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CATIONIC RHODIUM(I) ORGANIC COMPLEXES WITH NITROGEN DONORS AND THEIR CARBONYLATION PRODUCTS

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Summary

The preparation and properties of eleven new cationic rhodium(I) complexes with mono- and bi-dentate nitrogen donor ligands are described. Their carbonylation at normal pressure leads to the corresponding dicarbonyl compounds, in which one of the CO groups can be replaced by PPh_3.

Introduction

Recently several series of cationic rhodium(I) organic complexes with 1,5-cyclooctadiene (COD) and other ligands with Group VB donor atoms, have been prepared. Their carbonylation reactions have also been studied. Amongst the nitrogen donors, pyridine and its substituted derivatives 1,2-bipyridine and 1,10-phenanthroline have been used [1—4].

The present paper reports cationic complexes of the type $[(COD)Rh(L—L)]^+$, (L—L) being ethylenediamine (en), 1,2-propylenediamine (pn), 1,3-propylenediamine (npn), *N,N,N′,N′*-tetramethylethylenediamine (tmen), 1,1′,2,2′-tetraethylethylenediamine (ntem), 1,2-diphenylethylenediamine (ndfen), *N,N′*-diphenylethylenediamine (dfen), 2,*N,N′*-triphenylethylenediamine (trfen), along with monodentate N-donor complexes of the type $[(COD)RhL_2]^+$, L being quinoline (quin), isoquinoline (iquin) and pyridine (py). The associated anion is in every case the perchlorate ClO_4^-.

Results and discussion

(a) Preparation and properties of the cationic complexes

The addition of N-donor ligands to $[(COD)_2Rh]ClO_4$ [1,5] dissolved in the minimal amount of dichloromethane results in the inmediate replacement of

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TABLE 1

ANALYTICAL DATA FOR THE COMPLEXES $[(1,5\text{-}C_8H_{12})RhL_2]ClO_4$

Complex	Found (calcd.) (%)			Λ_M (ohm^{-1} cm^2 mol^{-1})	M.p. (°C)
	C	H	N		
[(COD)Rh(en)]ClO$_4$ (I)	30.86	5.40	7.68	133	190 ^{b}
	(30.73)	(5.12)	(7.17)		(180—200)
[(COD)Rh(pn)]ClO$_4$ (II)	32.14	5.41	6.65	112	190 ^{b}
	(31.42)	(5.23)	(6.66)		(180—200)
[(COD)Rh(npn)]ClO$_4$ (III)	32.65	5.37	7.39	133	152 ^{b}
	(31.42)	(5.23)	(6.66)		(145—160)
[(COD)Rh(tmen)]ClO$_4$ (IV)	39.00	6.49	6.09	104	197 ^{b}
	(39.37)	(6.49)	(6.56)		(190—205)
[(COD)Rh(nt nen)]ClO$_4$ (V)	38.16	6.36	6.32	126	220 ^{b}
	(39.37)	(6.49)	(6.56)		(210—230)
[(COD)Rh(ndfen)]ClO$_4$ (VI)	49.05	5.05	5.15	124	195 ^{b}
	(50.05)	(5.35)	(5.35)		(190—200)
[(COD)Rh(dfen)]ClO$_4$ (VII)	47.76	4.92	4.75	126	207 ^{b}
	(49.86)	(5.60)	(4.97)		(200—215)
[(COD)Rh(trfen)]ClO$_4$ (VIII)	54.90	5.34	4.35	106	207 ^{b}
	(56.10)	(5.40)	(4.67)		(200—215)
[(COD)Rh(quin)$_2$]ClO$_4$ (IX)	53.69	4.64	4.57	116	185 ^{b}
	(54.86)	(4.57)	(4.92)		(180—190)
[(COD)Rh(iquin)$_2$]ClO$_4$ (X)	53.72	4.32	5.12	100	165 ^{b}
	(54.86)	(4.57)	(4.92)		(160—170)
[(COD)Rh(py)$_2$]ClO$_4$ (XI)	45.33	4.50	5.96	146	135 ^{a}
	(46.12)	(4.69)	(5.97)		

[a] Melts under decomposition. [b] Decomposes.

one mole of (COD) according to eq. 1.

$$[(COD)_2Rh]ClO_4 + (L\text{—}L) \rightarrow [(COD)Rh(L\text{—}L)]ClO_4 + (COD) \qquad (1)$$

The complexes can also be prepared by adding the ligand to an ethanol solution of $[(COD)RhCl]_2$. The precipitation of the cationic complex is then accomplished by adding sodium perchlorate.

