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Synthesis and characterization of dirhodium complexes with asymmetric bridging ligands

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Abstract

The new dirhodium complexes $[Rh_2(CO)_4(\mu\text{-}L)_2]$ (I: $L = CH_3CONC_6H_5$; II: $L = CH_3CSNC_6H_5$) have been prepared from $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ and the appropriate ligand obtained by deprotonation of the corresponding RCXNHPh compounds (X = O or S) with NaH. The complex I reacts with PPh_3 in hexane to give $[Rh_2(CO)_2(PPh_3)_2(\mu\text{-}L)_2]$ (III), which undergoes two one-electron oxidations at a platinum bead electrode in CH_2Cl_2. The first process is reversible and gives a monocation with a $[Rh_2]^{3+}$ core. Oxidation of III with $[Fe(\eta\text{-}C_5H_5)_2][PF_6]$ gives the paramagnetic complex $[Rh_2(CO)_2(PPh_3)_2(\mu\text{-}L)_2][PF_6]$ (IV).

Introduction

The structure and electrochemical properties of the dirhodium(I) complexes of the type $[Rh_2(CO)_4(\mu\text{-}L)_2]$ (L = RNNNR,R'NC(Me)NR') have been recently reported [1,2]. Such species and some of their group 5 donor ligand derivatives undergo up to three succesive, one-electron oxidations in which the $[Rh_2]^{z+}$ unit remains intact for $z = 2–5$. The paramagnetic monocations that have been fully characterized e.g $[Rh_2(CO)_2(PPh_3)_2(\mu\text{-}RNNNR)_2][PF_6]$ are delocalized mixed-valence complexes with a $[Rh_2]^{3+}$ core. The effects of asymmetry arising from the presence of different terminal ligands on the electrochemical properties and chemical reactivity of the dirhodium complexes have been described recently [3]. In order to examine further the effects of the asymmetric bridge we decided to explore the possibility of preparing new species of the type $[Rh_2(CO)_4(\mu\text{-}L)_2]$ containing acetanilide, thioacetanilide or 2-mercaptopyridine as the bridging ligand.

Results and discussion

The compounds $CH_3CONHC_6H_5$ (acetanilide or *N*-phenylacetamide), $CH_3CSNHC_6H_5$ (thioacetanilide) and C_5H_4NSH (2-mercaptopyridine) react with NaH in

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Table 1

Analytical and IR spectroscopic data

Compound [a]	Colour	Analysis (Found (calcd.) (%))			ν(CO) (cm^{-1}) [b]
		C	H	N	
$[Rh_2(CO)_4(\mu\text{-}L)_2]$ (I)	dark red	41.1 (41.0)	2.9 (2.8)	4.7 (4.8)	2086vs 2062s 2014vs
$[Rh_2(CO)_4(\mu\text{-}L')_2]$ (II)	purple	38.4 (38.8)	2.7 (2.6)	4.3 (4.5)	2082vs 2054s 2018vs
$[Rh_2(CO)_2(PPh_3)_2(\mu\text{-}L)_2]$ (III)	red-orange	60.4 (61.5)	4.6 (4.4)	2.6 (2.7)	1955 [c]br
$[Rh_2(CO)_2(PPh_3)_2(\mu\text{-}L)_2]$-$[PF_6]$ (IV) [d]	dark red	50.5 (51.4)	3.8 (3.8)	2.2 (2.2)	2036s 2013 [c]vs

[a] L = $CH_3CONC_6H_5$, L′ = $CH_3CSNC_6H_5$. [b] In hexane unless stated otherwise. [c] In CH_2Cl_2. [d] Analysed as a 1/CH_2Cl_2 solvate; s, strong; vs, very strong; br, broad.

THF to give solutions containing the potentially bridging anions $[CH_3CONC_6H_5]^-$, $[CH_3CSNC_6H_5]^-$, and $[C_5H_4NS]^-$. These anions were found to react immediately with $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ at low temperature (−78°C) to give deep red (L = $CH_3CONC_6H_5^-$) and purple (L = $CH_3CSNC_6H_5^-$, $C_5H_4NS^-$) solutions, from which only the species $[Rh_2(CO)_4(\mu\text{-}L)_2]$ with L = $CH_3CONC_6H_5^-$ (I) and L = $CH_3CSNC_6H_5^-$ (II) were isolated. Both of the new complexes were characterised by elemental analysis and IR spectroscopy (Table 1). The derivative with L = C_5H_4NS was identified by comparison of the IR spectra (ν(CO): 2083vs, 2060s, 2018vs cm^{-1}, in hexane) with those of I and II, but could not be isolated in the pure.

