Journal of Organometallic Chemistry, 234 (1982) 205—217
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

MONO- AND DINUCLEAR CATIONIC RHODIUM(I) COMPLEXES WITH PHOSPHINE OXIDES AND RELATED LIGANDS

R. USON, L.A. ORO, M.A. CIRIANO, F.J. LAHOZ and M.C. BELLO

Department of Inorganic Chemistry, University of Zaragoza, Zaragoza (Spain)

(Received March 2nd, 1982)

Summary

The syntheses of mononuclear cationic complexes of general formula $[Rh(COD)(OER_3)_2]ClO_4$ and $[Rh(COD)(OER_3)(PPh_3)]ClO_4$ (E = P, As) are described. Carbonylation of complexes of the types $[Rh(COD)(OER_3)_2]ClO_4$ and $[Rh(COD)(OPyR)_2]ClO_4$ (OPyR = substituted pyridine *N*-oxides), sometimes carried out in the presence of triphenylphosphine, leads to complexes of the types $[Rh(CO)_2(OER_3)_2]ClO_4$, $[Rh(CO)(OER_3)_2(PPh_3)]ClO_4$, $[Rh(CO)(OER_3)(PPh_3)_2]ClO_4$, $[Rh(CO)(OPyR)_2(PPh_3)]ClO_4$ and $[Rh(CO)(OPyR)(PPh_3)_2]ClO_4$. Dinuclear complexes of the general formula $[Rh_2(\mu\text{-}OER_3)_2(CO)_2(PPh_3)_2](ClO_4)_2$ are prepared from the solvate $[Rh(CO)(PPh_3)(Me_2CO)_x]ClO_4$ and the appropriate ligand. Related complexes of the type $[Rh_2(\mu\text{-}OER_3)_2(COD)_2](ClO_4)_2$ are similarly obtained.

Introduction

The coordination chemistry of phosphine oxides has been reviewed [1,2]. In particular, a large number of coordination metal complexes of the first series transition metals [3,4], lanthanides [5] and actinides [6,7] with phosphine oxides as ligands have been described; but complexes with metals of the second and third transition series have been less studied. On the other hand, phosphine oxides have been used in selective extraction processes of platinum metals [8—10] and as additives in some catalytic reactions [11—13]. These ligands are also formed during the preparation [14] or decomposition [15] of some phosphine rhodium(I) complexes. As far as we know, the only previously reported phosphine oxide rhodium(I) complex is $RhCl(CO)_2(OPCy_3)$ whose structure has been determined by X-ray diffraction [16]. A few rhodium(III) complexes of the type $RhCl(ylid)_2(OPR_3)$ [17] and $[Rh(dimethylglyoximate)_2(OPPh_3)]_2O_2$ [18] have been reported.

Following our earlier studies on rhodium(I) complexes with pyridine

0022-328X/82/0000—0000/$02.75

N-oxides as ligands [19], we describe below a family of rhodium(I) complexes incorporating phosphine oxides.

Results and discussion

Complexes of the $[Rh(COD)(OER_3)_2]ClO_4$ and $[Rh(COD)(OER_3)(PPh_3)]ClO_4$ types

Treatment of acetone solutions of the solvated species $[Rh(COD)(Me_2CO)_x]ClO_4$ [20] with either triarylphosphine oxides or triphenylarsine oxide gives yellow solutions from which complexes I—V can be isolated as yellow crystalline solids (eq. 1).

$$[Rh(COD)(Me_2CO)_x]ClO_4 + 2\ OER_3 \rightarrow [Rh(COD)(OER_3)_2]ClO_4 + x\ Me_2CO \quad (1)$$

$(OER_3 = OP(p\text{-}ClC_6H_4)_3$ (I), $OPPh_3$ (II), $OP(p\text{-}MeC_6H_4)_3$ (III),
$OP(p\text{-}MeOC_6H_4)_3$ (IV), $OAsPh_3$ (V))

Addition of stoichiometric amounts (1/1) of triphenylphosphine to dichloromethane solutions of the complexes I—V results in displacement of one mol of OER_3 and formation of the mixed complexes $[Rh(COD)(OER_3)(PPh_3)]ClO_4$ (complexes VI—X). Alternatively, these complexes can be obtained by successive additions of stoichiometric amounts of OER_3 and triphenylphosphine (1/1) to the solvated species $[Rh(COD)(Me_2CO)_x]ClO_4$ (eq. 2).

$$[Rh(COD)(Me_2CO)_x]ClO_4 + OER_3 + PPh_3 \rightarrow [Rh(COD)(OER_3)(PPh_3)]ClO_4 + x\ Me_2CO \quad (2)$$

