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MONO- AND POLYNUCLEAR RHODIUM(I) COMPLEXES WITH NITROGEN-DONOR LIGANDS

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Summary

The preparation of cationic rhodium(I) complexes of the type $[Rh(diolefin)L_2]ClO_4$ (L = 4-NH_2py, 2-NH_2py, 4-NMe_2py, 4-CNpy or 2-CNpy) and of polynuclear compounds of the type $[Rh_n(diolefin)_n(L\text{-}L)_n](ClO_4)_n$ (L-L = 4,4'-bipy, pyz or 4-CNpy), in which the metal centres are bridged by the nitrogen-donor ligands, are described. Related rhodium(I) mono- and polynuclear carbonyls are also reported.

Introduction

Several types of cationic rhodium(I) complexes containing diolefins along with mono- or bidentate nitrogen-donor ligands have been described [1]. The only hitherto described binuclear cation, which uses the bridging capacity of the 4-aminomethylpyridine for linking two rhodium atoms, corresponds to the formula $[Rh_2(COD)_2(NH_2CH_2py)_2]^{2+}$ [2].

In the present paper we describe several rhodium(I) complexes with a series of ligands. Each of these ligands contains two nitrogen atoms, which are potentially capable of coordination to the metal ion. The following ligands were used: 4-aminopyridine (4-NH_2py), 2-aminopyridine (2-NH_2py), 4-(dimethylamino)pyridine (4-NMe_2py), 4-cyanopyridine (4-CNpy), 2-cyanopyridine (2-CNpy), 4,4'-bipyridine (4,4'-bipy) and pyrazine(pyz).

Results and discussion

a) Cationic mononuclear complexes of the type $[Rh(diolefin)L_2]ClO_4$

Complexes of this type can be prepared by two methods, according to eqs. 1 and 2.

$$[Rh(diolefin)_2]ClO_4 + 2\ L \rightarrow [Rh(diolefin)L_2]ClO_4 + diolefin \qquad (1)$$

TABLE 1

ANALYTICAL RESULTS, MOLAR CONDUCTIVITIES, YIELDS AND IR DATA FOR MONONUCLEAR CATIONIC COMPLEXES

Complex	Analysis (found (calcd.) (%))			Λ_M (ohm^{-1} cm^2 mol^{-1})	Yield (%)	IR bands (cm^{-1})
	C	H	N			
$[Rh(TFB)(4\text{-}NH_2py)_2]ClO_4$ (I)	43.47 (42.84)	3.45 (2.94)	8.69 (9.08)	126	84	3492, 3367, 3232 ν(NH)
$[Rh(TFB)(2\text{-}NH_2py)_2]ClO_4$ (II)	43.74 (42.84)	3.40 (2.94)	8.48 (9.08)	116	86	3454, 3353 ν(NH)
$[Rh(TFB)(4\text{-}CNpy)_2]ClO_4$ (III)	44.18 (45.27)	2.42 (2.22)	7.81 (8.80)	123	75	2247 ν(CN)
$[Rh(TFB)(2\text{-}CNpy)_2]ClO_4$ (IV)	44.25 (45.27)	2.31 (2.22)	8.30 (8.80)	136	78	2242 ν(CN)
$[Rh(COD)(4\text{-}NH_2py)_2]ClO_4$ (V)	43.96 (43.34)	4.80 (4.85)	11.21 (11.23)	144	83	3475, 3380, 3250 ν(NH)
$[Rh(COD)(2\text{-}NH_2py)_2]ClO_4 \cdot Me_2CO$ (VI)	44.91 (45.26)	5.32 (5.38)	9.87 (10.05)	128	81	3448, 3350 ν(NH) 1710 ν(CO)
$[Rh(COD)(4\text{-}NMe_2py)_2]ClO_4$ (VII)	48.19 (47.62)	5.76 (5.81)	9.84 (10.09)	—	90	
$[Rh(COD)(4\text{-}CNpy)_2]ClO_4$ (VIII)	45.61 (46.30)	3.87 (3.88)	11.05 (10.80)	132	83	2247 ν(CN)
$[Rh(COD)(2\text{-}CNpy)_2]ClO_4$ (IX)	45.70 (46.30)	3.88 (3.88)	10.23 (10.80)	106	46	2248 ν(CN)
$[Rh(NBD)(4\text{-}NH_2py)_2]ClO_4$ (X)	41.93 (42.29)	4.35 (4.17)	12.04 (11.60)	136	87	3500, 3435, 3390 3360, 3250 ν(NH)
$[Rh(NBD)(2\text{-}NH_2py)_2]ClO_4$ (XI)	41.38 (42.29)	4.09 (4.17)	11.97 (11.60)	150	34	3470, 3360 ν(NH)
$[Rh(NBD)(4\text{-}CNpy)_2]ClO_4$ (XII)	44.35 (45.39)	3.72 (3.20)	10.42 (11.14)	—	74	2247 ν(CN)
$[Rh(CO)_2(4\text{-}NH_2py)_2]ClO_4$ (XIII)	33.02 (32.27)	2.74 (2.71)	13.19 (12.54)	—	62	3465, 3365, 3240 ν(NH) 2095, 2025 ν(CO)
$[Rh(CO)(4\text{-}NH_2py)_2(PPh_3)]ClO_4$ (XIV)	50.24 (51.15)	4.34 (3.99)	8.36 (8.22)	120	81	3475, 3375, 3250 ν(NH) 2000 ν(CO)
$[Rh(CO)(4\text{-}CNpy)_2(PPh_3)]ClO_4$ (XV)	52.57 (53.10)	3.61 (3.28)	7.58 (7.99)	122	74	2245 ν(CN) 2010 ν(CO)
$[Rh(CO)(4,4'\text{-}bipy)_2(PPh_3)]ClO_4$ (XVI)	57.20 (58.17)	4.03 (3.85)	7.27 (6.96)	—	80	2000 ν(CO)
$[Rh(CO)(pyz)(PPh_3)_2]ClO_4$ (XXVI)	58.17 (58.97)	4.20 (4.10)	3.47 (3.35)	—	48	2010 ν(CO)

