

The coordination behaviour of the squarate anion in rhodium(I) chemistry

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Abstract

Preparation of the neutral $[\text{Rh}_2(\mu\text{-sq})(\text{COD})_2]$ (**1**) (sq=squarate) and ionic $[\text{Rh}(\text{phen})(\text{COD})][\text{Rh}(\text{sq})(\text{COD})]$ (**2**) and $[\text{Rh}(\text{dppe})_2]_2[\text{sq}]$ (**3**) complexes is reported. Complex $[\text{Rh}_2(\mu\text{-sq})(\text{CNR})_4]$ (**4**) (R=*p*-tosylmethylisocyanide) has been prepared by substitution of the diolefinic ligands of complex **1**. Carbonylation of compounds **1** and **2** gave $[\text{Rh}_2(\mu\text{-sq})(\text{CO})_4]$ (**5**) and $[\text{Rh}(\text{phen})(\text{CO})_2][\text{Rh}(\text{sq})(\text{CO})_2]$ (**6**), respectively. Compound $[\text{Rh}_2(\mu\text{-sq})(\text{CO})_2(\text{PPh}_3)_2]$ (**7**) was prepared by addition of PPh_3 to complex **5**. Complex **7** undergoes oxidative addition of molecular iodine leading to the rhodium(III) compound $[\text{Rh}_2(\mu\text{-sq})\text{I}_2(\text{CO})_2(\text{PPh}_3)_2]$ (**8**).

Keywords: Rhodium complexes; Squarate anion complexes

1. Introduction

There is considerable interest in the chemical and physical properties of new anisotropic materials [1–3]. Several mononuclear bis-(carbonyl)rhodium(I) or iridium(I) complexes containing columnar stacking have been recently reported [4,5], including examples which possess intermolecular Rh–Rh interactions [6]. In particular the compounds $[\text{M}(\text{acac})(\text{CO})_2]$ (M=Rh, Ir) show properties characteristic of semiconductors [7] as a possible result of intermolecular conjugation. Compounds which possess sterically undemanding and/or planar ligands would appear to be favourable in the promotion of intermolecular metal–metal interactions and are thus of great interest.

With this in mind, we have reported a variety of rhodium complexes containing bidentate oxygen anions. Among those the synthesis and reactivity of rhodium(I) complexes containing oxalate [8,9] and chloranilate [10,11] type ligands have been described. As part of our interest in the chemistry of intermolecular metal–metal interactions, we have investigated the coordination properties of the squarate dianion $\text{C}_4\text{O}_4^{2-}$ [(dihydroxycyclobutenedionate(2–))] because this anionic ligand has been scarcely studied and could offer interesting possibilities in this field [12–15], since it is a planar ligand, chemically related to the oxalate ion [12,14]

which is likely to allow intermolecular metal–metal interactions.

We describe in this paper the synthesis of some mononuclear and binuclear squarate rhodium(I) complexes, as well as a study of iodine oxidative addition reactions on a representative binuclear complex.

2. Results and discussion

2.1. Squarate diolefin complexes

The binuclear complex $[\text{Rh}_2(\mu\text{-sq})(\text{COD})_2]$ (**1**) (sq=squarate, COD=1,5-cyclooctadiene) was prepared from the reaction of the mononuclear-solvate compound $[\text{Rh}(\text{COD})(\text{acetone})_2][\text{BF}_4]$ with the piperidine salt of squaric acid $[\text{Hpip}]_2[\text{sq}]$. Compound **1** was isolated as a microcrystalline yellow solid and its formulation is based on the analytical and spectroscopic data described below.

The molecular weight of compound **1** was established by mass spectroscopy as corresponding to a dimeric structure (*m/z* 534). The ¹H NMR spectrum exhibits only one signal (δ 3.96 ppm) for the eight olefinic protons of the cyclooctadiene ligands. The IR spectrum of complex **1** is dominated by the extremely broad and strong band extending over the region 1400–1550 cm^{-1} . This band can be assigned to a mixture of C=C–O and C=O stretching vibrations. The

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absence of a band above 1600 cm^{-1} most likely indicates all the CO groups are coordinated to metal atoms, and the D_{4h} symmetry of the squarate ion [16] is not greatly reduced on coordination. Furthermore, the expected square planar coordination for the metal centre in rhodium(I) complexes led us to propose the squarate ligand 1,2-bis-chelates a binuclear rhodium(I) complex in a similar fashion to those bridged by oxalate or chloranilate dianions [8,10,11] although more complex molecular arrangements cannot be excluded [17,18]. The suggested structure for complex **1** is, thus, represented in Fig. 1.

