Journal of Organometallic Chemistry, 217 (1981) 251—257
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

CATIONIC RHODIUM(I) COMPLEXES WITH DIOLEFIN AND SUBSTITUTED PYRIDINE *N*-OXIDES AS LIGANDS

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(Received March 2nd, 1981)

Summary

The preparations of cationic rhodium(I) complexes of the types $[Rh(COD)L_2]ClO_4$ and $[Rh(COD)L(PPh_3)]ClO_4$ (L = substituted pyridine *N*-oxides) and the reactions of $[Rh(COD)(4\text{-}MePyO)_2]ClO_4$ with N, P, As, Sb and S-donor ligands are described.

Introduction

A large number of metallic complexes containing pyridine *N*-oxides have been described [1,2] but no such rhodium(I) complexes were previously known. Drago et al. [3] have shown by calorimetric studies that the interaction between $[RhCl(COD)]_2$ and O-donor ligands is practically negligible except for the ligand Me_2SO (DMSO). The only hitherto isolated cationic rhodium(I) diolefin complexes with O-donor ligands are of the types $[Rh(diolefin)(DMSO)_x]A$ [4,5], $[Rh(diolefin)(sulfoxide)PPh_3]A$ [6] and $[Rh(diolefin)(Me_2CO)(PR_3)]A$ [6,7].

We describe below the preparation of complexes of the type $[Rh(COD)L_2]ClO_4$ (COD = 1,5-cyclooctadiene; L = a substituted pyridine *N*-oxide) and of the related mixed-ligand complexes $[Rh(COD)LL']ClO_4$ (L′ = N or P-donor ligand).

Results and discussion

$[Rh(COD)L_2]ClO_4$ complexes

i) Addition of the ligand L to acetone solutions of $[Rh(COD)(Me_2CO)_x]ClO_4$, obtained by treating $[RhCl(COD)]_2$ with $AgClO_4$ [8], leads (eq. 1) to yellow solutions from which yellow solids can be isolated (complexes I—X; L = PyO (I); 2-MePyO (II); 3-MePyO (III); 4-MePyO (IV); 4-MeOPyO (V); 4-t-BuPyO (VI); 4-NO_2PyO (VII); 4-CNPyO (VIII); 2-BzPyO (IX) or 4-ClPyO (X)).

$$[Rh(COD)(Me_2CO)_x]ClO_4 + 2\ L \rightarrow [Rh(COD)L_2]ClO_4 + x\ Me_2CO \qquad (1)$$

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ii) An alternative route (eq. 2) gives poorer yields, and no reaction takes place with L = 4-NO_2PyO and 2-BzPyO.

$$[Rh(COD)_2]ClO_4 + 2\ L \rightarrow [Rh(COD)L_2]ClO_4 + COD \qquad (2)$$

iii) Attempts to prepare the corresponding BPh_4^- derivatives proved unsuccessful, since one of the phenyl groups of BPh_4^- becomes coordinated to the rhodium atom [9,10], displacing the ligands L to give the neutral complex Rh(COD)($PhBPh_3$) (eq. 3).

$$[Rh(COD)L_2]^+ + BPh_4^- \rightarrow Rh(COD)(PhBPh_3) + 2\ L \qquad (3)$$

The analytical results, conductivities, and yields for complexes I—X are listed in Table 1.

[Rh(COD)L(PPh_3)]ClO_4 complexes

i) Addition of PPh_3 to the complexes I—X results in displacement of one mole of pyridine *N*-oxide and formation of mixed complexes of the type [Rh(COD)L(PPh_3)]ClO_4. It is not necessary to isolate the complexes I—X, since the PPh_3 (1 mol) can directly be added to the solutions prepared according to eq. 2. Though 2-BzPyO does not react according to eq. 2, subsequent addition of PPh_3 causes a change in colour (from red to yellow) and the mixed complex can be isolated from the solution. No such reaction takes place for L = NO_2-PyO.