The complexes obtained by both methods are listed in Table 1. They are yellow solids, which decompose before melting and behave as completely dissociated 1/1 electrolytes in acetone. The vibrations which could be assigned in the IR spectra of complexes with (L—L) = diamine, along with the $\Delta\nu$(N—H) of the free and of the coordinated ligand, are listed in Table 2.

The reaction of complexes (I—XI) with triphenylphosphine or triphenylphosphite leads to substitution of the nitrogen donor (eq. 2), whereas, in the case

$$[(COD)Rh(L\text{—}L)]^+ + 2PR_3 \rightarrow [(COD)Rh(PR_3)_2]^+ + (L\text{—}L) \qquad (2)$$

of $[(COD)Rh(bipy)]^+$ the reaction with these ligands gives rise to the replacement of the (COD) [3]. No reaction takes place with triphenylarsine.

(b) Carbonylation reactions

The bubbling of carbon monoxide at ordinary pressure through suspensions or solutions of complexes I—XI leads to the displacement of the (COD) and to the formation of the corresponding dicarbonyl derivative according to

TABLE 2

IR DATA FOR THE COMPLEXES $[(1.5\text{-}C_8H_{12})Rh(diamine)]ClO_4$

Assignation (cm^{-1})	Complex							
	I	II	III	IV	V	VI	VII	VIII
ν(N—H)	3320	3285	3300		3280	3280		
ν(N—H)	3265	3240	3250		3240	3240	3200	3200
$\Delta\nu$(N—H)	60	65	80		60	60		
$\Delta\nu$(N—H)	35	50	50		40	20	200	180
1,5-C_8H_{12}	1330, 1310	1320, 1300	1330, 1300	1340, 1310	1330, 1300	1330, 1300	1330, 1300	1330, 1300
ClO_4^-	1080, 615	1080, 600	1080, 610	1090, 610	1080, 610	1080, 610	1090, 600	1090, 610

eq. 3. These compounds XII—XIX can also be obtained from $AgClO_4$ and

$$[(COD)Rh(L\text{—}L)]ClO_4 + 2CO \rightarrow (COD) + [(CO)_2Rh(L\text{—}L)]ClO_4 \qquad (3)$$

$[(CO)_2RhCl]_2$ in acetone. The precipitated AgCl is filtered off, and the N-donor ligand added to the filtrate to give $[(CO)_2Rh(L\text{—}L)]ClO_4$.

Table 3 lists the analytical data for complexes XII—XXII. The measured conductivities show the complexes to be 1/1 electrolytes. The ν(C=O) absorptions appeared in every case as two strong bands in the 2100—2000 cm^{-1}

TABLE 3

ANALYTICAL DATA FOR THE COMPLEXES $[(CO)_2RhL_2]ClO_4$

Complex	Found (calcd.) (%)			Λ_M (ohm^{-1} cm^2 mol^{-1})	M.p. (°C)	ν(C≡O) (cm^{-1})
	C	H	N			
$[(CO)_2Rh(en)]ClO_4$ (XII)	15.70	2.60	8.70	106	157 [b]	2080—2000
	(15.07)	(2.51)	(8.79)		(155—160)	
$[(CO)_2Rh(pn)]ClO_4$ (XIII)	19.47	3.34	8.45	125	165 [b]	2080—2000
	(18.05)	(3.03)	(8.42)		(160—170)	
$[(CO)_2Rh(npn)]ClO_4$ (XIV)	18.89	3.28	7.95	112	98 [a]	2080—2010
	(18.05)	(3.03)	(8.42)			
$[(CO)_2Rh(tmen)]ClO_4$ (XV)	25.61	4.90	7.23	124	165 [b]	2080—2010
	(25.63)	(4.27)	(7.40)		(163—170)	
$[(CO)_2Rh(ntmen)]ClO_4$ (XVI)	25.06	4.26	7.16	116	205 [b]	2080—2000
	(25.63)	(4.27)	(7.40)		(200—210)	
$[(CO)_2Rh(ndfen)]ClO_4$ (XVII)	40.18	3.45	6.00	109	190 [b]	2080—2000
	(40.80)	(3.40)	(5.95)		(185—195)	
$[(CO)_2Rh(dfen)]ClO_4$ (XVIII)	39.45	3.44	5.67	106	205 [b]	2080—2000
	(40.80)	(3.40)	(5.95)		(203—207)	
$[(CO)_2Rh(trfen)]ClO_4$ (XIX)	45.72	3.90	5.94	112	178 [b]	2080—2000
	(46.12)	(3.66)	(5.12)		(178—185)	
$[(CO)_2Rh(quin)_2]ClO_4$ (XX)	48.30	3.51	5.25	131	125 [b]	2090—2015
	(46.55)	(2.71)	(5.42)		(120—130)	
$[(CO)_2Rh(iquin)_2]ClO_4$ (XXI)	45.11	3.01	5.43	126	137 [b]	2080—2020
	(46.55)	(2.71)	(5.42)		(130—145)	
$[(CO)_2Rh(py)_2]ClO_4$ (XXII)	33.89	2.62	6.37	140	120 [b]	2095—2015
	(34.59)	(2.40)	(6.72)		(110—130)	