$$1/2[\mathrm{RhCl(diolefin)}]_2 \xrightarrow[\mathrm{CH_2Cl_2/Me_2CO}]{\mathrm{AgClO_4}}$$

$$[\mathrm{Rh(diolefin)(Me_2CO)}_x]\mathrm{ClO_4} \xrightarrow[-\mathrm{Me_2CO}]{2\mathrm{L}} [\mathrm{Rh(diolefin)L_2}]\mathrm{ClO_4} \quad (2)$$

(diolefin = TFB; L = 4-NH_2py(I), 2-NH_2py(II), 4-CNpy(III), 2-CNpy(IV).
diolefin = COD; L = 4-NH_2py(V), 2-NH_2py(VI), 4-NMe_2py(VII), 4-CNpy(VIII), 2-CNpy(IX).
diolefin = NBD; L = 4-NH_2py(X), 2-NH_2py(XI), 4-CNpy(XII))

Table 1 lists the analytical and other data for the yellow air-stable complexes I—XII, which are 1 : 1 electrolytes in acetone. In all cases the ligand is linked to the metal atom via the heterocyclic nitrogen, since the absorption due to ν(C≡N) in the free ligand is not changed by coordination. Moreover, the ^{1}H NMR spectra of the aminopyridine ligands show peaks due to the protons of the -NH_2 and -NMe_2 groups with chemical shifts rather similar to those for the free ligands (see Table 2). Complex VI crystallizes together with a molecule of Me_2CO (ν(C=O) at 1710 cm^{-1} (Table 1); ^{1}H NMR peak due to Me at 7.9 ppm).

Carbonylation (at room temperature and normal pressure) of dichloromethane solutions of complexes I—XII leads to the displacement of the diolefin and formation of a solution of $[\mathrm{Rh(CO)_2L_2}]\mathrm{ClO_4}$. Complex XIII, with L = 4-NH_2py, has been isolated (ν(C≡O): 2090 and 2028 cm^{-1} (CH_2Cl_2 solution); 2095 and 2025 cm^{-1} (Nujol mulls)). Its dichloromethane solutions react with one mole of triphenylphosphine to give the mixed complex $[\mathrm{Rh(CO)(4\text{-}NH_2py)_2(PPh_3)}]\mathrm{ClO_4}$ (XIV). Similar mixed complexes (XIV—XVI) can be obtained by the reaction represented in eq. 3.

$$1/2[\mathrm{RhCl(CO)(PPh_3)}]_2 \xrightarrow[\mathrm{CH_2Cl_2/Me_2CO}]{\mathrm{AgClO_4}}$$

$$[\mathrm{Rh(CO)(PPh_3)(Me_2CO)}_x]\mathrm{ClO_4} \xrightarrow[-\mathrm{Me_2CO}]{+2\mathrm{L}} [\mathrm{Rh(CO)L_2(PPh_3)}]\mathrm{ClO_4} \quad (3)$$