The complexes VI—X were isolated as yellow crystalline solids. Table 1 lists the analytical results, molar conductivities, yields and IR data for the complexes I—X. Their spectroscopic data are in accordance with square-planar structures around the rhodium atom. Thus, their IR spectra show $\nu(PO)$ or $\nu(AsO)$ of the coordinated phosphine or arsine oxide [21] as an intense band in the 1170—1140 region or at ca. 870 cm^{-1}, respectively, shifted towards lower wavenumbers than those of the free ligands. In addition, the bands at ca. 1100 and 620 cm^{-1} are characteristic of the uncoordinated anion ClO_4^- [22]. Consequently, the complexes are 1/1 electrolytes [23] in acetone. The ^{31}P NMR spectrum of the complex II displays a singlet resonance at 39.7 ppm * from two phosphorus nuclei in equivalent environments. On the other hand, the ^{31}P NMR of the complex VII shows the expected two resonances from triphenylphosphine oxide and triphenylphosphine at 39.5 ppm * (s) and 28.6 ppm (d, $^1J(Rh\text{—}P)$ 155 Hz), respectively.

Complexes of the $[Rh(CO)_2L_2]ClO_4$ type

(i) L = Phosphine and arsine oxides. Bubbling of carbon monoxide at atmospheric pressure through dichloromethane solutions of the complexes $[Rh(COD)(OER_3)_2]ClO_4$ (I—V) results in displacement of 1,5-cyclooctadiene and formation in solution (eq. 3) of *cis*-dicarbonyl species, which were detected

(Continued on p. 210)

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* The possible coupling $^2J(Rh\text{—}P)$ was not observed.

TABLE 1

ANALYTICAL RESULTS, MOLAR CONDUCTIVITIES, YIELDS AND IR DATA FOR THE COMPLEXES $[Rh(COD)(OER_3)_2]ClO_4$ AND $[Rh(COD)(OER_3)(PPh_3)]ClO_4$

Complex		Found (Calcd.) (%)		Λ_M (ohm^{-1} cm^2 mol^{-1})	Yield (%)	ν(EO) (cm^{-1})
		C	H			
I	$[Rh(COD)\{OP(p\text{-}ClC_6H_4)_3\}_2]ClO_4$	49.3 (49.2)	3.7 (3.4)	129	88	1168s
II	$[Rh(COD)(OPPh_3)_2]ClO_4$	60.8 (60.9)	5.0 (4.9)	129	73	1150vs
III	$[Rh(COD)\{OP(p\text{-}MeC_6H_4)_3\}_2]ClO_4$	62.5 (63.1)	6.1 (5.7)	131	64	1145vs
IV	$[Rh(COD)\{OP(p\text{-}MeOC_6H_4)_3\}_2]ClO_4$	57.7 (57.3)	5.5 (5.2)	123	88	1142sh
V	$[Rh(COD)(OAsPh_3)_2]ClO_4$	55.0 (55.3)	4.4 (4.4)	135	88	870s
VI	$[Rh(COD)\{OP(p\text{-}ClC_6H_4)_3\}(PPh_3)]ClO_4$	54.5 (55.4)	4.3 (4.1)	136	72 [a]	1149s
VII	$[Rh(COD)(OPPh_3)(PPh_3)]ClO_4$	62.6 (62.1)	5.0 (5.0)	136	85 [b]	1152vs
VIII	$[Rh(COD)\{OP(p\text{-}MeC_6H_4)_3\}(PPh_3)]ClO_4$	62.5 (63.2)	5.8 (5.4)	129	87 [a]	1149vs
IX	$[Rh(COD)\{OP(p\text{-}MeOC_6H_4)_3\}(PPh_3)]ClO_4$	59.8 (60.0)	5.4 (5.1)	125	86 [a]	1145s
X	$[Rh(COD)(OAsPh_3)(PPh_3)]ClO_4$	58.9 (59.0)	4.8 (4.7)	139	77 [b]	876vs

[a] Yields according to eq. 2. [b] Yields according to method (ii) (experimental part).

TABLE 2

ANALYTICAL RESULTS, MOLAR CONDUCTIVITIES, YIELDS AND IR DATA FOR THE COMPLEXES $[Rh(CO)_2L_2]ClO_4$, $[Rh(CO)L_2(PPh_3)]ClO_4$ AND $[Rh(CO)L(PPh_3)_2]ClO_4$

