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Reactivity of $[\{(\eta^5\text{-}C_5Me_5)RhCl(\mu\text{-}Cl)\}_2]$ towards some potentially bidentate ligands

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Abstract

The complex $[\{Cp^{\star}RhCl(\mu\text{-}Cl)\}_2]$ ($Cp^{\star} = \eta^5\text{-}C_5Me_5$) reacts in dichloromethane with the relevant neutral ligands to give the complexes $[Cp^{\star}RhCl_2L]$ [L (monodentate) = *o*-aminophenol (oap), *o*-aminothiophenol (oatp), 4-cyanopyridine (4-CNpy)], or 4-amino-2,6-dimethyl-5-oxo-3-thioxo-1,2,3,4-tetrahydro-1,2,4-triazine (taz)], $[\{Cp^{\star}RhCl_2\}_2(\mu\text{-ppda})]$ (ppda = *p*-phenylenediamine), and $[Cp^{\star}RhCl(L\text{-}L)]Cl$ [L–L (chelating bidentate) = *o*-phenylenediamine (opda), ethylenediamine (en), or tetramethylethylenediamine (tmen)]. Anion exchange occurs when the opda complex is treated with KPF_6, giving $[Cp^{\star}RhCl(opda)]PF_6$. The new complexes have been characterized by elemental analysis, thermogravimetry, conductance measurements, and spectroscopic (IR and ^1H- and ^{13}C-NMR) methods.

Introduction

$[\{Cp^{\star}RhCl(\mu\text{-}Cl)\}_2]$ undergoes a great variety of reactions in which the halide bridges are split by a donor ligand to give neutral mononuclear compounds, $[Cp^{\star}RhCl_2L]$ [1–4]. Use of an excess of the ligand leads to further displacement of halide to give the cationic complexes $[Cp^{\star}RhClL_2]^+$ [1–5]. On the other hand, treatment of $[\{Cp^{\star}RhCl(\mu\text{-}Cl)\}_2]$ with 1,2-bis(diphenylphosphino)ethane (dppe) in 1 : 1 molar ratio gives $[\{Cp^{\star}RhCl_2(\mu\text{-dppe})\}_2]$ [1].

The recent interest in the chemistry of $[Cp^{\star}Rh(ppy)L]^{n+}$-type complexes ($n = 1$, 2, ppy = an oligopyridine ligand; L = H_2O, OH^-, Cl^-, or I^-) [6,7] is due to their use as redox catalysts in, for example, the photoreduction of protons to hydrogen on colloidal TiO_2. The crystal structure of $[Cp^{\star}Rh(bipy)Cl]ClO_4$ has been reported recently [8].

In this paper we present the results obtained in the reaction between $[\{Cp^{\star}RhCl(\mu\text{-}Cl)\}_2]$ and the potentially bidentate ligands listed above, which have no or only a low ability to back-accept electron density from the metal centre.

Results and discussion

The addition of the corresponding ligand to $[\{Cp^{\star}RhCl(\mu\text{-}Cl)\}_2]$ in dichloromethane leads to the formation of the rhodium complexes shown in Scheme 1. Some

