carbonyl,  $\text{RhI}_3(\text{CO})\text{biq}$  ( $\nu(\text{CO})$  2073  $\text{cm}^{-1}$ ). This compound is very sparingly soluble in some common organic solvents, and may be recrystallised by Soxhlet extraction with dichloromethane as solvent. We have, however, been able to isolate both chloro- and bromo-carbonyl complexes of rhodium(I) of the type  $\text{RhX}(\text{CO})_2\text{biq}$  ( $X = \text{Cl}, \text{Br}$ ) starting from the dihalo-bridged diene complex  $[\text{RhX}(\text{COD})]_2$ . The orange-yellow diene complex reacts with biq in refluxing methanol to give dark red crystals of the neutral complex  $\text{RhX}(\text{COD})\text{biq}$ . It is noteworthy that a similar reaction with phen [15,16] gives the ionic compound  $[\text{Rh}(\text{phen})(\text{COD})]\text{Cl}$ . The carbonyl compounds  $\text{RhX}(\text{CO})_2\text{biq}$  ( $X = \text{Cl}, \text{Br}$ ) are easily prepared by bubbling carbon monoxide through an acetone solution of the red diene complex  $\text{RhX}(\text{COD})\text{biq}$ . The carbonyl compounds  $\text{RhX}(\text{CO})_2\text{biq}$  are non-electrolytes in nitrobenzene and show two  $\nu(\text{CO})$  bands between 1967 and 2053  $\text{cm}^{-1}$ . The chloro compound shows a  $\nu(\text{Rh}-\text{Cl})$  band at 305  $\text{cm}^{-1}$ , while the bromo compound shows a  $\nu(\text{Rh}-\text{Br})$  band at 214  $\text{cm}^{-1}$ . Attempts to isolate the iodorhodium(I) carbonyl complex,  $\text{RhI}(\text{CO})_2\text{biq}$ , by the metathetical reaction of  $\text{RhX}(\text{CO})_2\text{biq}$  ( $X = \text{Cl}, \text{Br}$ ) with  $\text{LiI}$  were unsuccessful. The chloro compound  $\text{RhCl}(\text{CO})_2\text{biq}$  reacts readily with silver perchlorate to form the cationic complex  $[\text{Rh}(\text{CO})_2\text{biq}]\text{ClO}_4$ .

The neutral dicarbonyl complexes  $\text{RhX}(\text{CO})_2\text{biq}$  ( $X = \text{Cl}, \text{Br}$ ) must have one

of the three configurations II to IV. Similar dicarbonyl complexes of rhodium(I)



containing bipy and phen of the type  $\text{RhX}(\text{CO})_2(\text{N}-\text{N})$  ( $\text{N}-\text{N}$  = bipy, phen;  $\text{X}$  = Cl, Br, I) have been reported by Mestroni et al. [17] and Gillard and coworkers [16].

The neutral dicarbonyl complexes  $\text{RhX}(\text{CO})_2\text{biq}$  ( $\text{X}$  = Cl, Br) add halogens in alcohol to give the corresponding rhodium(III) complexes  $\text{RhX}_3(\text{CO})\text{biq}$  ( $\text{X}$  = Cl, Br). The orange-yellow products show a single  $\nu(\text{CO})$  peak around  $2100\text{ cm}^{-1}$ . Two configurations V and VI are possible for these compounds. Results of their far infrared spectra are listed in Table 1. Assignments have been made by comparison with those for rhodium(III) complexes containing rhodium-halogen and rhodium-nitrogen bonds [16,18-24]. These results support configuration VI for the new rhodium(III) carbonyl compounds.

Reactions between the rhodium(I) carbonyl compounds and molecular oxygen, nitrogen, and hydrogen were investigated by bubbling these gases through an acetone solution of the complexes,  $\text{RhX}(\text{CO})_2\text{biq}$ . It was found that in all the

TABLE 1  
FAR-INFRARED SPECTRAL DATA FOR CARBONYL COMPLEXES OF RHODIUM(I) AND RHODIUM(III)

Compound	$\nu(\text{Rh}-\text{X})^a$ ( $\text{cm}^{-1}$ )	Other bands
$\text{RhCl}(\text{CO})_2\text{biq}$	305vs	276w, 265m, 199w, 210w, 170m, 138m, 109m
$\text{RhBr}(\text{CO})_2\text{biq}$	214s	420w, 398m, 320w, 240w
$\text{RhCl}_3(\text{CO})\text{biq}$	330vs (Cl trans N) 351vs (Cl trans Cl)	434m, 415s, 310(sh), 157m, 140m
$\text{RhBr}_3(\text{CO})\text{biq}$	246vs (Br trans N) 281s (Br trans Br)	413s, 293s 271(sh), 161m

<sup>a</sup> Far-infrared spectra taken in polyethylene powder: w, weak; s, strong; vs, very strong; m, medium; (sh), shoulder.