Complex		Found (calcd.) (%)			Λ_M (ohm^{-1} cm^2 mol^{-1})	Yield (%)	Characteristic IR bands (cm^{-1})	
		C	H	N			ν(CO)	Other
XI	$[Rh(CO)_2(OPPh_3)_2]ClO_4$	55.7 (56.0)	3.8 (3.7)	—	136	80 ^{a}	2100,2025	1145vs
XII	$[Rh(CO)_2(OAsPh_3)_2]ClO_4$	50.2 (50.5)	3.4 (3.3)	—	132	86 ^{a}	2090,2005	860s
XIII	$[Rh(CO)_2\{OP(p\text{-}ClC_6H_4)_3\}_2]ClO_4$	44.2 (44.7)	2.6 (2.4)	—	122	50 ^{b}	2102, 2030	1155s,sh
XIV	$[Rh(CO)_2\{OP(p\text{-}MeC_6H_4)_3\}_2]ClO_4$	59.5 (58.8)	5.1 (4.7)	—	123	30 ^{b}	2100, 2022	1157m,sh
XV	$[Rh(CO)(OPPh_3)_2(PPh_3)]ClO_4$	62.3 (63.0)	4.5 (4.3)	—	132	82	1978	1155s
XVI	$[Rh(CO)(OAsPh_3)_2(PPh_3)]ClO_4$	57.9 (58.1)	3.9 (4.0)	—	117	89	1964	846m
XVII	$[Rh(CO)(4\text{-}MePyO)_2(PPh_3)]ClO_4$	52.9 (52.4)	4.6 (4.1)	3.4 (3.9)	137	90	2000	1207m
XVIII	$[Rh(CO)(4\text{-}MeOPyO)_2(PPh_3)]ClO_4$	50.6 (50.1)	4.5 (3.9)	3.4 (3.8)	126	74	1987	1200s
XIX	$[Rh(CO)\{OP(p\text{-}ClC_6H_4)_3\}(PPh_3)_2]ClO_4$	57.4 (58.1)	3.9 (3.7)	—	134	72 ^{c}	1987	1176m

XX	$[Rh(CO)(OPPh_3)(PPh_3)_2]ClO_4$	63.8 (63.9)	4.8 (4.4)	—	134	97^d	1986	1166s
XXI	$[Rh(CO)\{OP(p\text{-}MeC_6H_4)_3\}(PPh_3)_2]ClO_4$	64.5 (64.8)	5.2 (4.8)	—	138	90^c	1985	1158m
XXII	$[Rh(CO)\{OP(p\text{-}MeOC_6H_4)_3\}(PPh_3)_2]ClO_4$	62.0 (62.0)	4.7 (4.6)	—	121	77^c	1994	1160m
XXIII	$[Rh(CO)(OAsPh_3)(PPh_2)_2]ClO_4$	60.6 (61.3)	4.3 (4.2)	—	137	67^c	1980	880m
XXIV	$[Rh(CO)(4\text{-}NO_2PyO)(PPh_3)_2]ClO_4$	56.7 (56.4)	4.0 (3.8)	3.2 (3.1)	141	90^c	1990	1224s
XXV	$[Rh(CO)(4\text{-}MePyO)(PPh_3)_2]ClO_4$	59.8 (59.8)	4.6 (4.3)	1.8 (1.6)	139	93^c	2000	1210m
XXVI	$[Rh)(CO)(4\text{-}MeOPyO)(PPh_3)_2]ClO_4$	58.3 (58.7)	4.6 (4.2)	1.9 (1.6)	138	90^c	1988	1203m
XXVII	$[Rh(CO)(DMSO)(PPh_3)_2]ClO_4$	56.1 (56.2)	4.3 (4.4)	—	137	68	1980	
XXVIII	$[Rh(CO)(diox)(PPh_3)_2]ClO_4$	57.8 (58.4)	4.4 (4.5)	—	139	66	1990	
XXIX	$[Rh(CO)(THT)(PPh_3)_2]ClO_4$	58.0 (58.4)	4.5 (4.5)	—	138	60	2010	
XXX	$[Rh(CO)(SPPh_3)(PPh_3)_2]ClO_4$	63.6 (63.0)	4.3 (4.3)	—	137	43	2010	
XXXI	$[Rh(CO)(SEt_2)(PPh_3)_2]ClO_4$	58.3 (58.3)	4.3 (4.8)	—	141	61	1990	

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[a] Yields according to eq. 3. [b] Yields according to method (ii) (experimental part). [c] Yields according to eq. 5. [d] Yields according to eq. 6.

by IR spectroscopy.

$$[Rh(COD)(OER_3)_2]ClO_4 + 2\ CO \rightleftharpoons [Rh(CO)_2(OER_3)_2]ClO_4 + COD \qquad (3)$$

By addition of a large volume of ether with carbon monoxide bubbling through the solution, complexes XI and XII are precipitated as yellow crystalline solids (see Table 2). Solid mixtures of the dicarbonyl complexes and the starting material are obtained in other cases, suggesting that the reaction in eq. 3 is an equilibrium. Confirming this, addition of 1,5-cyclooctadiene to complexes XI and XII leads to $[Rh(COD)(OER_3)_2]ClO_4$ derivatives.

The dicarbonyl complexes XI—XIV can also be obtained by addition of the appropriate phosphine or arsine oxide to acetone solutions of $[Rh(CO)_2(Me_2CO)_x]ClO_4$ obtained by treating $[RhCl(CO)_2]_2$ with silver perchlorate.