TABLE 1

ANALYTICAL RESULTS, MOLAR CONDUCTIVITIES AND YIELDS FOR THE COMPLEXES $[Rh(COD)L_2]ClO_4$

Complex	Found (calcd.) (%)			Λ_M (ohm^{-1} cm^2 mol^{-1})	Yield (%)
	C	H	N		
$[Rh(COD)(PyO)_2]ClO_4$ (I)	43.77	4.55	5.74	132	53
	(43.18)	(4.43)	(5.59)		
$[Rh(COD)(2\text{-}MePyO)_2]ClO_4$ (II)	45.29	4.92	5.51	139	74
	(45.43)	(4.96)	(5.30)		
$[Rh(COD)(3\text{-}MePyO)_2]ClO_4$ (III)	44.70	4.85	5.36	129	40
	(45.43)	(4.96)	(5.30)		
$[Rg(COD)(4\text{-}MePyO)_2]ClO_4$ (IV)	45.30	4.93	5.36	138	95
	(45.43)	(4.96)	(5.30)		
$[Rh(COD)(4\text{-}MeOPyO)_2]ClO_4$ (V)	42.79	4.66	5.05	128	94
	(42.83)	(4.67)	(4.99)		
$[Rh(COD)(4\text{-}t\text{-}BuPyO)_2]ClO_4$ (VI)	51.09	6.24	4.72	135	41
	(50.95)	(6.25)	(4.57)		
$[Rh(COD)(4\text{-}NO_2PyO)_2]ClO_4$ (VII)	36.79	3.31	9.36	129	65
	(36.60)	(3.41)	(9.48)		
$[Rh(COD)(4\text{-}CNPyO)_2]ClO_4$ (VIII)	44.09	3.87	9.87	145	69
	(43.62)	(3.66)	(10.17)		
$[Rh(COD)(2\text{-}PhCH_2PyO)_2]ClO_4$ (IX)	55.67	4.95	4.15	140	81
	(56.44)	(5.03)	(4.11)		
$[Rh(COD)(4\text{-}ClPyO)_2]ClO_4$ (X)	[a]			146	73
	(37.95)	(3.54)	(4.92)		

[a] This complex explodes violently in the microanalyzer.

ii) The addition of L + PPh_3 (1/1) to acetone solution of [Rh(COD)($Me_2CO)_x$]ClO_4, prepared as described above, is more generally applicable in all the cases it gives higher yields of the mixed complexes, and it allows the preparation even of complex XVIII (L = 4-NO_2PyO).

$$[Rh(COD)(Me_2CO)_x]ClO_4 + L + PPh_3 \rightarrow [Rh(COD)L(PPh_3)]ClO_4 + x\ Me_2CO \quad (4)$$

The analytical and other data for complexes XI—XX are listed in Table 2.

Reactivity

The behavior of [Rh(COD)(4-MePyO$)_2$]ClO_4 towards various ligands has been studied. This complex can also be prepared by addition of 4-MePyO to complexes of the type [Rh(COD)(nitrile$)_2$]ClO_4 (nitrile = BzCN or 4-MeC_6H_4-CN) [11].

The reaction of an excess of py, bipy, phen or PPh_3 with complex IV results in displacement of 4-MePyO and formation of the corresponding previously reported complexes [12—14]. Addition of 1 mol of 2-methylimidazole (2-MeIm) or 4-aminopyridine (4-NH_2Py) to complex IV leads to novel mixed complexes, whilst poorer N-donors, such as 4-CNPy, C_5Cl_5N, BzCN or 4-Me-C_6H_4CN do not react. This seems to indicate that the coordination capacity of the "PyO" ligands towards Rh^I is between that of pyridine and nitrile ligands.