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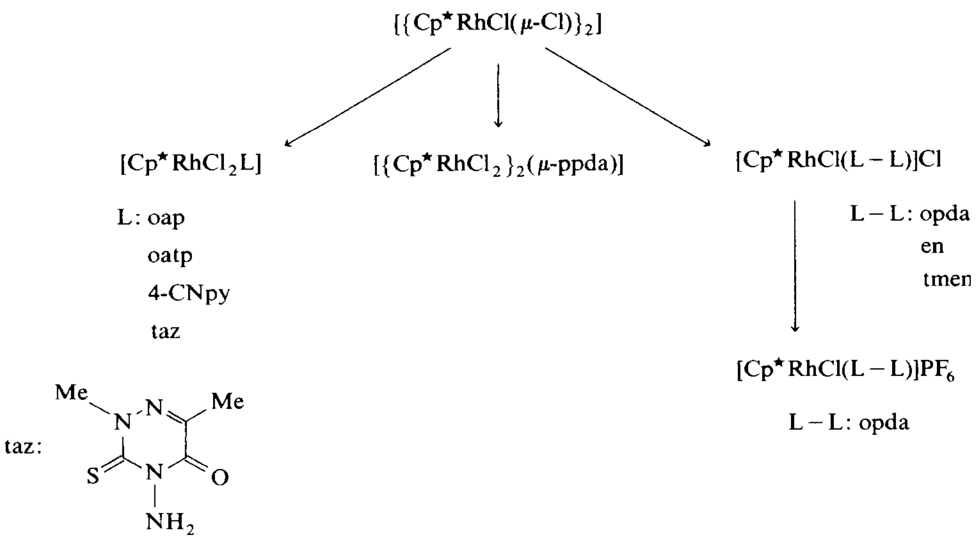

Scheme 1. ($Cp^\star = \eta^5 - C_5Me_5$).

of the compounds are hydrated, with the water content shown in Table 1; the water is assumed to come from the commercial ligand used. All attempts made to isolate a 2-cyanopyridine complex were unsuccessful, probably owing to steric factors. Chloride in complex VI was replaced by PF_6^- by reaction with potassium hexafluorophosphate, to give complex VII.

Table 1

Analytical data, yields and conductivities of the rhodium complexes

Compound	Colour	Yield (%)	Analysis [Found (calc.) (%)]			Λ_e (Ω^{-1} cm^2 mol^{-1})
			C	N	H	
$[Cp^\star RhCl_2(oap)] \cdot 0.5H_2O$ (I)	orange	83	45.2 (45.0)	5.1 (5.4)	3.1 (3.3)	7 [a]
$[Cp^\star RhCl_2(oatp)] \cdot 2H_2O$ (II)	orange	80	41.1 (41.4)	5.0 (5.1)	2.8 (3.2)	10 [a]
$[Cp^\star RhCl_2(4\text{-}CNpy)]$ (III)	orange	82	46.3 (46.5)	4.5 (4.6)	6.8 (6.8)	13 [a]
$[Cp^\star RhCl_2(taz)]$ (IV)	yellow	71	37.6 (37.4)	4.9 (4.8)	11.5 (11.6)	18 [a]
$[\{Cp^\star RhCl_2\}_2(\mu\text{-}ppda)]$ (V)	yellow	89	42.9 (43.0)	5.5 (5.2)	6.1 (5.9)	2 [a]
$[Cp^\star RhCl(opda)]Cl$ (VI)	yellow	82	45.8 (46.0)	5.8 (5.5)	6.7 (6.7)	56 [b]
$[Cp^\star RhCl(opda)]PF_6$ (VII)	orange	69	36.8 (36.5)	3.7 (3.6)	5.3 (5.3)	145 [a]
$[Cp^\star RhCl(en)]Cl \cdot 2H_2O$ (VIII)	yellow	95	39.1 (39.0)	6.5 (6.2)	7.9 (7.6)	15 [a]
$[Cp^\star RhCl(tmen)]Cl \cdot 2H_2O$ (IX)	orange	80	41.7 (41.6)	7.7 (7.6)	6.0 (6.1)	11 [a]

[a] In $(CH_3)_2CO$ ($c = 5 \times 10^{-4}$ M). [b] In CH_3CN ($c = 5 \times 10^{-4}$ M).