The analytical results, molar conductivities, yields and IR data for the complexes XI—XIV are given in Table 2. Their IR spectra exhibit two intense ν(CO) bands typical of *cis*-dicarbonyl rhodium complexes [24], the ν(PO) or ν(AsO) band for the coordinated oxigen-donor ligand and the characteristic absorptions of the uncoordinated perchlorate anion. In accord with the proposed structure, the ^{31}P NMR spectrum of complex XI shows a singlet signal at 47.1 ppm.

(ii) L = Pyridine N-oxides. Bubbling of carbon monoxide through dichloromethane solutions of the complex $[Rh(COD)(OPyR)_2]ClO_4$ [19] (OPyR = 4-NO_2PyO, 4-MePyO, 4-MeOPyO) gives the *cis*-dicarbonyl complexes which display two intense ν(CO) bands in the 2100—2000 cm^{-1} region. However, attempts to isolate them were unsuccesful, and the starting materials were recovered.

Complexes of the $[Rh(CO)L_2(PPh_3)]ClO_4$ type

(i) L = Phosphine and arsineoxides. Treatment of dichloromethane solutions of the complexes of the type $[Rh(COD)(OER_3)_2]ClO_4$ (I—V) with carbon monoxide and subsequent addition of the stoichiometric amount of triphenylphosphine leads to the complexes of the type $[Rh(CO)(OER_3)_2(PPh_3)]ClO_4$ (eq. 4).

$$[Rh(COD)(OER_3)_2]ClO_4 + CO + PPh_3 \rightarrow [Rh(CO)(OER_3)_2(PPh_3)]ClO_4 + COD \qquad (4)$$

The complexes XV and XVI are isolated from the solution as reasonably pure yellow solids, whilst the analogous derivatives with ligands of the type $OP(p\text{-}RC_6H_4)_3$ are contaminated with $[Rh(CO)(OER_3)(PPh_3)_2]ClO_4$ derivatives. The latter are the result of repeated recrystallizations of the mixtures.

An alternative route for the preparation of the complexes XV and XVI involves the addition of a stoichiometric amount of triphenylphosphine (1/1) to dichloromethane solutions of complexes XI and XII. Their IR spectra show a single band ν(CO) along with ν(PO) or ν(AsO) of the oxygen-donor ligand and the characteristic bands of the perchlorate ion. They are 1/1 electrolytes (see Table 2). The ^{31}P NMR spectrum of complex XV consists of two resonances: a doublet at 48.6 ppm (d, ^1J(Rh—P) 182 Hz) from the triphenyl phosphine and a broad band centered at 40.5 ppm from both oxygen-donor ligands, which are apparently equivalent.

(ii) L = Pyridine N-oxides. Carbonylation of the complexes of the type $[Rh(COD)(OPyR)_2]ClO_4$ followed by careful addition of triphenylphosphine similarly leads to the formation of the compounds $[Rh(CO)(OPyR)_2(PPh_3)]ClO_4$. The complexes XVII and XVIII are isolated from the solutions as yellow crystalline solids (see Table 2). However, a mixture of $[Rh(CO)(4\text{-}NO_2PyO)_2(PPh_3)]ClO_4$ and $[Rh(CO)(4\text{-}NO_2PyO)(PPh_3)_2]ClO_4$ is obtained when the pyridine ring bears an electron withdrawing substituent such as a nitro group. Recrystallization of the mixture gives the latter complex.

The IR spectra of the complexes XVII and XVIII shows a single $\nu(CO)$ band between 2000—1980 cm^{-1} and an intense absorption $\nu(NO)$ around 1200 cm^{-1}, characteristic of coordinated pyridine *N*-oxide [19], in accord with the proposed formula.

Complexes of the $[Rh(CO)L(PPh_3)_2]ClO_4$ type

Carbonylation of the complexes of the type $[Rh(COD)(OER_3)_2]ClO_4$ (I—V) and $[Rh(COD)(OPyR)_2]ClO_4$ [19] (OPyR = $4\text{-}NO_2PyO$, 4-MePyO, 4-MeOPyO) in dichloromethane at atmospheric pressure followed by addition of triphenylphosphine in molar ratio 1/2 gives directly (eq. 5) the complexes of the type $[Rh(CO)L(PPh_3)_2]ClO_4$, which were isolated as yellow crystalline solids (complexes XIX—XXVI, Table 2).

$$[Rh(COD)L_2]ClO_4 + CO + 2\ PPh_3 \rightarrow [Rh(CO)L(PPh_3)_2]ClO_4 + COD + L \qquad (5)$$

They can also be prepared by replacement of acetone in the complex $[Rh(CO)(Me_2CO)(PPh_3)_2]ClO_4$ [25] by the oxygen-donor ligand L (eq. 6).