TABLE 2

ANALYTICAL RESULTS, MOLAR CONDUCTIVITIES AND YIELDS FOR THE COMPLEXES [Rh(COD)L(PPh_3)]ClO_4

Complex	Found (calcd.) (%)			Λ_M (ohm^{-1} cm^2 mol^{-1})	Yield (%)
	C	H	N		
[Rh(COD)(PyO)(PPh_3)]ClO_4 (XI)	55.45	4.97	2.30	123	87 [a]
	(55.74)	(4.83)	(2.10)		
[Rh(COD)(2-MePyO)(PPh_3)]ClO_4 (XII)	56.05	5.13	2.40	136	74 [a]
	(56.36)	(5.02)	(2.05)		
[Rh(COD)(3-MePyO)(PPh_3)]ClO_4 (XIII)	55.98	5.04	2.60	131	73 [a]
	(56.36)	(5.02)	(2.05)		
[Rh(COD)(4-MePyO)(PPh_3)]ClO_4 (XIV)	56.59	5.23	2.12	125	86 [b]
	(56.36)	(5.02)	(2.05)		
[Rh(COD)(4-MeOPyO)(PPh_3)]ClO_4 (XV)	55.10	5.23	2.05	131	70 [b]
	(55.07)	(4.91)	(2.01)		
[Rh(COD)(4-t-BuPyO)(PPh_3)]ClO_4 (XVI)	57.50	5.68	2.19	130	36 [a]
	(58.06)	(5.57)	(1.93)		
[Rh(COD)(4-NO_2PyO)(PPh_3)]ClO_4 (XVII)	52.45	4.49	3.91	132	79 [b]
	(52.23)	(4.38)	(3.93)		
[Rh(COD)(4-CNPyO)(PPh_3)]ClO_4 (XVIII)	54.27	4.58	4.19	146	94 [b]
	(55.46)	(4.51)	(4.04)		
[Rh(COD)(2-$PhCH_2$PyO)(PPh_3)]ClO_4 (XIX)	60.05	5.46	2.01	120	47 [a]
	(60.21)	(5.05)	(1.85)		
[Rh(COD)(4-ClPyO)(PPh_3)]ClO_4 (XX)	[c]			136	81 [b]
	(53.01)	(4.45)	(1.99)		

[a] Yields according to i). [b] Yields according to eq. 4. [c] This complex exploded violently in the microanalyzer.

TABLE 3

IR DATA FOR THE CATIONIC COMPLEXES (cm^{-1})

L	σ_{PyO} [a]	Ligand [b]	$[Rh(COD)L_2]ClO_4$			$[Rh(COD)L(PPh_3)]ClO_4$		
		ν(NO)	ν(NO)	$\Delta\nu$(NO) [c]	Other bands	ν(NO)	$\Delta\nu$(NO) [c]	Other bands
4-NO_2PyO	+1,19	1294, 1283	1226, 1217	67	490, 394	1222, 1211	72	501, 430
4-CNPyO	+0,94	1282	1219	63	483, 371	1219	63	493, 413
4-ClPyO	+0,206	1251	1195	56	434, 388	1193	58	490, 420
PyO	0	1246	1199	47	393	1199	47	490, 423
4-MePyO	–0,24	1247	1203	44	413, 387	1200	47	492, 423
4-MeOPyO	–0,603	1232	1201	31	380	1196	36	493, 420
4-t-BuPyO		1245	1210	35	388	1181	64	495, 422
2-MePyO	–0,111	1244	1195	49	400, 376	1183	61	493, 423
2-$PhCH_2$PyO		1247	1193	54	400, 374	1186	61	493, 423
3-MePyO	–0,139	1278, 1268	1271, 1254	10	390	1284, 1275	–6	495, 422

[a] Hammett constants [2]. [b] Data from ref. 26. [c] $\Delta\nu(NO) = \nu(NO)(\text{ligand}) - \nu(NO)(\text{complex})$.

No reaction takes place with $AsPh_3$, $SbPh_3$, $SPPh_3$, SEt_2 or tht (tetrahydrothiophen).