L = 4-NH_2py(XIV), 4-CNpy(XV), 4,4′-bipy(XVI)

b) Polynuclear complexes of the type $[\mathrm{Rh}_n(\mathrm{diolefin})_n(\mathrm{L\text{-}L})_n](\mathrm{ClO_4})_n$

If reactions 1 and 2 are carried out with bidentate non-chelating ligands, such as 4,4′-bipyridine (4,4′-bipy) or pyrazine(pyz), polynuclear complexes of the

TABLE 2

^{1}H NMR SPECTRA [a] FOR $[\mathrm{Rh(COD)L_2}]\mathrm{ClO_4}$ AND RhCl(COD)L COMPLEXES

Complex	Aminopyridine ligand		Cyclooctadiene	
	Aromatic	Amino	CH	CH_2
$[\mathrm{Rh(COD)(4\text{-}NH_2py)_2}]\mathrm{ClO_4}$	8.1 (H_α), 6.65 (H_β)	6.2 (NH_2)	4.0	2.6, 1.9
$[\mathrm{Rh(COD)(2\text{-}NH_2py)_2}]\mathrm{ClO_4}$	8.55 (H_α), 6.65 (H_β), 7.45 (H_γ)	6.95 (NH_2)	4.2	2.6, 1.9
$[\mathrm{Rh(COD)(4\text{-}NMe_2py)_2}]\mathrm{ClO_4}$	8.2 (H_α), 6.67 (H_β)	3.04 (NMe_2)	3.9	2.6, 1.9
RhCl(COD)(4-NH_2py)	7.95 (H_α), 6.4 (H_β)	6.5 (NH_2)	3.9	2.3, 1.7
RhCl(COD)(2-NH_2py)	8.1 (H_α), 6.5 (H_β), 7.27 (H_γ)	5.8 (NH_2)	4.14	2.5, 1.8
RhCl(COD)(4-NMe_2py)	8.18 (H_α), 6.40 (H_β)	2.98 (NMe_2)	4.1	2.4, 1.8

[a] δ values (ppm).

general formula $[\mathrm{Rh}_n(\mathrm{diolefin})_n(\text{L-L})_n](\mathrm{ClO_4})_n$ (diolefin = TFB or NBD, L-L = 4,4′-bipy or pyz; diolefin = COD, L-L = pyz) (XVII—XXI) are obtained.

Complexes XVII—XXI are yellow air-stable solids, which are conducting in nitromethane. Thus, for $[\mathrm{Rh}_n(\mathrm{TFB})_n(4,4'\text{-bipy})_n](\mathrm{ClO_4})_n$ the conductivity/concentration plot gives a slope of 620 (Onsager's equation [3]). In the solid state these complexes probably have $n > 2$, but their nitromethane solutions give rather lower values. Owing to their low solubility in other solvents no additional data could be obtained.

The reaction of complexes XVII—XXI with carbon monoxide at room temperature and normal pressure gives rise to complete displacement of the diolefin group and formation of $[\mathrm{Rh}_n(\mathrm{CO})_{2n}(\text{L-L})_n](\mathrm{ClO_4})_n$ (complexes XXII—XXIII). The IR spectra of both complexes show two strong bands due to $\nu(\mathrm{C{\equiv}O})$ at 2100 and 2040 or at 2120 and 2050 $\mathrm{cm^{-1}}$, respectively, as expected for *cis*-dicarbonyls [4].

Complex XXIII can also be prepared by the following reaction (eq. 4).

$$n/2[\mathrm{RhCl(CO)_2}]_2 \xrightarrow[\mathrm{CH_2Cl_2/Me_2CO}]{\mathrm{AgClO_4}}$$

$$n[\mathrm{Rh(CO)_2(Me_2CO)}_x]\mathrm{ClO_4} \xrightarrow[-\mathrm{Me_2CO}]{\mathrm{pyz}} [\mathrm{Rh}_n(\mathrm{CO})_{2n}(\mathrm{pyz})_n](\mathrm{ClO_4})_n \quad (4)$$

Addition of triphenylphosphine to complex XXII ($\mathrm{Rh/PPh_3} = 1/1$) causes displacement of half of the CO groups and formation of $[\mathrm{Rh}_n(\mathrm{CO})_n(4,4'\text{-bipy})_n(\mathrm{PPh_3})_n](\mathrm{ClO_4})_n$ (XXIV), with retention of the structure. The same reaction with complex XXIII leads to more profound changes, since only the mononuclear complex $[\mathrm{Rh(CO)(pyz)(PPh_3)_2}]\mathrm{ClO_4}$ (XXVI) can be isolated. However, the polynuclear complex with pyz (XXV) analogous to XXIV can be prepared by the following reaction (eq. 5).