The same complexes were obtained by addition of Et_3N to a solution of $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ and thioacetanilide or 2-mercaptopyridine, but no deprotonation of the ligand was observed in the case of acetanilide.

The lower IR carbonyl stretching frequencies of I or II compared with those observed for the RNNNR derivative [1] suggest that the former should also have lower oxidation potentials, but the instability in solution of these species in CH_2Cl_2 or THF prevented their study by cyclic voltammetry. Complex I was not oxidised by $[Fe(\eta\text{-}C_5H_5)_2][PF_6]$ in CH_2Cl_2 and the use of stronger oxidants such as NO^+ resulted only in decomposition.

The reaction of $[Rh_2(CO)_4(\mu\text{-}CH_3CONC_6H_5)_2]$ with PPh_3 in hexane resulted in disubstitution, giving $[Rh_2(CO)_2(PPh_3)_2(\mu\text{-}CH_3CONC_6H_5)_2]$ (III), which was identified by elemental analysis and IR spectroscopy (Table 1).

The ^{31}P NMR spectrum in $CDCl_3$ of III showed, however, that III was a mixture of two isomers, isomer IIIa with two equivalent phosphorus atoms (doublet centered at 44.6 ppm (J(P–Rh) 161 Hz)), and isomer IIIb with two different phosphorus atoms (two doublets centered at 48.28 ppm (J(P–Rh) 195 Hz) and 29.08 ppm (J(P–Rh) 127 Hz)). These data are consistent with two possible structures for IIIa, as shown in Fig 1a, and three structures for IIIb, shown in Fig. 1b–1d. The most probable structure for IIIb is that with two phosphorus *trans*, as shown in Fig. 1b. Such a structure is adopted [4] by $[Rh_2(CO)_2(PPh_3)_2(\mu\text{-}RNNNR)_2]$ (R = p-totyl).

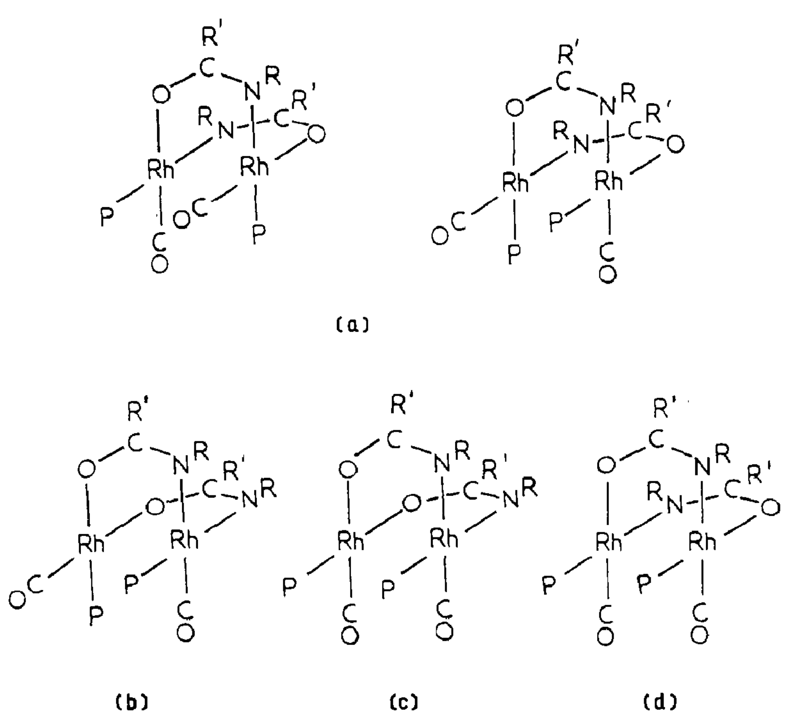

Fig. 1. Possible structures for $[Rh_2(CO)_2(PPh_3)_2(\mu\text{-}CH_3CONC_6H_5)_2]$ (a) isomer IIIa and (b), (c) and (d) isomer IIIb. $R = C_6H_5$; $R' = CH_3$; $P = PPh_3$.

