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SYNTHESIS OF NEW CATIONIC COMPLEXES OF RHODIUM(I)

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SUMMARY

New rhodium(I) cationic complexes containing 2,2'-bipyridine and 1,10-phenanthroline in 1/1 metal/chelate ratios have been prepared and their reactions studied. Displacement reactions are discussed in terms of the nature of the entering ligands.

Our interest has been recently focused on the synthesis and reactivity of transition metal complexes of bidentate chelating systems having delocalized electronic structures. A 1/1 metal/chelate ratio has been selected as a useful system for studying the effect of the chelating agent on the free coordination positions[1]. Syntheses of some complexes of this kind are reported in literature[2], but their reactivity has received little attention. However, some communications[3] on the topic appeared during the course of our work.

We describe below results on the chemical behaviour of some new cationic complexes of rhodium(I) containing bidentate chelating ligands.

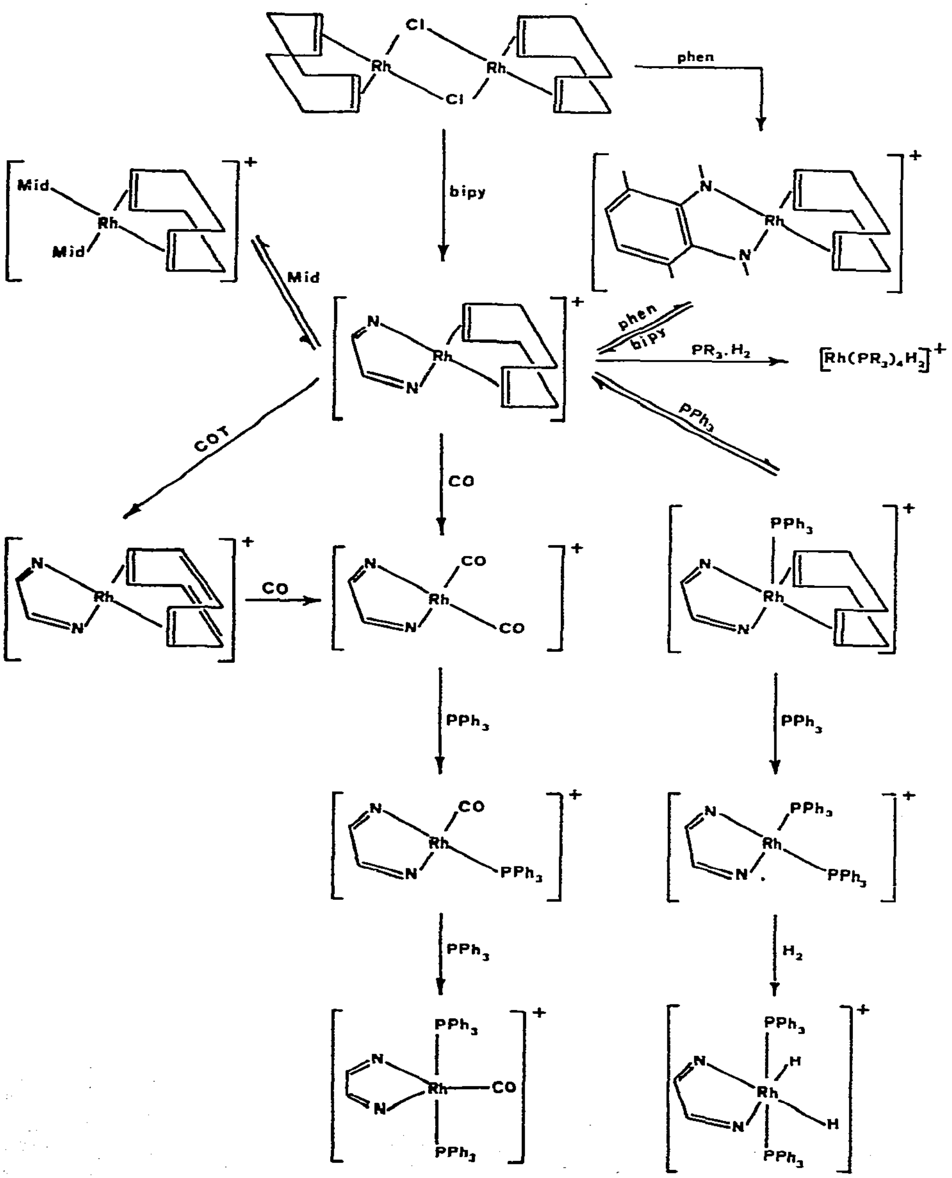
RESULTS AND DISCUSSION

As starting products we chose the complexes $[\mathrm{Rh^I BipyCOD}]\mathrm{ClO_4}$ and $[\mathrm{Rh^I PhenCOD}]\mathrm{Cl}$ (Bipy = 2,2'-bipyridine, Phen = 1,10-phenanthroline, COD = 1,5-cyclooctadiene), previously prepared by Chatt and Venanzi[4]. As those authors pointed out, the agreement between analytical data and calculated values was not satisfactory, and so we reexamined the preparation of these compounds. Good analyses can be obtained of the complexes of the type $[\mathrm{Rh^I ChelCOD}]\mathrm{X}$ (Chel = Bipy or Phen, $\mathrm{X} = \mathrm{ClO_4^-}$, $\mathrm{PF_6^-}$, $\mathrm{BPh_4^-}$), using the method of preparation described by Chatt and Venanzi, These complexes can be more easily made, however, by treating $[\mathrm{Rh^I CODCl}]_2$ in methanol with an excess of chelate, followed by the addition of the corresponding anion. All the compounds are red crystalline solids, slightly soluble in methanol, acetone, dichloromethane and chloroform. IR spectra show the characteristic bands of the coordinate chelate and of the ionic anion. There is also a doublet in the 360–340 $\mathrm{cm^{-1}}$ region, which is possibly to be attributed to the coordinated COD[5].