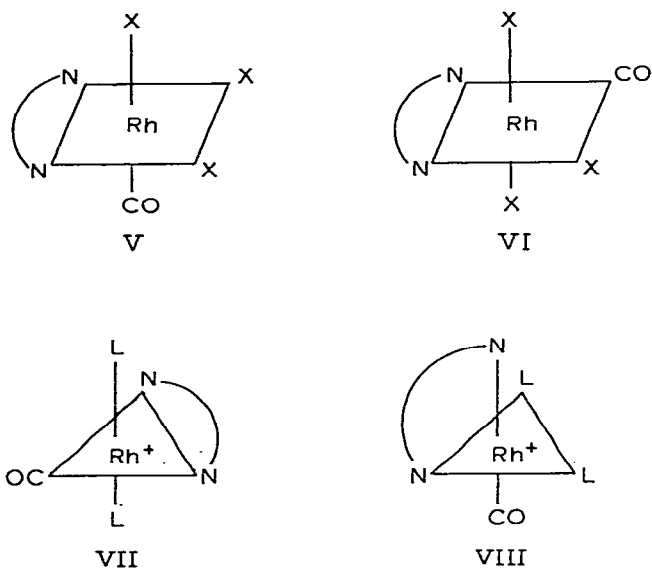
TABLE 2. PHYSICAL PROPERTIES AND ANALYTICAL DATA FOR CARBONYL COMPLEXES OF RHODIUM(I) AND RHODIUM(III)

Compound	Colour	M.p. or dec. (°C)	$\Lambda^a$	$\nu(\text{CO})^b$ ( $\text{cm}^{-1}$ )	Analytical data (Found (calcd.)) (%)			
					C	H	N	
$[\text{Rh}(\text{CO})_2\text{biq}]\text{ClO}_4$	Orange	>190	26.0	2040, 2100	46.7 (46.7)	2.3 (2.4)		5.7 (5.4)
$\text{Biq} \cdot \text{ClO}_4$	Yellow	310-312	28.5	1100 <sup>c</sup>	60.5 (60.5)	3.5 (3.7)		7.8 (7.9)
$\text{Rh}(\text{COD})\text{biqCl}$	Dark red	221	—	—	61.8 (62.1)	4.7 (4.8)		5.6 (5.6)
$\text{Rh}(\text{COD})\text{biqBr}$	Dark brown	216-218	—	—	56.9 (57.1)	4.3 (4.4)		5.2 (5.1)
$\text{RhCl}(\text{CO})_2\text{biq}$	Orange red	>180	—	1967, 2050	53.4 (53.3)	2.5 (2.7)		6.2 (6.2)
$\text{RhBr}(\text{CO})_2\text{biq}$	Brown	>165	—	1980, 2053	48.4 (48.5)	2.5 (2.4)		5.6 (5.7)
$\text{RhCl}_3(\text{CO})\text{biq}$	Yellow	>165	—	2120	47.1 (46.2)	2.5 (2.5)		4.7 (5.2)
$\text{RhBr}_3(\text{CO})\text{biq}$	Orange red	>170	—	2100	36.0 (36.4)	1.9 (2.1)		4.4 (4.5)
$\text{RhI}_3(\text{CO})\text{biq}$	Black	>170	—	2073	29.9 (29.7)	1.6 (1.6)		3.6 (3.6)
$[\text{Rh}(\text{CO})\text{biq}(\text{Ph}_3\text{P})_2]\text{ClO}_4$	Red	200-201	22.4	1940	64.7 (65.3)	4.5 (4.2)		2.7 (2.8)
$[\text{Rh}(\text{CO})\text{biq}(p\text{-tol}_3\text{P})_2]\text{ClO}_4$	Yellow	205-208	26.6	1921	66.1 (66.9)	4.8 (5.0)		2.5 (2.7)
$[\text{Rh}(\text{CO})\text{biq}(\text{Ph}_3\text{Sb})_2]\text{ClO}_4$	Orange red	>250	23.3	1980	55.3 (55.4)	3.6 (3.6)		2.3 (2.4)
$[\text{Rh}(\text{CO})\text{biq}(\text{Ph}_3\text{As})_2]\text{ClO}_4$	Red	233-234	22.5	1936	59.3 (60.1)	4.2 (3.9)		2.1 (2.6)
$[\text{Rh}(\text{CO})\text{biq}(\text{Ph}_2\text{MeAs})_2]\text{ClO}_4$	Rose	234-236	22.9	1920	55.7 (55.4)	4.1 (3.9)		2.8 (2.9)
$[\text{Rh}(\text{CO})\text{biq}(\text{Ph}_2\text{EtAs})_2]\text{ClO}_4$	Orange red	219-221	23.8	1913	56.4 (56.3)	4.2 (4.2)		2.9 (2.8)
$[\text{Rh}(\text{CO})\text{biq}(\text{Ph}_2\text{PrAs})_2]\text{ClO}_4$	Chocolate	223-225	22.5	1937	57.0 (57.1)	4.7 (4.5)		2.8 (2.7)
$[\text{Rh}(\text{CO})\text{biq}(\text{Ph}_2\text{BuAs})_2]\text{ClO}_4$	Grey	205-207	22.4	1933, 1947	57.0 (57.9)	4.7 (4.8)		2.7 (2.7)
$[\text{Rh}(\text{CO})\text{biq}(\text{Cy}_3\text{As})_2]\text{ClO}_4$	Light grey	185-188	21.6	(split) 1914, 1906	58.5 (58.2)	6.8 (6.9)		2.8 (2.5)