The formation of more than one isomer has been observed in other dirhodium species containing bridging anions similar to those used in this work [5–8].

The cyclic voltammogram of the mixture of isomers III at a platinum bead electrode in CH_2Cl_2 shows two one-electron oxidations, the first of which is reversible (Table 2). The shape of the current-voltage curves suggests that the two isomers are oxidised at approximately the same potential, Similar results were reported for other binuclear species [6,7].

Table 2 also shows the data for the RNNNR and R′NC(Me)NR′ derivatives analogue.

It is interesting to note that the oxidation of III to the monocation occurs at a potential more negative than that for the RNNNR derivative and close to that for the R′NC(Me)NR′ complex. This implies that RNNNR is a worse σ-donor or better π-acceptor than R′NC(Me)NR′ or CH_3CONR', which is also mirrored in the higher

Table 2

Cyclic voltammetric data for $[Rh_2(CO)_2(PPh_3)_2(\mu\text{-}L)_2]$

L	Process	E^0 (V)	Process	E^0 (V)[a]	Process	E^0 (V)
RNNNR[b,c]	$0 \rightleftharpoons +1$	0.18	$+1 \rightleftharpoons +2$	1.28(*R*)	$+2 \rightleftharpoons +3$	1.57
R′NC(Me)NR′[c,d]	$0 \rightleftharpoons +1$	−0.08	$+1 \rightleftharpoons +2$	1.26(*I*)[e]	–	–
CH_3CONR'(III)	$0 \rightleftharpoons +1$	0.04	$+1 \rightleftharpoons +2$	1.22(*I*)[e]	–	–

[a] (*R*), reversible; (*I*), irreversible. [b] R = *p*-tolyl. [c] Data taken from ref. 1. [d] R′ = Ph. [e] Ep_k for irreversible process at $\nu = 200$ mV s^{-1}.

IR carbonyl stretching frequencies observed [1] for $[Rh_2(CO)_2(PPh_3)_2(\mu\text{-}RNNNR)_2]$ compared with those for the R′NC(Me)NR′ and CH_3CONR' analogues.

The cyclic voltammograms of the R′NC(Me)NR′ and CH_3CONR' compounds show only one irreversible wave in addition to that for the formation of the monocation, whereas the RNNNR derivative shows a second reversible wave corresponding to the formation of the dication, and a third irreversible wave corresponding to the formation of the trication.

The data for complex III suggested that it should be possible to form the monocation readily by use of mild chemical oxidants, and it was found that the paramagnetic salt $[Rh_2(CO)_2(PPh_3)_2(\mu\text{-}CH_3CONC_6H_5)_2][PF_6]$ (IV) was indeed produced by reaction of solid $[Fe(\eta\text{-}C_5H_5)_2][PF_6]$ with (III) in CH_2Cl_2. Compound IV was characterised by elemental analysis and IR and ESR spectroscopy (Table 1). The room temperature ESR spectrum of IV in CH_2Cl_2/thf (1/2) showed a broad single line with $g_{av} = 2.10$; no hyperfine coupling was observed even in the spectrum of the frozen solution.

Experimental

The preparation, purification and reactions of the complexes were carried out under dry nitrogen.

The compounds $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ [9], and $[Fe(\eta\text{-}C_5H_5)_2][PF_6]$ [10] were prepared by published methods. The ligands *N*-phenyl-acetamide, *N*-phenylthioacetamide and 2-mercaptopyridine were purchased from the Aldrich Chemical Co., Inc.

Infrared spectra were recorded on a Nicolet MX-5 FT spectrometer. X-Band ESR spectra were recorded on a Varian Associates 4502/15 instrument and were calibrated against a solid sample of the diphenylpicrylhydrazyl radical.

Phosphorus-31 NMR spectra were recorded at 36 MHz on a JEOL FX 90Q instrument, with H_3PO_4 as external standard.