As expected the coordinatively unsaturated $[\mathrm{RhBipyCOD}]\mathrm{ClO_4}$ (I) is kinetically labile, and useful for the synthesis of new cationic derivatives of $\mathrm{Rh^I}$. We discovered that cyclooctadiene and bipyridine can be easily replaced by π-acids and heterocyclic Lewis bases respectively. Thus complex (I) reacts with cyclooctatetraene (COT) to give the orange-coloured [RhBipy COT]ClO_4. Both complexes react with carbon monoxide to give the yellow complex [RhBipy$(CO)_2$]ClO_4 [ν(CO) 2103–2044; lit. 2108–2050[3] cm^{-1}] in high yield. IR spectra are in agreement with the proposed structures.

Complex (I) reacts also with an excess of triphenylphosphine to give the pentacoordinate adduct [RhBipyCODPPh_3]ClO_4. This reaction is reversible.

SCHEME 1



If it is carried out under hydrogen the white crystalline complex $[Rh^{III}Bipy(PPh_3)_2H_2]ClO_4$ [ν(Rh-H) 2058–2041 cm^{-1}] can be isolated suggesting the existence of an $[Rh^{I}$-$Bipy(PPh_3)_2]^+$ intermediate.

From the reaction of $[RhBipy(CO)_2]ClO_4$ with triphenylphosphine in 1/1 ratio the corresponding adduct cannot be isolated because an easy replacement of one CO molecule occurs, to give the complex $[RhBipy(PPh_3)CO]ClO_4$ [ν(CO) 1985 cm^{-1}], in equilibrium with the starting product and the pentacoordinated $[RhBipy(PPh_3)_2CO]ClO_4$ derivative [ν(CO) 1912 cm^{-1}]. The last complex can be obtained in a high yield by use of an excess of triphenylphosphine, as previously reported by Reddy *et al.*[3].

Complex (I) reacts with nitrogen-donor ligands as *N*-methylimidazole (Mid), imidazole, pyridine and phenanthroline to give the corresponding $[(L)_2RhCOD]^+$, the Bipy being the only chelate replaced. All these reactions are reversible.