$$[Rh(CO)(Me_2CO)(PPh_3)_2]ClO_4 + L \rightarrow [Rh(CO)L(PPh_3)_2]ClO_4 + Me_2CO \qquad (6)$$

The complexes XIX—XXVI are 1/1 electrolytes in acetone, and their spectra support square-planar structures in which the two phosphine ligands are in positions *trans*. Thus, the ^{31}P NMR spectrum of complex XX shows a resonance at 38.5 ppm due to the phosphine oxide and a doublet signal at 28.0 ppm (d, $^1J(Rh—P)$ 125 Hz) characteristic of *trans*-bisphosphine rhodium(I) complexes [26]. All the complexes display in their IR spectra a single $\nu(CO)$ band, $\nu(PO)$, $\nu(AsO)$ or $\nu(NO)$ bands of the coordinated oxygen-donor ligand, and bands of the perchlorate anion (see Table 2).

The complexes $[Rh(CO)(DMSO)(PPh_3)_2]ClO_4$ (XXVII) and $[Rh(CO)(diox)(PPh_3)_2]ClO_4$ (XXVIII) were prepared similarly by carbonylation (DMSO = dimethylsulfoxide and diox = dioxane). The related compounds with sulfur-donor ligands $[Rh(CO)(THT)(PPh_3)_2]ClO_4$ (XXIX), $[Rh(CO)(SPPh_3)(PPh_3)_2]ClO_4$ (XXX) and $[Rh(CO)(SEt_2)(PPh_3)_2]ClO_4$ (XXXI) (THT = tetrahydrothiophene; $SPPh_3$ = triphenylphosphine sulfide; SEt_2 = diethylthioether) are similarly obtained.

Dinuclear complexes of the $[Rh_2(\mu\text{-}OER_3)_2(CO)_2(PPh_3)_2](ClO_4)_2$ type

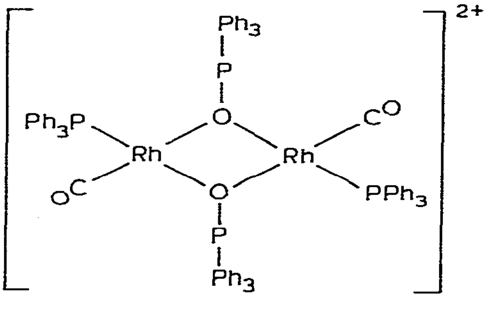
Bubbling of carbon monoxide through dichloromethane solutions of the complexes of the type $[Rh(COD)(OER_3)(PPh_3)]ClO_4$ (VI—X) gives rise to complex reactions. Two $\nu(CO)$ bands characteristic of *cis*-dicarbonyl rhodium(I) complexes, among others, are detected in solution. These solutions yield yellow solids which are a mixture of apparently monocarbonyl rhodium(I) complexes. Recrystallization of the crude solids gives complexes of the general formula $[Rh_2(\mu\text{-}OER_3)_2(CO)_2(PPh_3)_2](ClO_4)_2$ (complexes XXXII—XXXVI, Table 3) which were the main products.

These dinuclear complexes are obtained directly by reaction of the species $[Rh(CO)(PPh_3)(Me_2CO)_x]ClO_4$ with the appropriate phosphine oxide or triphenylarsine oxide (eq. 7), and are isolated as orange-yellow solids.

$$2\,[Rh(CO)(PPh_3)(Me_2CO)_x]ClO_4 + 2\,OER_3 \rightarrow [Rh_2(\mu\text{-}OER_3)_2(CO)_2(PPh_3)_2](ClO_4)_2 + 2\,x\,Me_2CO \qquad (7)$$

Measurements of the equivalent conductivities in nitromethane or acetone solutions of the complexes XXXII—XXXVI at different concentrations give plots of the Onsager equation ($\Lambda_o - \Lambda_e = B\sqrt{C}$), for which B values are characteristic of 2/1 electrolytes in these solvents [27,28] (see Table 3). Their IR spectra show only one ν(CO) band in the region of terminal carbonyls, suggesting a structure for the complex ion in which the ligands OER_3 act as bridges between the two rhodium atoms and each carbonyl and triphenylphosphine ligands is bonded to one rhodium atom. Structures with phosphine oxides bridging two metal atoms have been previously proposed for complexes of the type $[M(OPPh_3)_4](ClO_4)_2$ M = Fe, Co, Ni [29]. Similar structures with pyridine *N*-oxides of the type $[Cu(\mu\text{-}OPy)Cl_2]_2$ have been confirmed by X-ray diffraction studies [30]. For copper complexes with pyridine *N*-oxides there is not a clearcut difference between the position of ν(NO) for bridging and terminal ligands. No substantial differences in the position of ν(PO) and ν(AsO) are found between complexes XXXII—XXXVI and complexes in which the ligands are terminal.