Attempts to prepare compound **1** by reaction of $[\text{Rh}_2(\mu\text{-OMe})_2(\text{COD})_2]$ or $[\text{Rh}(\text{acac})(\text{COD})]$ with squaric acid were unsuccessful probably due to the solubility problems of the squaric acid in common solvents.

Compound $[\text{Rh}_2(\mu\text{-sq})(\text{COD})_2]$ (**1**) readily reacts with the bidentate nitrogen donor ligand 1,10-phenanthroline leading to the formation of the ionic derivative $[\text{Rh}(\text{COD})(\text{phen})][\text{Rh}(\text{sq})(\text{COD})]$ (**2**). The electrical conductivity of compound **2** shows it to be a 1/1 electrolyte (see Section 3). The cation of this complex $[\text{Rh}(\text{COD})(\text{phen})][\text{Rh}(\text{sq})(\text{COD})]$ is reported to be of high stability [19]. The IR spectrum of **2** shows moderate bands at 1740 cm^{-1} . The absorption may be assigned to a C=O stretching mode, suggesting a C_{2v} symmetry for the squarate ion, as that observed for metal squarate complexes involving the mono-chelate coordination mode of the squarate ion [20] (see Fig. 2).

The addition of bis(diphenylphosphino)ethane to a dichloromethane suspension of compound **1**, in a molar ratio Rh/dppe of 1/2, leads to the displacement of the cyclooctadiene ligands and to the formation of $[\text{Rh}(\text{dppe})_2]_2[\text{sq}]$ (**3**). Compound **3** has been characterised on the basis of elemental analysis and the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum. The stable $[\text{Rh}(\text{dppe})_2]^+$ cation exhibits one doublet at $\delta 58.2\text{ ppm}$ ($J_{\text{RhP}} 133\text{ Hz}$) corresponding to four equivalent phosphorus nuclei which are coupled to the rhodium centre [21].

The addition of *p*-tosylmethylisocyanide to compound **1** led to the displacement of both diolefin ligands and to the formation of $[\text{Rh}_2(\mu\text{-sq})(\text{CNR})_4]$ ($\text{R} = p\text{-tosylmethyl}$) (**4**). Compound **4** has been characterised by analytical and spectroscopic data.

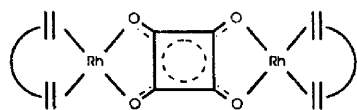


Fig. 1. Suggested structure for complex **1**.

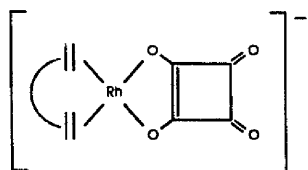


Fig. 2. Suggested structure for $[\text{Rh}(\text{sq})(\text{COD})]^-$ anion.

2.2. Squarate carbonyl complexes

Bubbling carbon monoxide through a dichloromethane suspension of compound **1** leads to the displacement of the coordinated diolefins causing an instantaneous change of colour from yellow to dark blue and precipitation of dark blue microcrystals formulated as $[\text{Rh}_2(\mu\text{-sq})(\text{CO})_4]_x$ (**5**).

The planarity of the squarate ligand probably favours the presence of an intermolecular rhodium–rhodium interaction in complex **5** as is suggested by the dark colour and complex IR spectrum in nujol ($\nu(\text{C}\equiv\text{O})$ (nujol): 2095, 2034 and 2027 cm^{-1}). This type of intermolecular interaction has also been found in other binuclear rhodium(I) complexes containing planar ligands bridging both metal centres [8,22]. Unfortunately, the low solubility of compound **5** prevented us from obtaining molecular weight measurements. Furthermore, all attempts to prepare monocrystals of compound **5** suitable for X-ray analysis were unsuccessful.