$$n/2[\mathrm{RhCl(CO)(PPh_3)}]_2 \xrightarrow[\mathrm{CH_2Cl_2/Me_2CO}]{\mathrm{AgClO_4}}$$

$$n[\mathrm{Rh(CO)(PPh_3)(Me_2CO)}_x]\mathrm{ClO_4} \xrightarrow[-\mathrm{Me_2CO}]{\text{L-L}} [\mathrm{Rh}_n(\mathrm{CO})_n(\text{L-L})_n(\mathrm{PPh_3})_n](\mathrm{ClO_4})_n \quad (5)$$

L-L = 4,4′-bipy, pyz

The same method also allows the synthesis of XXIV.

The reaction between the mononuclear complex XVI, which contains 4,4′-bipy as unidentate ligand, and $[\mathrm{Rh(CO)(PPh_3)(Me_2CO)}_x]\mathrm{ClO_4}$ gives rise to the displacement of the acetone and to formation of XXIV (eq. 6).

$$n/2[\mathrm{Rh(CO)(PPh_3)}(4,4'\text{-bipy})_2]\mathrm{ClO_4} + n/2[\mathrm{Rh(CO)(PPh_3)(Me_2CO)}_x]\mathrm{ClO_4} \rightarrow$$

$$nx/2\ \mathrm{Me_2CO} + [\mathrm{Rh}_n(\mathrm{CO})_n(4,4'\text{-bipy})_n(\mathrm{PPh_3})_n](\mathrm{ClO_4})_n \quad (6)$$

Addition of triphenylphosphine to complex XXIV ($\mathrm{Rh/PPh_3} = 1/1$ ratio) yields the binuclear complex $[\mathrm{Rh_2(CO)_2}(4,4'\text{-bipy})(\mathrm{PPh_3})_4](\mathrm{ClO_4})_2$, which was previously prepared by a different route [5]. The binuclear complex $[\mathrm{Rh_2(COD)_2}(4\text{-CNpy})_2](\mathrm{ClO_4})_2$ (XXVII) was synthesized by using $[\mathrm{Rh(COD)}(4\text{-CNpy})_2]$-

TABLE 3

ANALYTICAL RESULTS, YIELDS AND IR DATA FOR POLYNUCLEAR CATIONIC COMPLEXES

Complex	Analysis. Found (calcd.) (%)			Yield (%)	IR bands (cm^{-1})
	C	H	N		
$[Rh_n(TFB)_n(4,4'\text{-bipy})_n](ClO_4)_n$ (XVII)	44.87 (45.19)	2.54 (2.41)	4.76 (4.79)	95	
$[Rh_n(TFB)_n(pyz)_n](ClO_4)_n$ (XVIII)	36.96 (37.78)	2.12 (1.98)	5.35 (5.51)	88	
$[Rh_n(COD)_n(pyz)_n](ClO_4)_n$ (XIX)	37.11 (36.89)	4.08 (4.12)	7.24 (7.17)	66	
$[Rh_n(NBD)_n(4,4'\text{-bipy})_n](ClO_4)_n$ (XX)	43.47 (45.30)	3.55 (3.55)	6.35 (6.21)	92	
$[Rh_n(NBD)_n(pyz)_n](ClO_4)_n$ (XXI)	34.22 (35.27)	3.27 (3.23)	7.64 (7.47)	86	
$[Rh_n(CO)_{2n}(4,4'\text{-bipy})_n](ClO_4)_n$ (XXII)	34.35 (34.76)	2.20 (2.43)	6.39 (6.75)	62	2100, 2040 ν(CO)
$[Rh_n(CO)_{2n}(pyz)_n](ClO_4)_n$ (XXIII)	22.47 (21.29)	1.61 (1.19)	7.84 (7.27)	61	2120, 2050 ν(CO)
$[Rh_n(CO)_n(4,4'\text{-bipy})_n(PPh_3)_n](ClO_4)_n$ (XXIV)	51.26 (51.81)	4.10 (3.54)	3.98 (4.31)	85	2000 ν(CO)
$[Rh_n(CO)_n(pyz)_n(PPh_3)_n](ClO_4)_n$ (XXV)	47.06 (48.23)	3.31 (3.34)	4.67 (4.89)	65	2010 ν(CO)
$[Rh_2(COD)_2(4\text{-CNpy})_2](ClO_4)_2$ (XXVII)	40.64 (40.55)	3.93 (3.89)	6.30 (6.75)	60	2284 ν(CN)
$[Rh_2(COD)_2(4\text{-CNpy})(PPh_3)_2](ClO_4)_2$ (XXVIII)	55.60 (55.74)	4.69 (4.61)	2.33 (2.24)	83	