<sup>a</sup> Molar conductance ( $\text{ohm}^{-1} \text{cm}^2 \text{mole}^{-1}$ ) in nitrobenzene at ca. 25°C. <sup>b</sup> IR spectra taken in Nujol. <sup>c</sup>  $\nu(\text{ClO}_4^-)$ .

cases, both the carbon monoxide molecules were eliminated as shown by the infrared spectra of the resulting insoluble solids, which appeared to be polymeric in nature. There was, however, no indication for the addition of  $O_2$ ,  $N_2$  or  $H_2$  to the metal.

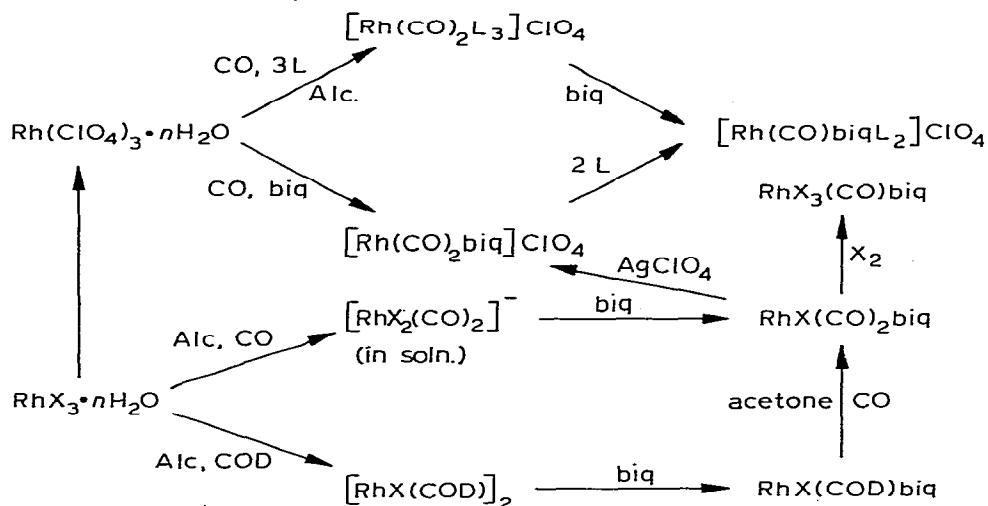
We have also carried out a series of substitution reactions of the cation  $[Rh(CO)_2biq]^+$  with a variety of tertiary phosphines and arsines. The dicarbonyl cation reacts in alcohol with tertiary phosphines and arsines to give five-coordinate cationic complexes of the type  $[Rh(CO)biqL_2]ClO_4$  where  $L = PPh_3, p\text{-tol}_3P, Ph_3Sb, Ph_3As, Ph_2MeAs, Ph_2EtAs, Ph_2PrAs, Ph_2BuAs$  and  $Cy_3As$ . Several of these substituted cations have also been prepared by treatment of the five-coordinate cationic complexes  $[Rh(CO)_2L_3]ClO_4$  ( $L =$  tertiary phosphine or arsine) with  $biq$  in alcohol. The products show a single  $\nu(CO)$  peak around  $1950\text{ cm}^{-1}$  (Table 2) and a  $\nu(ClO_4^-)$  band at  $1100\text{ cm}^{-1}$ , and behave as 1/1 electrolytes in nitrobenzene. The PMR spectrum of the complex containing  $Ph_2MeAs$  shows a single methyl resonance at  $\tau$  8.5 ppm suggesting that the two arsines are *trans* to each other (configuration VII). The corresponding  $Ph_2EtAs$  derivative shows a methyl triplet centred at  $\tau$  8.9 ppm and a methylene quartet centred around  $\tau$  7.97 ppm. Similarly, the  $Ph_2PrAs$  analogue shows a methyl triplet at  $\tau$  9.15 ppm and a complex methylene resonance between  $\tau$  8.0 and 8.8 ppm, favouring the *trans* disposition of the two ligands. Hence it is suggested that the cations have configuration VII, (but configuration VIII cannot be totally ruled out, since the two arsine ligands are in identical environments).