The reaction of complex $[\text{Rh}(\text{COD})(\text{phen})][\text{Rh}(\text{sq})(\text{COD})]$ (**2**) with carbon monoxide leads to the formation of $[\text{Rh}(\text{CO})_2(\text{phen})][\text{Rh}(\text{sq})(\text{CO})_2]$ (**6**). The complex IR spectrum in the carbonyl stretching frequency region along with the dark green colour of the compound in the solid state suggest an ionic chain-like structure involving metal–metal interactions. The observed IR absorptions seem to be the result of the superimposed individual *cis*-dicarbonyl bands of $[\text{Rh}(\text{CO})_2(\text{phen})]^+$ [19] and $[\text{Rh}(\text{sq})(\text{CO})_2]^-$. Compound **6** behaves as a 1:1 electrolyte in solution.

Addition of triphenylphosphine to a dichloromethane suspension of $[\text{Rh}_2(\mu\text{-sq})(\text{CO})_4]_x$ (**5**) caused the evolution of carbon monoxide and formation of the orange compound $[\text{Rh}_2(\mu\text{-sq})(\text{CO})_2(\text{PPh}_3)_2]$ (**7**). The $^{31}\text{P}\{^1\text{H}\}$ spectrum shows the presence of one doublet corresponding to two equivalent phosphorus atoms coupled to the nearest rhodium atom ($\delta 30.9$, $J_{\text{RhP}} 131\text{ Hz}$). The presence of only one signal at 1980 cm^{-1} in the IR spectrum also suggests a *trans* disposition of the terminal ligands [23].

2.3. Molecular iodine oxidative addition reaction to $[\text{Rh}_2(\mu\text{-sq})(\text{CO})_2(\text{PPh}_3)_2]$ (**7**)

The addition of molecular iodine to a dichloromethane solution of compound **7** with an Rh/I₂ 1/1 molar ratio, progressively causes the colour of the solution to change from orange to green. After stirring for 30 min the IR spectrum shows only one band at 2090 cm^{-1} corresponding to terminal carbonyl ligands, while the band at 1980 cm^{-1} of the starting material has completely disappeared. The increase in the carbonyl stretching wave numbers ($\Delta\nu(\text{CO}) 110\text{ cm}^{-1}$) parallels the increase of the formal oxidation numbers from I to III. Despite the larger number of potential isomers possible for **8**, the NMR spectrum indicates that only one is present in solution. The $^{31}\text{P}\{^1\text{H}\}$ spectrum shows a doublet at $\delta 25.2$ ($J_{\text{RhP}} 90\text{ Hz}$) arising from a symmetrical compound. This implies the coordination of two iodide groups to each

rhodium metal centre and formation of $[\text{Rh}_2(\mu\text{-sq})\text{I}_4(\text{CO})_2(\text{PPh}_3)_2]$ (**8**).

The planarity shown by the squarate dianion in these binuclear systems leads to a large intra-metal separation within the molecule. Each metal centre might behave, thus, relatively independently with respect to its neighbour. Consequently we considered the possibility of preparing mixed valent compounds. However, the reaction of molecular iodine with $[\text{Rh}_2(\mu\text{-sq})(\text{CO})_2(\text{PPh}_3)_2]$ (**7**), in an Rh/I₂ 2/1 molar ratio gave only an equimolecular mixture of unreacted material **7** and the rhodium(III) derivative **8**. A similar result has recently been observed in the oxidative addition reactions on binuclear rhodium systems containing a chloranilate ligand bridging both metal centres [11].

3. Experimental

All reactions were carried out under nitrogen using standard Schlenk techniques and were monitored by solution IR spectroscopy (carbonyl stretching region). $[\text{Rh}_2(\mu\text{-Cl})(\text{COD})_2]$ [**24**] was prepared according to literature methods. Solvents were purified according to standard procedures and distilled under nitrogen prior to use. All other reagents were purchased from Aldrich and used as received. Solution IR spectra were recorded on a Nicolet Magna 550 spectrometer. ¹H and ³¹P{¹H} NMR spectra were carried out in CDCl₃ solutions at room temperature on a Varian XL 300 spectrometer. ³¹P chemical shifts are positive downfield from external 85% H₃PO₄ in D₂O. Elemental analyses were carried out with a Perkin-Elmer 240B microanalyser. Conductivity measurements were carried out with a Philips 9509 conductimeter. Fast atom bombardment (FAB) mass spectra were recorded on a AUTOSPEC V6 spectrometer.