TABLE 4

ANALYTICAL RESULTS, MOLECULAR WEIGHTS, YIELDS AND IR DATA FOR MONONUCLEAR NEUTRAL COMPLEXES

Complex	Analysis (found (calcd.) (%))			Mol. wt. ($CHCl_3$) (found (calcd.))	Yield (%)	IR bands (cm^{-1})
	C	H	N			
RhCl(TFB)(4-NH_2py) (XXIX)	44.83	2.69	5.84	483	72	3425, 3315, 3210 ν(NH)
	(44.51)	(2.63)	(6.11)	(459)		
RhCl(TFB)(2-NH_2py) (XXX)	44.80	2.87	6.05	423	52	3405, 3310 ν(NH)
	(44.51)	(2.63)	(6.11)	(459)		312 ν(RhCl)
RhCl(COD)(4-NH_2py) (XXXI)	45.60	5.31	8.73	368	68	3430, 3330, 3220 ν(NH)
	(45.83)	(5.32)	(8.22)	(341)		298 ν(RhCl)
RhCl(COD)(4-NMe_2py) (XXXII)	49.40	5.96	7.76	364	92	
	(48.86)	(6.01)	(7.60)	(369)		
RhCl(COD)(4,4'-bipy) (XXXIII)	52.86	4.91	6.55	401	90	
	(53.68)	(5.00)	(6.95)	(403)		
RhCl$(CO)_2$(4-NH_2py) (XXXIV)	28.76	2.25	9.63	—	59	3475, 3370, 3240 ν(NH)
	(29.14)	(2.09)	(9.71)			2095, 2020 ν(CO)(CH_2Cl_2)
$Rh_2Cl_2(CO)_4$(4,4'-bipy) (XXXV)	31.22	1.55	5.45	—	71	
	(30.86)	(1.48)	(5.14)			

ClO_4 as precursor (eq. 7)

$$[Rh(COD)(4\text{-}CNpy)_2]ClO_4 + [Rh(COD)_2]ClO_4 \rightarrow [Rh_2(COD)_2(4\text{-}CNpy)_2](ClO_4)_2 + COD \quad (7)$$

The 4-cyanopyridine ligand in the resulting complex is also coordinated via the nitrile group, since the vibration $\nu(CN)$ is shifted towards higher energies ($\Delta\nu(CN) = 37$ cm^{-1}), pointing to coordination through the N atom of the nitrile group [6,7].

Complex XXVII reacts with triphenylphosphine ($Rh/PPh_3 = 1/1$) to give $[Rh_2(COD)_2(4\text{-}CNpy)(PPh_3)_2](ClO_4)_2$ (XXVIII).

Analytical and other * data for the above-described complexes are listed in Table 3.

Other neutral complexes

Several neutral rhodium(I) complexes were made by the following reaction (eq. 8).

$$1/2[RhCl(diolefin)]_2 + L \rightarrow RhCl(diolefin)L \quad (8)$$

diolefin = TFB; L = 4-NH_2py (XXIX), 2-NH_2py (XXX)
diolefin = COD; L = 4-NH_2py (XXXI), 4-NMe_2py (XXXII), 4,4′-bipy (XXXIII)

The molecular weights (in $CHCl_3$) of these complexes show them as mononuclear, with L acting as a monodentate ligand. The ^1H NMR data for RhCl(COD)(4-NH_2py), RhCl(COD)(4-NMe_2py) and RhCl(COD)(2-NH_2py) confirm their coordination via the nitrogen of the pyridine group (see Table 2).

In dichloromethane solution complex XXXI reacts with carbon monoxide to give $RhCl(CO)_2(4\text{-}NH_2py)$ (XXXIV), which can also be prepared according to eq. 9.

$$1/2[RhCl(CO)_2]_2 + 4\text{-}NH_2py \rightarrow RhCl(CO)_2(4\text{-}NH_2py) \quad (9)$$

The reaction of XXXIII with carbon monoxide, however, gives an orange-coloured, non-conducting solid, which corresponds to the formulation $Rh_2Cl_2(CO)_4(4,4'\text{-}bipy)$ (XXXV), and was previously obtained by treating $[RhCl(CO)_2]_2$ with 4,4′-bipy [8].

The analytical and other properties for the neutral complexes are listed in Table 4.