Various reactions involving the carbonyl complexes are shown in Scheme 1.

It is seen that  $biq$  reacts with rhodium halides in more or less the same way as  $bipy$  and  $phen$  in spite of the fact that there is considerable steric crowding around the nitrogen atoms. The  $biq$ -containing compounds are generally less soluble in alcohols than their  $bipy$  or  $phen$  analogues [2]. The comparative ease of isolation of the  $biq$ -containing compounds as solids may be attributed to this lower solubility.

Scheme 1



(L = tertiary phosphine or arsine; X = Cl, Br; Alc = Alcohol)

## Experimental

The infrared (Nujol mull), far infrared (polyethylene powder) and NMR (in  $\text{CDCl}_3$ ) spectral measurements were carried out with Carl Zeiss UR 10, Polytec FIR 30 Fourier spectrophotometers and a Varian T-60 instrument, respectively. Conductivity measurements were made with Toshniwal Instruments Conductivity Bridge Type CL 01.02.

The complexes of the type  $[\text{Rh}(\text{CO})_2\text{L}_3]\text{ClO}_4$  and  $[\text{RhX}(\text{COD})]_2$  were made by published methods [2,25]. Microanalyses were carried out at the University of Surrey (England) and the University of Sussex (England).

### *Dicarbonyl-2,2'-biquinolylrhodium(I) perchlorate, $[\text{Rh}(\text{CO})_2\text{biq}]\text{ClO}_4$*

Carbon monoxide was passed through a warm ethanolic solution of rhodium perchlorate for 1 h. The calculated amount of biq was added, and the passage of carbon monoxide was continued. Orange red crystals of the required compound separated.

### *Carbonyl-2,2'-biquinolylbis(tertiary phosphine or arsine)rhodium(I) perchlorate, $[\text{Rh}(\text{CO})\text{biqL}_2]\text{ClO}_4$*

To an ethanolic suspension of  $[\text{Rh}(\text{CO})_2\text{biq}]\text{ClO}_4$  or  $[\text{Rh}(\text{CO})_2\text{L}_3]\text{ClO}_4$ , the calculated amount of the ligand L or biq was added and the mixture was refluxed on a steam-bath for 1 h. The solution was evaporated to small volume under reduced pressure, and the required compound deposited.

### *Halo-2,2'-biquinolyl-1,5-cyclooctadienerhodium(I), $\text{RhX}(\text{COD})\text{biq}$ (X = Cl, Br)*

The calculated amount of biq was added to a methanolic solution of  $[\text{RhX}-$

(COD)]<sub>2</sub>. The mixture was refluxed on a steam-bath for 1 h, and shining red crystals separated.

*Halodicarbonyl-2,2'-biquinolylrhodium(I), RhX(CO)<sub>2</sub>biq (X = Cl, Br)*

Carbon monoxide was bubbled through an acetone solution of RhX(COD)biq until the colour changed to yellow. The excess of solvent was removed under reduced pressure, and the required compound separated out as red or brown crystals.

*Trihalocarbonyl-2,2'-biquinolylrhodium(III), RhX<sub>3</sub>(CO)biq (X = Cl, Br, I)*

To an ethanolic suspension of RhX(CO)<sub>2</sub>biq either chlorine in carbon tetrachloride or bromine in ethanol was added in the mole ratio 1/1. The mixture was refluxed on a steam-bath for 1 h, when shining yellow or orange yellow crystals of the compound separated out.

The iodo compound RhI<sub>3</sub>(CO)biq was prepared as follows. Carbon monoxide was bubbled through a refluxing ethanolic solution of RhCl<sub>3</sub> · nH<sub>2</sub>O until the solution turned pale yellow. An excess of LiI was added, followed by an equimolar amount of biq and bubbling of carbon monoxide was continued. Dark shining crystals separated out.

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