3.1. Preparation of $[\text{Rh}_2(\mu\text{-sq})(\text{COD})_2]$ (**1**)

A methanolic solution of $[\text{Hpip}]_2[\text{sq}]$ (8.2 mmol) (prepared by addition of piperidine (0.81 ml, 8.2 mmol) to a stirred suspension of squaric acid (463 mg, 4.06 mmol) in methanol (20 ml)) was added to a solution of $[\text{Rh}(\text{COD})(\text{acetone})_x][\text{BF}_4]$ (8.12 mmol), prepared in situ by reaction of $[\text{Rh}_2(\mu\text{-Cl})_2(\text{COD})_2]$ (2 g, 4.06 mmol) with AgBF₄ (1.58 g, 8.12 mmol), in acetone (30 ml). The resulting yellow suspension was stirred for 20 min. Concentration of the solvent to 1 ml and addition of diethyl ether (20 ml) led to complete precipitation of a yellow solid which was separated by filtration, washed with diethyl ether and dried under vacuum. Yield 1.85 g (85%). *Anal.* Calc. for C₂₀H₂₄O₄Rh₂: C, 45.01; H, 4.55. Found: C, 44.58; H, 4.40%. IR (nujol): $\nu(\text{C}=\text{O})$ and $\nu(\text{C}=\text{C})$ 1550–1400 (vs, br) cm⁻¹. ¹H NMR (CDCl₃): 3.96 (b, HC=), 2.63 (b, H₂C-), 1.71 (m, H₂C-). *m/z* = 534.

3.2. Preparation of $[\text{Rh}(\text{phen})(\text{COD})][\text{Rh}(\text{sq})(\text{COD})]$ (**2**)

A solution of 1,10-phenanthroline (37 mg, 0.19 mmol) in dichloromethane (3 ml) was added to a stirred suspension of $[\text{Rh}_2(\mu\text{-sq})(\text{COD})_2]$ (**1**) (100 mg, 0.18 mmol) in acetonitrile (8 ml). The initial yellow solution changed to a dark red suspension following the addition. Stirring was continued at room temperature for 45 min, and the dark red precipitate was filtered, washed with diethyl ether and vacuum dried. Yield 99 mg (74%). *Anal.* Calc. for C₃₂H₃₂N₂O₄Rh₂: C, 53.81; H, 4.52; N, 3.90. Found: C, 53.25; H, 4.38; N, 3.82%. IR (nujol): $\nu(\text{C}=\text{O})$ 1740 cm⁻¹. Δ_M (acetone) = 60 ohm⁻¹ cm² mol⁻¹.

3.3. Preparation of $[\text{Rh}(\text{dppe})_2][\text{sq}]$ (**3**)

Dppe (150 mg, 0.38 mmol) was added to a stirred suspension of $[\text{Rh}_2(\mu\text{-sq})(\text{COD})_2]$ (**1**) (50 mg, 0.09 mmol) in dichloromethane (10 ml). The initial suspension immediately changed to an orange solution and stirring was continued for 2 h. The solution was concentrated in vacuo to ~1 ml and the addition of diethyl ether (15 ml) precipitated a yellow solid, separated by filtration, washed with diethyl ether and dried under vacuum. Yield 164 mg (92%). *Anal.* Calc. for C₁₀₈H₉₆O₄P₈Rh₂: C, 67.92; H, 5.10. Found: C, 67.02; H, 5.10%. ³¹P{¹H} NMR (CDCl₃): 58.2 (d, J_{RhP} 133 Hz).

3.4. Preparation of $[\text{Rh}_2(\mu\text{-sq})(\text{CNR})_4]$ (**4**) (*R* = *p*-tosylmethyl)

A solution of CNR (72 mg, 0.37 mmol) in dichloromethane (3 ml) was added to a suspension of $[\text{Rh}_2(\mu\text{-sq})(\text{COD})_2]$ (**1**) (50 mg, 0.093 mmol) in dichloromethane (10 ml). The initial yellow suspension changed to a dark blue solution and was stirred for 2 h. The solvent was concentrated in vacuo to ~1 ml and addition of hexane (8 ml) precipitated a dark blue solid, which was separated by filtration, washed with hexane and vacuum dried. Yield 80 mg (78%). *Anal.* Calc. for C₄₀H₃₆N₄O₁₂Rh₂S₄: C, 43.71; H, 3.32; N, 5.12. Found: C, 43.62; H, 3.71; N, 5.92%. IR (nujol): $\nu(\text{CN})$: 2200 cm⁻¹. ¹H NMR (CDCl₃): 7.77 (m, Ph), 4.69 (b, CH₂), 2.30 (s, CH₃).