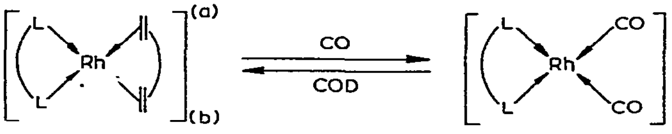
Use of trialkylphosphine gives the corresponding pentacoordinated adducts $[RhBipyCODPR_3]ClO_4$ [$PR_3 = PEt_2Ph$, PEt_3, PPr_3, PBu_3]. If these reactions are performed under hydrogen, Rh^{III} complexes of formula $[Rh^{III}(PR_3)_4H_2]ClO_4$ were obtained*. The NMR spectrum of the PBu_3 derivative, resembled that described by Schrock and Osborn[7] for $[Rh(PMe_3)_4H_2]^+$, and indicates that in this series the two hydrogens are also in *cis* position.

The derivative with diethylphenylphosphine appears to be a useful hydrogenation catalyst, a phosphine molecule being easily cleaved from the complex, to give a catalyst for the reduction of ethylene to ethane. The chemical behaviour of these compounds will be described in a separate paper.

As can be seen from a survey of the reactions carried out with $[RhBipyCOD]ClO_4$ (see Scheme 1), π-acceptor ligands displace π-coordinate olefins, while mainly σ-donor ligands displace bipyridine; as a rule, the entering ligand displaces only a chelate of a similar nature.

An explanation may be that a π-acceptor group while entering weakens the metal–olefin bond, thus favouring its displacement; on the other hand the entrance of mainly σ-donor ligands, by increasing the charge density on the rhodium atom, should strengthen the π-olefinic and weaken the metal–nitrogen bond, favouring the displacement of bipyridine. This behaviour means that the preparation of well-known complexes such as $[RhBipy_2]^+$[8] or $[Rh(PPh_3)_2(CO)_2]^+$[9] is not possible, but it enables a study to be made of substitution reactions of π-acid ligands without bipyridine displacement.

Complexes of the type [RhChel(diolefin)] (Chel = acetylacetonate[10], oxinate[11], salicylaldoximate[11] and salicylaldiminates[12]) show similar behaviour. However the lability of monoanion chelates has not yet been taken into consideration.



(a) LL = Bipy (b) LL=Acac

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* The existence of $[Rh(PBu_3)_4H_2]BPh_4$ has recently been reported[6].

It is interesting to note the different behaviour of Rh–Bipy and Rh–Acac systems with respect to the COD→CO exchange reaction.

It is known that $[AcacRh(C_2H_4)_2]$ reacts with carbon monoxide to give the corresponding dicarbonyl derivative[13], showing that the Rh–CO is more stable than the $Rh–C_2H_4$ bond, while with a chelating diolefin the reaction proceeds in the opposite direction (see b). Such behaviour can be ascribed predominantly to entropy effects, but when L–L = Bipy the reaction is again shifted towards the right in spite of the unfavourable variation of entropy. Furthermore, the stretching frequencies of corresponding series of carbonyl derivatives[10,12] (see Table 1) reveal that the Rh–CO bond is weaker in complexes with bipyridine than in the acetylacetonate derivatives. These facts can be explained assuming a decreased back-donation from rhodium to π-ligands, owing to the smaller charge density induced on the metal by bipyridine than by the monoanion chelate.

TABLE 1

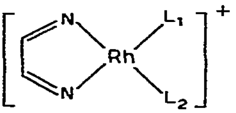
CO STRETCHING FREQUENCIES OF CARBONYL DERIVATIVES (NUJOL)

Complex	ν(C=O) (cm^{-1})
$[RhBipy(CO)_2]ClO_4$	2103–2044
$[RhBipy(PPh_3)CO]ClO_4$	1985
$[RhAcac(CO)_2]$	2083–2015[a]
$[RhAcac(PPh_3)CO]$	1980
$[Rh(Sal{=}N{-}Ph)(CO)_2]$	2090–2031
$[RhSal{=}N{-}Ph(PPh_3)CO]$	1962

[a] In petroleum ether.

As the π-acceptor capacity of the diolefin is more important than its σ-donor capacity in determining the strength of the metal–olefin bond[14], so in these complexes of bipyridine the Rh–diolefin system is much more weakened than the Rh–CO bond, and this favours the displacement of the coordinated diolefin.