[a] Melts under decomposition. [b] Decomposes;

region, characteristic for terminal carbonyls. The bands due to the ClO_4^- group (T_d) [6], along with those due to the respective N-donor, were observed in all cases. It is noteworthy that the IR spectrum of the previously described [4] $[(CO)_2Rh(py)_2]PF_6$ was reported to show bands in the 1800 cm^{-1} region which were attributed to the formation of dimeric cations of the type  $[(py)_2CORh\begin{smallmatrix}\diagup CO \diagdown\\ \diagdown CO \diagup\end{smallmatrix}RhCO(py)_2]^{2+}$. In the case of $[(CO)_2Rh(py)_2]ClO_4$ we did not observe any bands in the 1800 cm^{-1} region, whereas two intense bands along with two weak ones were recorded in the 2100—2000 cm^{-1} region.

Comparison of the ν(CO) absorptions of the complexes XII—XXII with those for the analogous complexes with (L—L) = bipy [3] reveals that these absorptions are shifted towards lower energies in the sequence bipy > py ~ quin ~ iquin > diamine; i.e. the order in which the π-acceptor capacity of the nitrogen donor ligand decreases. Therefore, the lower the π-acid character of the nitrogen ligand, the higher is the strength of the Rh—CO bond. This observation can probably be extended to the Rh—(COD) bonds of complexes I—XI, since PR_3 is able to displace [3] the (COD) of $[(COD)Rh(bipy)]^+$ but not the (COD) of $[(COD)Rh(L—L)]^+$ (see eq. 2).

(c) Displacement of one CO group

The addition of equimolar amounts of PPh_3 to dichloromethane solutions of the complexes XIV—XVI and XX—XXIII results in the formation of compounds of the $[CO(PPh_3)RhL_2]ClO_4$ type. The analytical data for the complexes are shown in Table 4. The compounds are yellow air-stable crystals, the IR spectra of which show a single band due to the vibration ν(CO) in the 2000 cm^{-1} region. The displacement of the second CO group could not be accomplished even by using an excess of triphenylphosphine.

TABLE 4

ANALYTICAL DATA FOR THE COMPLEXES $[COPPh_3RhL_2]ClO_4$

Complex	Found (calcd.) (%)			Λ_M (ohm^{-1} cm^2 mol^{-1})	M.p. (°C)	ν(C≡O) (cm^{-1})
	C	H	N			
$[COPPh_3Rh(npn)]ClO_4$ (XXIII)	47.41 (46.61)	4.77 (4.44)	4.55 (4.94)	105	187 [b] (185—190)	1998
$[COPPh_3Rh(tmen)]ClO_4$ (XXIV)	48.68 (49.31)	5.15 (5.13)	4.46 (4.60)	138	197 [b] (195—200)	2000
$[COPPh_3Rh(ntmen)]ClO_4$ (XXV)	48.92 (49.31)	5.28 (5.13)	4.30 (4.60)	130	207 [b] (205—210)	1998
$[COPPh_3Rh(quin)_2]ClO_4$ (XXVI)	58.45 (59.18)	4.79 (3.86)	3.25 (3.73)	126	127 [b] (125—130)	1995
$[COPPh_3Rh(iquin)_2]ClO_4$ (XXVII)	57.34 (59.18)	4.38 (3.86)	3.14 (3.73)	125	135 [b] (130—140)	1994
$[COPPh_3Rh(py)_2]ClO_4$ (XXVIII)	52.74 (53.52)	4.33 (3.84)	4.03 (4.30)	120	118 [a]	1994

[a] Melts under decomposition. [b] Decomposes.