Experimental

C, H and N analyses were carried out with a Perkin-Elmer 240 microanalyzer. IR spectra were recorded on a Perkin-Elmer 577 spectrophotometer (over the range 4000—200 cm^{-1}) using Nujol mulls between polyethylene sheets. Conductivities were measured in 5×10^{-4} *M* nitromethane or acetone solution with a Philips 9501/01 conductimeter. Molecular weights were determined osmometrically with a Perkin-Elmer 115 instrument.

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* *Caution:* Violent explosions occurred on heating some of the complexes, especially $[Rh_n(CO)_{2n}(pyz)_n](ClO_4)_n$.

Preparation of complexes of the type $[Rh(diolefin)L_2]ClO_4$ (I—XII)

These complexes were each prepared by two routes, which are illustrated below for two representative compounds.

i) Preparation of $[Rh(NBD)(4\text{-}NH_2py)_2]ClO_4$. Addition of 25.3 mg (0.26 mmol) of 4-NH_2py in 2 ml of acetone to 49.6 mg (0.128 mmol) of $[Rh(NBD)_2]ClO_4$ [9] in 5 ml of the same solvent caused a change in colour from red to yellow. After 30 min stirring the solution was concentrated to ca. 1 ml, and slow addition of ether gave a precipitate of a yellow solid, which was filtered off, washed with ether, and air-dried.

ii) Preparation of $[Rh(COD)(4\text{-}CNpy)_2]ClO_4$. To a solution of 46.6 mg (0.094 mmol) of $[RhCl(COD)]_2$ [10] in 10 ml of dichloromethane was added silver perchlorate (39.8 mg; 0.192 mmol) in 10 ml of acetone, silver chloride was immediately precipitated. After 45 min stirring the silver chloride was filtered off and the filtrate was added to 39.8 mg (0.382 mmol) of 4-CNpy in 2 ml of acetone. The resulting yellow solution was concentrated to ca. 2 ml; the precipitation of yellow crystals was completed by adding ether. The yellow microcrystalline complex was filtered, washed with ether, and air-dried.

Preparation of $[Rh(CO)_2(4\text{-}NH_2py)_2]ClO_4$ (XIII)

Carbon monoxide at normal pressure was bubbled through a suspension of $[Rh(TFB)(4\text{-}NH_2py)_2]ClO_4$ in dichloromethane for 30 min, during which the solid dissolved and small crystals separated. Ether was added to complete the precipitation of the complex, which was washed with ether, and air-dried.

Preparation of complexes of the type $[Rh(CO)L_2(PPh_3)]ClO_4$ (XIV—XVI)

These complexes of this type were each made by two routes, which are illustrated below.

i) Preparation of $[Rh(CO)(4\text{-}NH_2py)_2(PPh_3)]ClO_4$. A stoichiometric amount of triphenylphosphine in dichloromethane was added to a solution of $[Rh(CO)_2(4\text{-}NH_2py)_2]ClO_4$ (obtained by 10 min bubbling of carbon monoxide through a dichloromethane solution of $[Rh(COD)(4\text{-}NH_2py)_2]ClO_4$). After 20 min stirring followed by concentration to ca. 1 ml, ether was added to complete the precipitation of a pale-yellow solid, which was filtered off, washed with ether and air-dried.

ii) Preparation of $[Rh(CO)(4,4'\text{-}bipy)_2(PPh_3)]ClO_4$. To a solution of $[RhCl(CO)(PPh_3)]_2$ [11] (87.1 mg; 0.101 mmol) in 10 ml of dichloromethane was added silver perchlorate (96 mg, 0.463 mmol) in 10 ml of acetone. The silver chloride (which precipitated immediately) was filtered off after 45 min stirring and the filtrate was added to 96.6 mg (0.618 mmol) of 4,4'-bipy in 5 ml of dichloromethane. After 10 min stirring and concentration to ca. 2 ml, addition of pentane gave a yellow oil which was kept under vacuum. The resulting solid was filtered off and air-dried.