Table 2

Some relevant infrared data (cm^{-1}) for the rhodium complexes

Compound	ν(NH)	Other bands
$[Cp^{\star}RhCl_2(oap)]\cdot 0.5H_2O$ (I)	3300m, 3250sh, 3200br	3560br,m (ν(OH))
$[Cp^{\star}RhCl_2(oatp)]\cdot 2H_2O$ (II)	overlapped	3360br,m (ν(OH))
$[Cp^{\star}RhCl_2(4\text{-}CNpy)]$ (III)		2240 (ν($C\equiv N$)), 1605m 1540m, 1410s (ring C–C and C–N str), 1025m, (ring breathing), 845s (out of plane def.)
$[Cp^{\star}RhCl_2(taz)]$ (IV)	3120m, 3060sh	1730vs (ν(C=O)) 1360s (ν(C=S))
$[\{Cp^{\star}RhCl_2\}_2(\mu\text{-}ppda)]$ (V)	3350s, 3280m, 3190m, 3170sh, 3140w, 3100m	
$[Cp^{\star}RhCl_2(opda)]$ (VI)	3250s, 3140m	
$[Cp^{\star}RhCl(opda)]PF_6$ (VII)	3280s, 3190s, 3170s, 3100s	
$[Cp^{\star}RhCl_2(en)]\cdot 2H_2O$ (VIII)	3220s, 3150s, 3100s	3400s (ν(OH))
$[Cp^{\star}RhCl_2(tmen)]\cdot 2H_2O$ (IX)		3360br, m (ν(OH))

The new pentamethylcyclopentadienyl derivatives of rhodium(III) are yellow or orange air-stable solids, but complexes IV and IX are stable only under nitrogen. Complex IV is soluble in chloroform and all the isolated complexes are slightly soluble in acetone and acetonitrile but very soluble in coordinating solvents such as dimethylsulfoxide or dimethylformamide. As expected, complexes I–V are non-conducting in acetone solution, but the non-conducting nature of complexes VIII and IX is inconsistent with their proposed formulae. On the other hand, complex VII behaves as a 1 : 1 electrolyte in acetone solution [9] but the conductance of complex VI in acetonitrile solution is low for a 1 : 1 electrolyte. However, on ^{1}H-NMR investigation described below can account for these apparent discrepancies.

The infrared spectra of the complexes show the characteristic absorptions of the neutral ligands. Table 2 shows that the N–H stretching vibrations of coordinated amines appear at frequencies lower than those observed for the free ligands. In the case of complexes I, V, VII and VIII the number of infrared bands in this region is larger than the two bands expected for the antisymmetric and symmetric vibrational modes of the primary amines, and this may be due to hydrogen-bonding interactions between the coordinated amine and PF_6^- or H_2O, respectively. The presence of water in some of the complexes is confirmed by the appearance of strong absorptions at 3450–3350 cm^{-1} due to ν(OH), and a strong, broad band at 830 cm^{-1} in the spectrum of complex VII is assignable to the PF_6^- anion [10]. The $C\equiv N$ stretching frequency of free 4-CNpy is virtually unaltered in complex III, suggesting that the ligand is not nitrile bonded, and the blue shift of the ring C–C and C–N stretching vibrations indicates coordination through the pyridine nitrogen [11]. The important infrared bands of uncoordinated taz are found at 3320, 3220 (ν(NH)), 1665 (ν(C=O)), and 1380 (the thioamide band II [12,13]) cm^{-1}. As can be seen in Table 2, the 4-NH_2-nitrogen of taz is involved in coordination, but the C=O stretching vibration is shifted to higher wavenumber, indicating that the carbonyl group remains uncoordinated and that the C=O oxygen of the free ligand is likely to be involved in hydrogen bonding. However, the presence of a band at 1360 cm^{-1} is