TABLE 5

ANALYTICAL DATA FOR OTHER CATIONIC RHODIUM(I) COMPLEXES

Complex	Found (calcd.) (%)			Λ_M (ohm^{-1} cm^2 mol^{-1})	M.p. (°C)	ν(C≡O) (cm^{-1})
	C	H	N			
[(COD)RhPPh$_3$(quin)]ClO$_4$ (XXIX)	58.61	4.92	2.00	126	170 [b]	
	(59.89)	(4.84)	(1.99)		(160—180)	
[(COD)RhPPh$_3$(iquin)]ClO$_4$ (XXX)	59.31	5.15	2.08	135	135 [b]	
	(59.89)	(4.84)	(1.99)		(130—140)	
[(COD)RhPPh$_3$(py)]ClO$_4$ (XXXI)	57.39	5.24	2.23	127	150 [a]	
	(57.12)	(4.91)	(2.15)			
[(CO)$_2$RhPPh$_3$(quin)]ClO$_4$ (XXXII)	54.21	4.02	2.12	130	125 [b]	2090,
	(53.60)	(3.39)	(2.15)		(120—130)	2020,
						2000
[(CO)$_2$RhPPh$_3$(iquin)]ClO$_4$ (XXXIII)	52.91	3.81	2.07	123	115 [b]	2092,
	(53.60)	(3.39)	(2.15)		(110—120)	2018,
						1995

[a] Melts under decomposition. [b] Decomposes.

(d) Other substitution products

The addition of stoichiometric amounts of PPh$_3$ to complexes IX, X and XI leads to compounds of the type [(COD)RhL(PPh$_3$)]ClO$_4$. Their analytical data are listed in Table 5. On treating the latter with a carbon monoxide at normal pressure the (COD) is replaced and dicarbonylated complexes of the [(CO)$_2$RhL(PPh$_3$)]ClO$_4$ type are obtained (complexes XXXII and XXXIII). The complex with L being py was not isolated because it decomposes almost instantaneously. The IR spectra of the solid complexes show three bands due to ν(CO) in the 2100—2000 cm^{-1} region, probably because of lattice effects in the solids; the solutions show only the expected two bands.

The reaction of compounds of the [CORhL$_2$PPh$_3$]ClO$_4$ type (XXVI—XXVIII) and of the [(CO)$_2$RhL(PPh$_3$)]ClO$_4$ type (XXXII and XXXIII) with a mole of PPh$_3$ leads to complexes of the general formula [CORhL(PPh$_3$)$_2$]$^+$, previously described by Reddy and Ramesh [7].

Experimental

The C, H and N analyses were made with a Perkin—Elmer 240 microanalyzer. The IR spectra were recorded on a Beckman IR 20A spectrophotometer (over the range 4000—250 cm^{-1}) using Nujol mulls between NaCl discs. Conductivities were measured with a Philips PW 9501/01 conductimeter. Melting points were determined with a Reichert/Austria apparatus provided with microscope and heating device.

Synthesis of complexes of the type [(COD)RhL$_2$]ClO$_4$ (I—XI)

Upon addition of a stoichiometric amount of the ligand to a dichloromethane solution of di-1,5-cyclooctadienerhodium perchlorate the originally orange-red solution turned yellow. Reaction was inmediate at room temperature. The resulting complexes were precipitated by adding ether or n-pentane, filtered off, and washed with ether or n-pentane.

Synthesis of complexes of the type $[(CO)_2RhL_2]ClO_4$ (XII—XXII)

Complexes XII—XIX and XXI were prepared by bubbling carbon monoxide (1 atm) for 30 minutes through a dichloromethane solution or suspension of $[(COD)RhL_2]ClO_4$ at room temperature. The complexes were precipitated by adding ether or n-pentane, filtered off, and washed with ether or n-pentane.

The method was slightly modified in the case of complex XX and XXII. Carbon monoxide (1 atm) was bubbled for 4 h (XX) or for 1 h (XXII) through an n-pentane suspension of the appropriate $[(COD)RhL_2]ClO_4$ at room temperature. The resulting compound was filtered off and washed with n-pentane.

Synthesis of complexes of the type $[COPPh_3RhL_2]ClO_4$ (XXIII—XXVIII)

A stoichiometric amount of triphenylphosphine was added to a dichloromethane solution of the appropriate $[(CO)_2RhL_2]ClO_4$. The complexes were precipitated by adding ether or n-pentane, filtered off, and washed with ether or n-pentane.

Synthesis of complexes of the type $[(COD)RhPPh_3L]ClO_4$ (XXIX—XXXI)

A stoichiometric amount of triphenylphosphine was added to a dichloromethane solution of the appropriate $[(COD)RhL_2]ClO_4$. The resulting solution was stirred for a few minutes and the complexes were precipitated by adding ether, filtered off, and washed with ether.

Synthesis of complexes of the type $[(CO)_2RhPPh_3L]ClO_4$ (XXXII and XXXIII)

Carbon monoxide (1 atm) was bubbled for 1 h through a dichloromethane solution of the appropriate $[(COD)RhPPh_3L]ClO_4$. The complexes were precipitated by adding n-pentane, filtered off, and washed with n-pentane.

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