As expected, addition of t-BuNC or dpe to solutions of IV leads to the formation of $[Rh(t\text{-}BuNC)_4]ClO_4$ [15] or $[Rh(dpe)_2]ClO_4$, respectively [16]. Finally, reaction with Tlcp or with pyrazole yields Rh(COD)(cp) [17] or $[Rh(\mu\text{-}Pz)(COD)]_2$, respectively [18].

IR spectra

All the complexes I—XX show the bands characteristic of the uncoordinated anion ClO_4^- (Td) [19] at 1110 (ν_3) and 620 (ν_4) cm^{-1}, along with the absorptions of the coordinated diolefin group, as well as those due to the respective pyridine *N*-oxides or the ancillary ligands.

The values of ν(N—O) for the free and the coordinated ligands along with the corresponding $\Delta\nu$(N—O) are listed in Table 3. The coordination causes a reduction of ν(N—O), [1,20] except for L = 3-MePyO (complexes III and XIII), in accord with previous observations [21].

The sequence of the values of $\Delta\nu$(N—O) for the 4-substituted pyridine *N*-oxide complexes is the same as that for the Hammett constants for the substituents. Thus, electron-withdrawing substituents give the higher $\Delta\nu$(N—O) values and electron-releasing substituents lower ones. As expected [2], the absorption due to δ(N—O) at 880—830 cm^{-1} is almost insensitive to the nature of the ligands.

Table 3 also lists vibrations in the 500—370 cm^{-1} region, which could be due to ν(Rh—O). Those at lower energies do not vary with the substituents in any of the two series of complexes I—X and XI—XX. The bands at higher energies for complexes I—X appear at increasingly lower energies the more electron-releasing is the substituent in the 4-substituted pyridine *N*-oxides, as observed by Drago et al. [20] for nickel complexes.

The relation between ν(Rh—O) and $\Delta\nu$(N—O) is similar to that observed by James et al. [6] between ν(M—O) and $\Delta\nu$(S—O) for sulfoxide metal complexes. It is noteworthy, that for complexes XI—XX the ν(Rh—O) band almost independent of the substituent.

Experimental

C, H and N analyses were carried out with a Perkin-Elmer 240 microanalyzer. IR spectra were recorded (over the range 4000—200 cm^{-1}) on a Perkin-Elmer 599 spectrophotometer, using Nujol mulls between polyethylene disks or KBr pellets. Conductivities were measured in ca. 5×10^{-4} *M* acetone solutions with a Philips PW 9501/01 conductimeter. $[RhCl(COD)]_2$ and $[Rh(COD)_2]ClO_4$ were prepared as described elsewhere [22,23]. Pyridine *N*-oxide and its derivatives were prepared by standard methods [24,25] and vacuum-distilled or recrystallized before use. The solvents were distilled before use. All the reactions were carried out at room temperature.

Preparation of complexes of the type $[Rh(COD)L_2]ClO_4$ (I—X)

i) To a solution of $[Rh(COD)(Me_2CO)_x]ClO_4$ (obtained by treating $[RhCl(COD)]_2$ (0.0493 g, 0.1 mmol) with $AgClO_4$ (0.0415 g, 0.2 mmol) in 10 ml of acetone and removing the precipitated AgCl) was added 0.4 mmol of the corresponding pyridine *N*-oxide. The yellow solution was concentrated under vacuum and Et_2O was added. The yellow crystals were filtered off, washed with ether and air-dried. (Complexes II, III, VI and IX gave oils which were crystallized by prolonged stirring (>2 h)). This method gave the higher yields (see Table 1).

ii) To a solution of $[Rh(COD)_2]ClO_4$ (0.0418 g, 0.1 mmol) in 10 ml of CH_2Cl_2 was added 0.2 mmol of the appropriate ligand. Evaporation to dryness led to yellow oils, which were crystallized by stirring with ether. (Complexes VII and IX could not be synthesized by this method).