As far as the oxidative addition reactions of molecular hydrogen are concerned, complexes of the type:



$L_1 = L_2 = 1/2\ COD$
$L_1 = L_2 = CO$
$L_1 = CO, L_2 = PPh_3$
$L_1 = L_2 = PPh_3$

allow the synthesis of stable hydride derivatives of Rh^{III}, only when $L_1 = L_2 = PPh_3$. They have a structure similar to the corresponding cobalt complexes[1].

A more detailed study on these reactions will be reported together with the corresponding iridium complexes in our next paper.

EXPERIMENTAL

Unless otherwise noted preparations were performed at room temperature in the air. Analytical data are listed in Table 2.

TABLE 2

ANALYTICAL DATA FOR THE ISOLATED COMPLEXES

Number	Complex	Colour	Analyses found (calc) (%)			
			C	H	N	P
(I)	$[RhBipyCOD]ClO_4$	Red	46.2	4.31	6.12	
			(46.32)	(4.30)	(6.00)	
(II)	$[RhBipyCOD]PF_6$	Red	41.9	3.91	5.61	
			(42.20)	(3.93)	(5.47)	
(III)	$[RhBipyCOD]BPh_4$	Red	73.1	5.62	4.11	
			(73.4)	(5.87)	(4.08)	
(IV)	$[RhPhenCOD]ClO_4$	Red	48.7	4.15	5.70	
			(48.95)	(4.11)	(5.71)	
(V)	$[RhBipyCOT]ClO_4$	Orange	46.0	3.27	5.93	
			(46.72)	(3.47)	(6.05)	
(VI)	$[RhBipy(CO)_2]ClO_4$	Yellow	34.0	1.95	6.74	
			(34.76)	(1.94)	(6.76)	
(VII)	$[RhBipyCOD(PPh_3)]ClO_4$	Red	58.8	4.79	3.92	
			(59.30)	(4.84)	(3.84)	
(VIII)	$[RhBipy(PPh_3)_2H_2]ClO_4$	White	60.6	4.54	3.18	
			(62.40)	(4.55)	(3.17)	
(IX)	$[RhBipy(PPh_3)CO]ClO_4$	Yellow	53.0	3.47	4.32	
			(53.69)	(3.57)	(4.31)	
(X)	$[RhBipy(PPh_3)_2CO]ClO_4$	Light yellow	61.9	4.05	3.06	
			(61.96)	(4.21)	(3.07)	
(XI)	$[Rh(C_4H_6N_2)_2COD]BPh_4$	Yellow	68.9	6.22	8.35	
			(69.19)	(6.38)	(8.06)	
(XII)	$[RhBipyCOD(PEt_2Ph)]ClO_4$	Orange	52.8	5.55	4.57	
			(53.14)	(5.57)	(4.42)	
(XIII)	$[RhBipyCOD(PEt_3)]ClO_4$	Red	48.9	6.15	4.93	
			(49.28)	(6.03)	(4.79)	
(XIV)	$[RhBipyCOD(PPr_3)]ClO_4$	Yellow	51.3	6.48	4.52	
			(51.72)	(6.59)	(4.46)	
(XV)	$[RhBipyCOD(PBu_3)]ClO_4$	Cream	54.0	7.17	4.21	
			(53.85)	(7.08)	(4.19)	
(XVI)	$[Rh(PEt_2Ph)_4H_2]ClO_4$[a]	White	53.3	6.90		14.51
			(55.28)	(7.19)		(14.26)
(XVII)	$[Rh(PEt_3)_4H_2]ClO_4$[a]	White	40.1	8.93		16.91
			(42.58)	(9.23)		(18.30)
(XVIII)	$[Rh(PPr_3)_4H_2]ClO_4$[a]	White	48.8	9.91		14.17
			(51.15)	(10.25)		(14.66)
(XIX)	$[Rh(PBu_3)_4H_2]ClO_4$	White	57.4	11.26		12.50
			(56.85)	(10.94)		(12.23)

[a] These complexes lose phosphine easily.

[RhCODCl]$_2$ was prepared by Chatt and Venanzi's procedure[4].

[RhBipyCOD]X ($X = ClO_4^-$, PF_6^-, BPh_4^-) [(I)–(III)] 0.47 g (3 mmoles) Bipy were added to 0.49 g (1 mmole) of $[RhCODCl]_2$ suspended in 30 ml methanol or ethanol, to give a deep red solution. On addition of an aqueous solution of the anion the complexes separated as red crystals. They were recrystallized from hot methanol.