Preparation of complexes of the type $[Rh_n(diolefin)_n(L\text{-}L)_n](ClO_4)_n$ (XVII—XXI)

These complexes were each prepared by the two routes illustrated below.

i) Preparation of $[Rh_n(COD)_n(pyz)_n](ClO_4)_n$. To a solution of 35.8 mg (0.085 mmol) of $[Rh(COD)_2]ClO_4$ [12] in 5 ml of acetone were added 8.3 mg

(0.103 mmol) of pyz in 2 ml of the same solvent, whereupon the colour changed immediately from reddish to yellow and a yellow solid appeared. After 20 min stirring the solid was filtered off, washed with acetone and air-dried.

ii) Preparation of $[Rh_n(TFB)_n(4,4'\text{-}bipy)_n](ClO_4)_n$. Addition of 23.1 mg (0.111 mmol) of silver perchlorate in 10 ml of acetone to a suspension of 40 mg (0.055 mmol) of $[RhCl(TFB)]_2$ [13] in 10 ml of the same solvent gave an immediate precipitate of silver chloride. The suspension was stirred for 30 min, the precipitate was filtered off, and the filtrate was added to 8.6 mg (0.055 mmol) of 4,4'-bipy in 2 ml of acetone. The resulting intense-yellow solution was stirred for further 15 min and vacuum-concentrated to half its volume, whereupon a yellow solid separated. The precipitation was completed by adding ether, and the complex was filtered off, washed with ether, and air-dried.

Preparation of complexes of the type $[Rh_n(CO)_{2n}(L\text{-}L)_n](ClO_4)_n$ *(XXII—XXIII)*

Both complexes were made by the two routes described below.

i) Preparation of $[Rh_n(CO)_{2n}(4,4'\text{-}bipy)_n](ClO_4)_n$. Carbon monoxide at normal pressure was bubbled for 40 min through a suspension of 18 mg of $[Rh_n(TFB)_n(4,4'\text{-bipy})_n](ClO_4)_n$ in 10 ml of dichloromethane. The suspension was concentrated to ca. 4 ml and the precipitation was completed by addition of ether. The pale-yellow solid was filtered off, washed with ether, and air-dried.

ii) Preparation of $[Rh_n(CO)_{2n}(pyz)_n](ClO_4)_n$. Addition of 33.1 mg (0.160 mmol) of silver perchlorate in 10 ml of acetone to a solution of 31 mg (0.0797 mmol) of $[RhCl(CO)_2]_2$ [14] in 10 ml of dichloromethane gave an immediate precipitate of silver chloride. After 30 min stirring, the silver chloride was filtered off and the filtrate was added to 12.9 mg (0.161 mmol) of pyz in 2 ml of acetone. Addition of ether completed the precipitation of the complex, which was filtered off, washed with ether, and air-dried.

Preparation of complexes of the type $[Rh_n(CO)_n(L\text{-}L)_n(PPh_3)_n](ClO_4)_n$ *(XXIV—XXV)*

The three possible routes are described below.

Preparation of $[Rh_n(CO)_n(4,4'\text{-}bipy)_n(PPh_3)_n](ClO_4)_n$

i) 27 mg (0.103 mmol) of triphenylphosphine in dichloromethane were added to a solution of $[Rh_n(CO)_{2n}(4,4'\text{-bipy})_n](ClO_4)_n$ (prepared by bubbling carbon monoxide at normal pressure for 30 min through a dichloromethane solution of 48 mg of $[Rh_n(COD)_n(4,4'\text{-bipy})_n](ClO_4)_n$). After 20 min stirring and concentration to ca. 1 ml, the complex was precipitated by addition of ether. The pale-yellow compound was filtered off, washed with ether and air-dried.

ii) Addition of 8.96 mg (0.041 mmol) of silver perchlorate in 10 ml of acetone to 17 mg (0.019 mmol) of $[RhCl(CO)(PPh_3)]_2$ [11] in dichloromethane gave a precipitate of silver chloride, which after 45 min stirring was removed by filtration. The filtrate was added to 30.9 mg (0.038 mmol) of $[Rh(CO)(4,4'\text{-bipy})_2(PPh_3)]ClO_4$ in 5 ml of dichloromethane. Evaporation to ca. 1 ml and addition of ether gave a yellow solid, which was filtered off, washed with ether, and air-dried.

iii) Preparation of $[Rh_n(CO)_n(pyz)_n(PPh_3)_n](ClO_4)_n$

Addition of 13.5 mg (0.065 mmol) of silver perchlorate in 10 ml of acetone to a suspension of 25.7 mg (0.030 mmol) of $[RhCl(CO)(PPh_3)]_2$ in 10 ml of acetone gave a precipitate of silver chloride. After 45 min stirring this was filtered off and the filtrate was added to 5 mg (0.062 mmol) of pyz in 2 ml of acetone. The resulting solution was stirred for 20 min and concentrated to ca. 1 ml. The precipitation of the yellow solid was completed by addition of ether. The product was filtered off, washed with ether, and air-dried.