Preparation of complexes of the type [Rh(COD)L(PPh₃)]ClO₄

i) PPh_3 (1 : 1) was added to the above-described dichloromethane solutions of complexes I—X and the solutions were vacuum-concentrated to 1 ml. Slow addition of ether gave yellow solids, which were washed with ether and air-dried.

ii) To an acetone solution of equimolecular amount of PPh_3 and the corresponding pyridine *N*-oxide was added a stoicheiometric amount of $[Rh(COD)(Me_2CO)_x]ClO_4$, work-up was as in (i). The orange-coloured 4-NO_2PyO derivative could be obtained only by this route.

Reactivity of [Rh(COD)(4-MePyO)₂]ClO₄

i) The starting complex can also be prepared by addition of 0.2 mmol of 4-MePyO to a solution of 0.1 mmol of $[Rh(COD)(nitrile)_2]ClO_4$ [11] (nitrile = BzCN or 4-MeC_6H_4CN) in dichloromethane, vacuum-evaporation to 1 ml, and addition of diethyl ether.

ii) Addition of py (1 ml), bipy (1 mmol), phen (1 mmol), PPh_3 (0.2 mmol) or Tlcp (0.21 mmol) to acetone or dichloromethane solutions of 0.1 mmol of $[Rh(COD)(4\text{-}MePyO)_2]ClO_4$ led to the complete displacement of the pyridine *N*-oxide. Vacuum-evaporation and addition of diethyl ether gave the microcrystalline $[Rh(COD)(py)_2]ClO_4$ [12], $[Rh(COD)(bipy)]ClO_4$ [13], $[Rh(COD)(phen)]ClO_4$ [13], $[Rh(COD)(PPh_3)_2]ClO_4$ [14], or Rh(COD)(cp) [17].

iii) Addition of pyrazole (0.1 mmol), t-BuNC (0.07 ml, 0.6 mmol) or dpe (solid, 0.2 mmol) to acetone or dichloromethane solutions of 0.1 mmol of $[Rh(COD)(4\text{-}MePyO)_2]ClO_4$ in the first case resulted in displacement of the pyridine *N*-oxide and precipitation of $[Rh(\mu\text{-}Pz)(COD)]_2$ [18], and in the other two cases it resulted in displacement of all the ligands of the starting compound. Evaporation to dryness followed by recrystallization from CH_2Cl_2/Et_2O gave $[Rh(t\text{-}BuNC)_4]ClO_4$ (Found: C, 45.03; H, 6.70; N, 10.90. $C_{20}H_{36}N_4O_4ClRh$ calcd.: C, 44.91; H, 6.78; N, 10.47%) and $[Rh(dpe)_2]ClO_4$ [16].

iv) Addition of 0.1 mmol of 2-methylimidazole or 4-aminopyridine to 0.1 mmol of $[Rh(COD)(4\text{-}MePyO)_2]ClO_4$ in 10 ml of acetone gave yellow solutions, which after vacuum-concentration and addition of ether (where necessary with prolonged stirring) gave yellow crystals of $[Rh(COD)(4\text{-}MePyO)(2\text{-}MeIm)]ClO_4$ (Found: C, 42.71; H, 5.00; N, 8.33. $C_{18}H_{25}N_3O_5ClRh$ calcd.: C, 43.08; H, 5.02; N, 8.37%) or $[Rh(COD)(4\text{-}MePyO)(4\text{-}NH_2Py)]ClO_4$ (Found: C, 43.02; H, 4.76; N, 8.63. $C_{19}H_{25}N_3O_5ClRh$ calcd.: C, 44.42; H, 4.90; N, 8.18%), respectively.

v) No reaction took place between solution of the starting complex and $AsPh_3$, $SbPh_3$, $SPPh_3$, SEt_2 or tht (tetrahydrothiophen).

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