[RhPhenCOD]ClO$_4$ *(IV)* was similarly obtained. This complex can be also prepared treating (I) with an excess of Phen·H_2O in methanol.

Reaction of (I) with cyclooctatetraene

(I) 0.47 g (1 mmole) in a 1/1 mixture of methanol/dichloromethane was treated with 2 ml of cyclooctatetraene. After several hours the solvents were partially evaporated and the complex (V) separated.

Reaction of (I) or (V) with carbon monoxide

A deaerated suspension of 0.47 g (1 mmole) of (I) or (V) in 25 ml methanol was saturated with carbon monoxide to give a yellow solution, from which (VI) separated.

Reaction of (I) with triphenylphosphine

An ethereal solution (15 ml) of 0.2 g (0.8 mmoles) triphenylphosphine was added to a methanolic solution (15 ml) of 0.2 g (0.4 mmoles) of (I). The solid (VII), which separated, was filtered and washed with ether.

Reaction of (I) with triphenylphosphine and hydrogen

This reaction was carried out as above, but under hydrogen. After several hours a light yellow solution was formed, from which a crystalline solid (VIII) was precipitated by adding an aqueous solution of $NaClO_4$ and partially evaporating the solvent.

Reaction of $[RhBipy(CO)_2]ClO_4$ *with triphenylphosphine*

An ethanolic suspension (30 ml) of 0.4 g (1 mmole) of the dicarbonyl derivative was treated under nitrogen with 0.26 g (1 mmole) of triphenylphosphine. After 4 h a yellow solution was formed along with a yellow solid. From IR spectra it was identified as a mixture of $[RhBipy(CO)_2]ClO_4$, $[RhBipyCO(PPh_3)_2]ClO_4$ and $[RhBipyCO(PPh_3)]ClO_4$. From the filtered solution the complex $[RhBipyCO(PPh_3)]ClO_4$ (IX) was obtained by evaporation. With a 1/2 $[RhBipy(CO)_2]ClO_4/PPh_3$ ratio, only the light yellow solid $[RhBipyCO(PPh_3)_2]ClO_4$ (X) was obtained.

$[Rh(C_4H_6N_2)_2COD]BPh_4$ *(XI)*

N-Methylimidazole was added to 0.23 g (0.5 mmoles) of (I) suspended in 15 ml methanol, until a yellow solution formed. A methanolic solution of $NaBPh_4$ was added, and then water was added until precipitation began. The crystalline product was separated by evaporation.

The reactions with imidazole, pyridine, and phenanthroline were carried out similarly.

$[Rh(Bipy)CODPR_3]ClO_4$ *[(XII)–(XV)]* $(PR_3 = PEt_2Ph, PEt_3, PPr_3, PBu_3)$

(I) 0.46 g (1 mmole) in 50 ml of a 3/1 ether/methanol mixture treated with 0.4 ml of tertiary phosphine under nitrogen gave an orange solution, from which crystalline products precipitated. The solids were filtered off and washed with light petroleum ether.

$[Rh(Pr_3)_4H_2]ClO_4$ *[(XVI)–(XIX)]* $(PR_3 = PEt_2Ph, PEt_3, PPr_3, PBu_3)$

(I) 0.46 g (1 mmole) in 50 ml methanol treated with 0.6 ml of tertiary phosphine under hydrogen gave a colourless solution after several hours. Addition of aqueous $NaClO_4$ and evaporation of the solvent gave a white crystalline solid. This was filtered off and recrystallized by dissolving it in acetone/methanol and precipitation by concentration after addition of water.

Reaction of $[Rh(PEt_2Ph)_4H_2]ClO_4$ *with ethylene*

(XVI) dissolved in $CHCl_3$ gave a yellow solution with a strong IR absorption in the Rh–H region [ν(Rh–H) 2016 cm^{-1}]. When the mixture was saturated with ethylene it turned red and the Rh–H band disappeared. GSC of the gaseous phase showed that ethane was formed.

Techniques

IR spectra were recorded as Nujol mulls with a Perkin–Elmer 225 spectrophotometer.

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