Table 3

NMR data for complexes IV and VII

Complex	^{1}H δ (ppm) (SiMe$_4$)	^{13}C{^{1}H} δ (ppm) (SiMe$_4$)
[Cp*RhCl$_2$(taz)] [a] (IV)	11.76 (d, 1H, NH$_2$, J(HH) 8.6 Hz)	172.41 (s, CS)
	7.46 (d, 1H, NH$_2$, J(HH) 8.6 Hz)	151.56 (s, CO)
	3.90 (s, 3H, 2-CH$_3$ of taz)	150.86 (s, C–CH$_3$ of taz)
	2.31 (s, 3H, 6-CH$_3$ of taz)	97.97 (d, Cp* ring, J(RhC) 8.3 Hz)
	1.86 (s, 15 H, CH$_3$ of Cp*)	46.18 (s, 2-CH$_3$ of taz)
		16.55 (s, 6-CH$_3$ of taz)
		9.61 (s, CH$_3$ of Cp*)
[Cp*RhCl(opda)]PF$_6$ [b] (VII)	7.4 (m, 2H, 3- and 6-H of opda)	139.78 (s, C–NH$_2$)
	7.1 (m, 2H, 4- and 5-H of opda)	128.24 (s, C–H of opda)
	6.76 (d, 2H, NH$_2$, J(HH) 11 Hz)	127.37 (s, C–H of opda)
	5.97 (d, 2H, NH$_2$, J(HH) 11 Hz)	95.63 (d, Cp* ring, J(RhC) 8.4 Hz)
	1.95 (s, 15H, CH$_3$)	9.06 (s, CH$_3$)

[a] Solvent CDCl$_3$. [b] Solvent (CD$_3$)$_2$CO.

attributed to a weak interaction between the metal atom and the C=S sulphur atom. In the nickel complex [Ni(H$_2$O)$_2$(taz)$_2$]$^{2+}$, for which an X-ray diffraction study has shown the chelating nature of taz, the thioamide band II is found at 1340 cm^{-1} [14]. Finally, a band observed in the spectra of our complexes at ca. 280 cm^{-1} is assigned to the Rh–Cl stretching vibration [4].

The ^{1}H-NMR study shows the great stability of the starting compound [{Cp*RhCl(μ-Cl)}$_2$]. When some of the complexes are dissolved, partial or complete dissociation occurs and they revert to the parent complex. Thus the ^{1}H-NMR spectrum of complex VI exhibits two signals assignable to the Cp* protons at 1.60 and 1.74 ppm (with relative intensities of 2.5 : 1). The former is due to [{Cp*RhCl(μ-Cl)}$_2$], in good agreement with an early assignment [1], and the latter is attributed to the new complex VI. The equilibrium reaction represented by eq. 1

$$[\mathrm{Cp^{\star}RhCl(opda)}]\mathrm{Cl} \rightleftharpoons \tfrac{1}{2}\left[\{\mathrm{Cp^{\star}RhCl}(\mu\text{-}\mathrm{Cl})\}_2\right] + \mathrm{opda} \tag{1}$$

accounts for the experimental result. In fact, addition of opda to the solution causes the disappearance of the resonance peak at 1.60 ppm, i.e., the equilibrium reaction is shifted to the left-hand side. Complexes I–III, V, VIII and IX must be completely dissociated in DMSO-d_6 solution because only a resonance signal for the Cp* protons is found at 1.60 ppm. In contrast, complexes IV and VII give only singlets at 1.95 and 1.86 ppm, respectively, suggesting that they do not undergo dissociation. The ^{1}H- and ^{13}C-NMR data for IV and VII are listed in Table 3. The ^{1}H spectra clearly show that the N-bonded hydrogens in coordinated taz and opda behave as a pair of diastereotopic protons, indicating that there is hindered rotation of the neutral ligands about the Rh–N bond. This result provides further evidence for the presence of some Rh–S interaction in the taz complex. The conductance values given in Table 1 can be explained on the basis of the above results.

The thermogravimetric data for the rhodium complexes are shown in Table 4. The oatp and ppda complexes decompose directly to give metallic rhodium, but the others liberate the water of hydration and/or the neutral ligand to give [{Cp*RhCl(μ-Cl)}$_2$], which subsequently decomposes to yield metallic rhodium. This indicates that the chloro-bridged complex is also the most thermally stable.