The ^{31}P NMR spectrum of the complex XXXIII consists of a band centered at 41.1 ppm from the oxygen-donor ligands and a doublet resonance at 48.5 ppm (d, ^1J(Rh—P) 177 Hz) due to both triphenylphosphine ligands in equivalent environments. The data suggest the following structure:



In addition, complex XXXIII undergoes symmetrical bridge cleavage on treatment with triphenylphosphine, giving $[Rh(CO)(OPPh_3)(PPh_3)_2]ClO_4$.

Dinuclear complexes of the $[Rh_2(\mu\text{-}OER_3)_2(COD)_2](ClO_4)_2$ type

In analogy with the reactions represented in eq. 7, reaction of the solvate $[Rh(COD)(Me_2CO)_x]ClO_4$ with a stoichiometric amount of ligands OER_3 gives the complexes of the type $[Rh_2(\mu\text{-}OER_3)_2(COD)_2](ClO_4)_2$, which are iso-

TABLE 3

ANALYTICAL RESULTS, YIELDS, CONDUCTIVITY AND IR DATA FOR THE DINUCLEAR COMPLEXES $[Rh_2(\mu\text{-}OER_3)_2(CO)_2(PPh_3)_2](ClO_4)_2$ AND $[Rh_2(\mu\text{-}OER_3)_2(COD)_2](ClO_4)_2$

Complex		Found (calcd.) (%)		Yield (%)	Conductivity data		IR data (cm^{-1})	
		C	H		B [a]	Λ_M (ohm^{-1} cm^2 mol^{-1})	ν(CO)	ν(EO)
XXXII	$[Rh_2\{\mu\text{-}OP(p\text{-}ClC_6H_4)_3\}_2(CO)_2(PPh_3)_2](ClO_4)_2$	49.8 (50.8)	3.3 (3.1)	63	599 [b]	150 [b]	1988	1142vs,sh
XXXIII	$[Rh_2(\mu\text{-}OPPh_3)_2(CO)_2(PPh_3)_2](ClO_4)_2$	57.7 (57.6)	4.6 (3.9)	87	537 [b]	170 [b]	1980	1158,1136s
XXXIV	$[Rh_2\{\mu\text{-}OP(p\text{-}MeC_6H_4)_3\}_2(CO)_2(PPh_3)_2](ClO_4)_2$	58.8 (59.1)	5.1 (4.5)	58	583 [b]	164 [b]	1986	1148vs,sh
XXXV	$[Rh_2\{\mu\text{-}OP(p\text{-}MeOC_6H_4)_3\}_2(CO)_2(PPh_3)_2](ClO_4)_2$	55.8 (55.8)	4.9 (4.2)	52	487 [b]	156 [b]	1980	1145s
XXXVI	$[Rh_2(\mu\text{-}OAsPh_3)_2(CO)_2(PPh_3)_2](ClO_4)_2$	55.2 (54.5)	3.9 (3.7)	72	730 [c]	208 [c]	1963	844s
XXXVII	$[Rh_2\{\mu\text{-}OP(p\text{-}ClC_6H_4)_3\}_2(COD)_2](ClO_4)_2$	45.3 (45.1)	3.9 (3.5)	70	280 [b]	162 [b]	—	1155s,sh
XXXVIII	$[Rh_2(\mu\text{-}OPPh_3)_2(COD)_2]ClO_4)_2$	52.6 (53.0)	4.9 (4.6)	32	266 [b]	164 [b]	—	1154s
XXXIX	$[Rh_2\{\mu\text{-}OP(p\text{-}Me_6H_4)_3\}_2(COD)_2](ClO_4)_2$	55.8 (55.2)	5.8 (5.3)	60	246 [b]	146 [b]	—	1152s
XL	$[Rh_2\{\mu\text{-}OP(p\text{-}MeOC_6H_4)_3\}_2(COD)_2](ClO_4)_2$	51.5 (51.3)	5.1 (4.9)	90	195 [b]	156 [b]	—	1146s
XLI	$[Rh_2(\mu\text{-}OAsPh_3)_2(COD)_2](ClO_4)_2$	49.6 (49.3)	4.5 (4.3)	89	999 [c]	276 [c]	—	852s

[a] Slope found for Onsager's equation $\Lambda_e = \Lambda_0 - B\sqrt{C}$ [27]. [b] Measured in nitromethane solution. [c] Measured in acetone solution.

lated as hygroscopic yellow solids (complexes XXXVII—XLI). Their analyses, molar conductivities, yields and IR data are collected in Table 3.

Measurements of equivalent conductivities of nitromethane solutions of the complexes XXXVI—XL at various concentrations lead to values of coefficient B in the Onsager equation between those corresponding to 1/1 and 1/2 electrolytes. Evaporation of these solutions gives yellow solids different from the starting materials, which contain nitromethane, and consequently the low B values are not completely unexpected.