Preparation of $[Rh(CO)(pyz)(PPh_3)_2]ClO_4$ *(XXVI)*

A mixture of 15.6 mg (0.059 mmol) of triphenylphosphine in 2 ml of dichloromethane with a suspension of 20 mg of $[Rh_n(CO)_{2n}(pyz)_n](ClO_4)_n$ in 5 ml of dichloromethane was stirred for 20 min. The unchanged starting material was filtered off and the filtrate was concentrated to ca. 1 ml. Slow addition of ether caused precipitation of a yellow solid, which was filtered off, washed with ether, and air-dried.

Preparation of $[Rh_2(CO)_2(4,4'\text{-bipy})(PPh_3)_4](ClO_4)_2$

Carbon monoxide at normal pressure was bubbled for 10 min through a suspension of 11.8 mg of $[Rh_n(COD)_n(4,4'\text{-bipy})_n](ClO_4)_n$ in dichloromethane to give $[Rh_n(CO)_{2n}(4,4'\text{-bipy})_n](ClO_4)_n$. Addition of 13.2 mg (0.050 mmol) of triphenylphosphine in dichloromethane caused dissolution of the solid. After 15 min stirring the solution was concentrated to ca. 1 ml and ether was added to precipitate the yellow microcrystalline solid, which was filtered off, washed with ether and air-dried.

This complex was prepared previously by another method [5].

Preparation of $[Rh_2(COD)_2(4\text{-CNpy})_2](ClO_4)_2$ *(XXVII)*

Addition of 44.4 mg (0.085 mmol) of $[Rh(COD)(4\text{-CNpy})_2]ClO_4$ in 5 ml of acetone to a solution of 71.9 mg (0.172 mmol) of $[Rh(COD)_2]ClO_4$ [12] in 10 ml of the same solvent caused a change in colour from red to orange-yellow and formation of a precipitate. After 10 min stirring the suspension was concentrated to ca. 1 ml and precipitation was completed by addition of dichloromethane. The complex was filtered off, washed with dichloromethane, and air-dried.

Conductance studies gave a slope of 407 (Onsager's equation), which corresponds to a 1 : 2 electrolyte.

Preparation of $[Rh_2(COD)_2(4\text{-CNpy})(PPh_3)_2](ClO_4)_2$ *(XXVIII)*

A suspension of 9 mg (0.011 mmol) of $[Rh_2(COD)_2(4\text{-CNpy})_2](ClO_4)_2$ in 10 ml of acetone was stirred for 15 min together with 6.1 mg (0.023 mmol) of triphenylphosphine in 2 ml of the same solvent. Concentration to ca. 1 ml and slow addition of ether gave a precipitate of an orange-coloured solid, which was filtered off, washed with ether, and air-dried.

Preparation of complexes of the type RhCl(diolefin)L (XXIX—XXXIII)

The preparation of $RhCl(TFB)(2\text{-NH}_2py)$ is described as an example.

Addition of 8 mg (0.085 mmol) of 2-NH_2py in 2 ml of dichloromethane to a suspension of 30.6 mg (0.042 mmol) of $[RhCl(TFB)]_2$ in 10 ml of the same solvent caused immediate dissolution of the solid. After 15 min stirring the solution was vacuum-concentrated to give a yellow solid. The precipitation was completed by addition of ether. The complex was filtered off, washed with ether, and air-dried.

Preparation of $RhCl(CO)_2(4\text{-}NH_2py)$ (XXXIV)

The complex was prepared by two different routes, as follows:

i) Carbon monoxide at normal pressure was bubbled for ca. 30 min through a dichloromethane solution of 40 mg (0.117 mmol) of $RhCl(COD)(4\text{-}NH_2py)$. Addition of hexane gave an orange-yellow solid, and after 15 min stirring, this was filtered off, washed with pentane and air-dried.

ii) 19.8 mg (0.210 mmol) of $4\text{-}NH_2py$ in dichloromethane suspension were added to a solution of 40.6 mg (0.104 mmol) of $[RhCl(CO)_2]_2$ [14] in the same solvent. After 30 min stirring the solution was vacuum-concentrated to ca. 1 ml to give the orange-yellow complex, which was filtered off and air-dried.

Preparation of $Rh_2Cl_2(CO)_4(4,4'\text{-}bipy)$ (XXXV)

Carbon monoxide at normal pressure was bubbled for 30 min through a solution of 56.4 mg (0.140 mmol) of $RhCl(COD)(4,4'\text{-}bipy)$ in 10 ml of dichloromethane. Vacuum-concentration to ca. 5 ml gave an orange-reddish solid, whose precipitation was completed by addition of ether. The complex was filtered off, washed with ether, and air-dried.

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