Thermoanalytical data for the rhodium complexes [a]

Complex	Step	Temperature range (°C)	DTG_{max} (°C)	Weight loss (%)	Assignment	Weight loss calc. (%)
$[Cp^{*}RhCl_2(oap)]\cdot 0.5H_2O$	1	104–160	138	2.3	$0.5\ H_2O$	2.1
	2	180–264	251	24.5	oap	25.5
	3	297–630	371	48.0	$Cp^{*} + 2\ Cl$	48.2
	residue	> 700	–	25.1	Rh^0	24.1
$[Cp^{*}RhCl_2(oatp)]\cdot 2H_2O$	1	50–152	132	8.3	$2\ H_2O$	7.7
	2	185–450	219	69.2	$oatp + Cp^{*} + 2\ Cl$	70.4
	residue	> 500	–	22.5	Rh^0	22.9
$[Cp^{*}RhCl_2(4CNpy)]$	1	140–214	204	25.9	4CNpy	25.2
	2	288–474	327	43.4	$Cp^{*} + 2\ Cl$	49.9
	residue	> 700	–	30.5	Rh^0	24.9
$[\{Cp^{*}RhCl_2\}_2(\mu\text{-ppda})]$	1	200–450	298	72.3	$ppda + Cp^{*} + 2Cl$	71.6
			347			
			386			
	residue	> 500	–	27.7	Rh^0	28.4
$[Cp^{*}RhCl(opda)]Cl$	1	190–275	257	25.0	opda	25.9
	2	296–519	363	48.8	$Cp^{*} + 2\ Cl$	49.4
			443			
	residue	> 600	–	26.2	Rh^0	24.7
$[Cp^{*}RhCl(en)]Cl\cdot 2H_2O$	1	50–196	160	23.8	$2\ H_2O + en$	23.7
	2	249–580	273	49.0	$Cp^{*} + 2\ Cl$	50.9
			315			
			451			
	residue	> 600	–	27.2	Rh^0	25.4
$[Cp^{*}RhCl(tmed)]Cl\cdot 2H_2O$	1	40– 80	65	9.3	$2\ H_2O$	7.8
	2	80–197	95	22.3	tmed	25.1
	3	260–440	299	41.1	$Cp^{*} + 2\ Cl$	44.6
	residue	> 500	–	27.3	Rh^0	22.3

[a] Under dynamic nitrogen atmosphere (heating rate 10 °C/min).

Experimental

All the operations were carried out under nitrogen. The solvents were dried by conventional methods. With the exception of taz, which was prepared as described elsewhere [15], the neutral ligands were obtained from commercial sources. Pentamethylcyclopentadiene and dichloro(pentamethylcyclopentadienyl)rhodium were prepared by published procedures [1,16]. ^{1}H- and ^{13}C-NMR spectra were recorded on a Bruker AC 200E instrument. IR spectra were recorded on a Perkin–Elmer 1430 spectrophotometer as Nujol mulls. The C, H and N analyses were performed with a Perkin–Elmer 240C microanalyzer. Thermal decomposition studies were carried out on a Mettler TG-50 thermobalance. Conductivities were measured with a Crison 525 conductimeter.

Preparation of the complexes

The relevant ligand (0.32 mmol; but 0.16 mmol for ppda) was added to a dichloromethane (10 mL) solution of $[\{Cp^{\star}RhCl(\mu\text{-}Cl)\}_2]$ (100 mg; 0.16 mmol) under nitrogen and the mixture was stirred at room temperature for ca. 30 min. The expected rhodium complex either separated (opda, ppda, oap, and oatp complexes) during this period or was precipitated by addition of diethyl ether (en, tmen, 4-CNpy, and taz complexes). Except for the tmen and taz complexes, which were filtered off and dried under nitrogen, the solids were filtered off and dried in the air.

$[Cp^{\star}RhCl(opda)]PF_6$. Addition of an ethanol (5 mL) solution of complex VI (100 mg) to a solution of KPF_6 (100 mg) in water (5 mL) resulted in the formation of an orange-yellow precipitate, which was filtered off and dried in the air. The compound was recrystallized from acetone–ethanol.

The colours and yields of the complexes are listed in Table 1.

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