The ^{31}P NMR spectra of the complexes XXXVIII and XL display a resonance at 40.2 and 41.2 ppm, respectively, similar in position to the resonance of the related complex $[Rh_2(\mu\text{-}OPPh_3)_2(CO)_2(PPh_3)_2](ClO_4)_2$. On the other hand, conductivity data for acetone solutions of $[Rh_2(\mu\text{-}OAsPh_3)_2(COD)_2](ClO_4)_2$ (XLI) are compatible ($B = 999$) [28] with the proposed dinuclear structure.

Complexes XXXVI—XLI undergo symmetrical bridge cleavage with triphenylphosphine, giving the mononuclear species $[Rh(COD)(OER_3)(PPh_3)]ClO_4$.

Experimental

C, H and N analyses were carried out with a Perkin—Elmer 240 B microanalyzer. IR spectra were recorded on a Perkin—Elmer 577 spectrophotometer (over the range 4000—200 cm^{-1}) using Nujol mulls between polyethylene sheets or dichloromethane solutions in cells with NaCl windows. Conductivities were measured with a Philips PW 9501/01 conductimeter in ca. 5×10^{-4} M nitromethane or acetone solutions and, when stated, at various concentrations in the range 5×10^{-3}—10^{-4} M. The ^{31}P NMR spectra were recorded on a Varian FT-80A spectrometer using $CDCl_3$ solutions. Chemical shifts are given in ppm relative to external 85% H_3PO_4, with a positive sign indicating a shift to lower field.

$[RhCl(COD)]_2$ [31], $[RhCl(CO)(PPh_3)]_2$ [32], $[RhCl(CO)_2]_2$ [33], $RhCl(CO)(PPh_3)_2$ [34] and $[Rh(COD)(OPyR)_2]ClO_4$ [19] were prepared as described elsewhere.

The triarylphosphine oxides were prepared by oxidizing the phosphines in acetone with a slight excess of dilute hydrogen peroxide [35], purified by vacuum-melting and recrystallized from acetone. Triphenylphosphine oxide and triphenylarsine oxide were obtained from Fluka A.G. and recrystallized from acetone. Pyridine *N*-oxides were prepared by standard methods [36,37] and vacuum-distilled or recrystallized before use. The solvents were distilled before use. All the reactions were carried out at room temperature and atmospheric pressure with 0.1—0.2 mmol of the reagents.

Preparation of complexes of the type $[Rh(COD)(OER_3)_2]ClO_4$ (I—V)

The phosphine or arsine oxide (0.40 mmol) was added to a solution of $[Rh(COD)(Me_2CO)_x]ClO_4$ (obtained by treating $[RhCl(COD)]_2$ (0.049 g, 0.10 mmol) with $AgClO_4$ (0.041 g, 0.20 mmol) in 10 ml of acetone and removing the precipitated AgCl by filtration). Vacuum evaporation to dryness left yellow solids which were suspended in hexane, filtered off, washed with hexane, and air-dried.

Preparation of complexes of the type $[Rh(COD)(OER_3)(PPh_3)]ClO_4$ *(VI—X)*

(i) To an acetone solution of equimolecular amounts of PPh_3 and the respective phosphine or arsine oxide was added a stoichiometric amount of $[Rh(COD)(Me_2CO)_x]ClO_4$. The solutions were vacuum-concentrated to ca. 1 ml and slow addition of ether (VII and X) or hexane (VI, VIII and IX) gave yellow crystalline solids, which were filtered off, washed thoroughly with ether or hexane, and air-dried.

(ii) PPh_3 (1/1) was added to the above-described dichloromethane solutions of complexes I—V, work-up was as in (i). This method gave higher yields for complexes VII and X (see Table 1).

Preparation of complexes of the type $[Rh(CO)_2(OER_3)_2]ClO_4$ *(XI—XIV)*

(i) Bubbling of carbon monoxide for 15 min through a very concentrated dichloromethane/ether solution of $[Rh(COD)(OPPh_3)_2]ClO_4$ led to formation of a pale-yellow crystalline solid. Precipitation was completed by addition of ether and bubbling of carbon monoxide for another 15 min. The resulting crystals were filtered off, washed with ether and air-dried. Complex $[Rh(CO)_2(OAsPh_3)_2]ClO_4$ (XII) was synthesized in an analogous manner.

(ii) Addition of $OP(p\text{-}ClC_6H_4)_3$ (0.079 g, 0.21 mmol) to an acetone solution of $[Rh(CO)_2(Me_2CO)_x]ClO_4$ (obtained by treating $[RhCl(CO)_2]_2$ (0.020 g, 0.05 mmol) with $AgClO_4$ (0.021 g, 0.10 mmol) in the absence of light and under argon) led to a yellow solution. The precipitated AgCl was filtered off and the filtrate was concentrated to dryness to give an off-yellow oil. This was extracted with ca. 50 ml of ether, and the extract was evaporated to dryness and the resulting solid washed with hexane and vacuum-dried. Complex XIV was obtained in a similar way.