Cyclic voltammetry was carried out using an AMEL Electrochemolab in conjunction with a three-electrode cell. The working electrode was a platinum bead, the auxiliary electrode a platinum wire, and the reference an aqueous saturated calomel electrode (SCE) separated from the test solution by a fine-porosity frit and an agar bridge saturated with KCl. Solutions were 0.5×10^{-3} mol dm^{-3} in complex and 0.1 mol dm^{-3} in $[NBu^n_4][PF_6]$ as supporting electrolyte. After cyclic voltammetric measurements were carried out, $[Fe(\eta\text{-}C_5H_5)_2]$ was added to the test solution as an internal calibrant. Under the conditions described above, the E^0 value for the couple $[Fe(\eta\text{-}C_5H_5)_2]^+$-$[Fe(\eta\text{-}C_5H_5)_2]$ is 0.47 V

Microanalyses were carried out by the staff of the Microanalytical Service of the School of Chemistry University of Bristol.

$[Rh_2(CO)_4(\mu\text{-}CH_3CONC_6H_5)_2]$ (I)

N-Phenylacetamide (0.139 g, 1.03 mmol was added to a stirred suspension of NaH (0.050 g) in THF (20 cm^3). Evolution of H_2 was observed. After 10 min the solution was filtered into a stirred solution of $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$, (0.2 g, 0.51 mmol) in THF (10 cm^3) at −78 °C (CO_2-acetone). After 1 h the resulting dark red solution was evaporated to dryness and the residue extracted with n-hexane (60 cm^3).

Evaporation of the extract to low volume (15 cm^3) and cooling to 0 °C gave the complex as dark red crystals, yield 0.25 g (85%).

The solid is unstable in air, but can be stored under nitrogen at −10 °C for at least 10 days. The complex is soluble in hexane, CH_2Cl_2, and thf, giving red solutions which become brown when exposed to air.

$[Rh_2(CO)_4(\mu\text{-}CH_3CSNC_6H_5)_2]$ (II)

N-Phenylthioacetamide (0.154 g, 1.02 mmol) was added to a stirred suspension of NaH (0.050 g) in THF (20 cm^3). After 10 min the solution was filtered and added to a stirred solution of $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ (0.2 g, 0.51 mmol in THF (20 cm^3) at −78 °C). A very deep purple solution was immediately formed, and after 15 min it was evaporated to dryness. The residue was extracted with n-hexane (4 × 30 cm^3), and evaporation of the extract to low volume (15 cm^3) and cooling to 0 °C gave the complex as dark purple microcrystalline solid. Yield 0.26 g (84%). The complex is unstable in air, both in the solid state and in solution. It can be stored under nitrogen at −10 °C for a few days.

$[Rh_2(CO)_2(PPh_3)_2(\mu\text{-}CH_3CONC_6H_5)_2]$ (III)

Triphenylphosphine (0.092 g, 0.35 mmol) was added to a stirred solution of $[Rh_2(CO)_4(\mu\text{-}CH_3CONC_6H_5)_2]$ (0.103 g, 0.18 mmol) in n-hexane (70 cm^3). A red orange precipitate was immediately formed, and was filtered of, washed with n-hexane (3 × 20 cm^3), and dried. Recrystallization from CH_2Cl_2/n-hexane gave the complex as red-orange crystals. Yield 0.165 g (89%).

The complex is soluble in CH_2Cl_2, THF and toluene and insoluble in hexane.

$[Rh_2(CO)_2(PPh_3)_2(\mu\text{-}CH_3CONC_6H_5)_2][PF_6]$ (IV)

To a stirred solution of $[Rh_2(CO)_2(PPh_3)_2(\mu\text{-}CH_3CONC_6H_5)_2]$ (0.185 g, 0.18 mmol) in CH_2Cl_2 (40 cm^3) was added $[Fe(\eta\text{-}C_5H_5)_2][PF_6]$ (58 mg, 0.18 mmol). The solution immediately became dark-red. Filtration, addition of n-hexane (50 cm^3), and partial evaporation of the solvent in vacuo gave a dark-red precipitate. Recrystallization from CH_2Cl_2/n-hexane gave the product as dark-red crystals. Yield 0.18 g (84%).

The complex is air stable in the solid state, and dissolves in CH_2Cl_2 and thf to give solutions which decompose only very slowly in air.

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