3.5. Preparation of $[\text{Rh}_2(\mu\text{-sq})(\text{CO})_4]$ (**5**)

Carbon monoxide was bubbled through a suspension of complex **1** (0.90 mg, 1.70 mmol) in dichloromethane (20 ml) for 1 h, leading to the precipitation of a dark blue solid. The solvent was evaporated under vacuum to ~1 ml and hexane (10 ml) was added. The solid was filtered off, washed with hexane and vacuum dried. Yield 0.70 g (93%). *Anal.* Calc. for C₈O₈Rh₂: C, 22.35. Found: C, 23.02%. IR (nujol): $\nu(\text{C}\equiv\text{O})$ 2095, 2034 and 2027 cm⁻¹.

3.6. Preparation of $[Rh(phen)(CO)_2][Rh(sq)(CO)_2]$ (6)

Carbon monoxide was bubbled through a suspension of $[Rh(phen)(COD)] [Rh(sq)(COD)]$ (2) in dichloromethane (10 ml) for 30 min. The initial suspension changed from red to dark green. The green solid was separated by filtration, washed with diethyl ether and dried under vacuum. Yield 96 mg (84%). *Anal. Calc.* for $C_{20}H_8N_2O_8Rh_2$: C, 39.37; H, 1.32; N, 4.59. Found: C, 38.83; H, 1.43; N, 4.41%. IR (nujol): $\nu(C\equiv O)$ 2100 (b), 2070 (b), 2010 (b), 1980 (b) cm^{-1} . Δ_M (acetone) = 70 $ohm^{-1} cm^2 mol^{-1}$.

3.7. Preparation of $[Rh_2(\mu-sq)(CO)_2(PPh_3)_2]$ (7)

A stoichiometric amount of solid triphenylphosphine (737 mg, 2.80 mmol) was added to a suspension of $[Rh_2(\mu-sq)(CO)_4]_x$ (5) (600 mg, 1.40 mmol) in dichloromethane (10 cm^3). The resulting red–brown solution was stirred for 2 h. The solvent volume was concentrated in vacuo to ~1 ml. Addition of hexane (10 ml) to the concentrated solution gave an orange solid which was filtered, washed with hexane and dried under vacuum. Yield 1.14 g (91%). *Anal. Calc.* for $C_{42}H_{30}O_6P_2Rh_2$: C, 56.15; H, 3.37. Found: C, 56.40; H, 3.20%. IR (CH_2Cl_2): $\nu(C\equiv O)$ 1980 cm^{-1} . 1H NMR ($CDCl_3$): 7.42 (m, PPh_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): 30.9 (d, J_{RhP} 131 Hz).

3.8. Preparation of $[Rh_2(\mu-sq)I_4(CO)_2(PPh_3)_2]$ (8)

Iodine (58 mg, 0.22 mmol) was added to a solution of $[Rh_2(\mu-sq)(CO)_2(PPh_3)_2]$ (7) (100 mg, 0.11 mmol) in dichloromethane (15 ml). The resulting red–brown solution was stirred at room temperature. After 30 min the IR spectrum revealed the absence of starting material. Concentration of the solvent (1 ml) and addition of diethyl ether (3 ml) followed by hexane (5 ml) gave a green solid which was filtered, washed with hexane and dried under vacuum. Yield 106 mg (91%). *Anal. Calc.* for $C_{42}H_{30}I_4O_6P_2Rh_2$: C, 35.87; H, 2.15. Found: C, 35.62; H, 2.10%. IR (CH_2Cl_2): $\nu(C\equiv O)$ 2090 cm^{-1} . 1H NMR ($CDCl_3$): 7.22 (m, PPh_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): 25.2 (d, J_{RhP} 90 Hz).

4. Concluding remarks

We have presented the preparation of neutral and ionic rhodium complexes containing the squarate dianion. In the ionic compounds, 2 and 6, the squarate group chelates the metal centre, but remains as an uncoordinated anion in complex 3. The coordination around the metal centres, in the neutral binuclear systems, has been shown to be a bis-chelate coordination fashion for the squarate ligand. The IR spectra and properties of the neutral and ionic complexes containing the $Rh(CO)_2$ units suggest the presence of intermolecular Rh–Rh interactions.

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