Complexes XI and XII can be obtained by this method, but in lower yields.

Preparation of complexes of the type $[Rh(CO)L_2(PPh_3)]ClO_4$ *(XV—XVIII)*

A stoichiometric amount (1/1) of PPh_3 in dichloromethane was added to a solution of $[Rh(CO)_2L_2]ClO_4$ (obtained by 15 min bubbling of carbon monoxide through a dichloromethane solution of complexes of the type $[Rh(COD)L_2]ClO_4$, where L = OER_3 (complexes I—V) or L = OPyR [19]. After 30 min stirring the solution was concentrated under reduced pressure to ca. 1 ml. The complexes were crystallized by slow addition of ether. The yellow solids were filtered off, washed with ether, and air-dried.

Complexes in which L was a substituted pyridine *N*-oxide gave oils which were crystallized by prolonged stirring with ether.

Preparation of complexes of the type $[Rh(CO)L(PPh_3)_2]ClO_4$

Complexes XIX—XXVI. (i) Bubbling of carbon monoxide through a dichloromethane solution of $[Rh(COD)(OPPh_3)_2]ClO_4$ (0.052 g, 0.06 mmol) and subsequent addition of PPh_3 (0.031 g, 0.12 mmol) gave a intense yellow solution. After 30 min stirring, the solution was evaporated to dryness to give a yellow solid, which was suspended in hexane, filtered off, washed with hexane and vacuum-dried. The other complexes of this type were synthesized analogously using the corresponding $[Rh(COD)L_2]^+$ complexes as starting materials, but ether was used as precipitating agent for complexes with substituted pyridine *N*-oxides.

(ii) To an acetone solution of $[Rh(CO)(Me_2CO)(PPh_3)_2]ClO_4$ (0.100 g, 0.12 mmol) was added a stoichiometric amount of the relevant ligand (0.12 mmol). The solution was concentrated to ca. 1 ml, and slow addition of hexane (complexes XIX—XXIII) or ether (complexes XXIV—XXVI) yielded yellow crystalline solids, which were filtered off, washed with hexane or ether, and vacuum-dried.

Complexes XXVII—XXXI. A stoichiometric amount of the corresponding O- or S-donor ligand (0.10 mmol) was added to an acetone solution of $[Rh(COD)(Me_2CO)_x]ClO_4$ (0.10 mmol). Bubbling of carbon monoxide for 10 min through this solution and addition of PPh_3 (0.052 g, 0.20 mmol) gave a yellow solution which was stirred for 30 min and vacuum-evaporated to ca. 1 ml. These complexes were precipitated by slow addition of ether as yellow solids, which were filtered off, washed with ether and vacuum-dried.

Preparation of complexes of the type $[Rh_2(\mu\text{-}OER_3)_2(CO)_2(PPh_3)_2](ClO_4)_2$ (XXXII—XXXVI)

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

(i) A solution of $AgClO_4$ (0.025 g, 0.12 mmol) in 5 ml of acetone was treated with an acetone solution of $[RhCl(CO)(PPh_3)]_2$ (0.052 g, 0.06 mmol) in the absence of light and the mixture was stirred for 15 min. The precipitated AgCl was filtered off and a solution of triphenylphosphine oxide (0.033 g, 0.12 mmol) in 10 ml of acetone was slowly added to the filtrate. The solution was vacuum-evaporated to dryness and the resulting orange-yellow solid was washed with hexane and vacuum-dried. Complexes XXXII, XXXIV—XXXVI were prepared analogously. The preparations of these complexes, which are hygroscopic, were carried out under argon.

(ii) Bubbling of carbon monoxide for 15 min through dichloromethane solutions of $[Rh(COD)(OER_3)(PPh_3)]ClO_4$ (VI—X), followed by concentration under reduced pressure to ca. 1 ml and addition of hexane gave orange-yellow solids, which were filtered off, washed with hexane, and vacuum-dried. They were recrystallized twice from dichloromethane solutions by slow addition of hexane. The recrystallized complexes were washed with hexane and vacuum-dried.

Preparation of complexes of the type $[Rh_2(\mu\text{-}OER_3)_2(COD)_2](ClO_4)_2$ (XXXVII—XLI)

To an acetone solution of $[Rh(COD)(Me_2CO)_x]ClO_4$ under an argon atmosphere was slowly added the stoichiometric amount of an acetone solution of the OER_3 ligand (Rh/OER_3, 1/1). Evaporation to dryness gave dark-yellow oils which were kept under vacuum for 1 h. Addition of dichloromethane gave yellow solutions, which were vacuum-concentrated to dryness. The resulting yellow solids were washed several times with hexane and vacuum-dried. These complexes are hygroscopic, except for $[Rh_2(\mu\text{-}OAsPh_3)_2(COD)_2](ClO_4)_2$.

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