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RHODIUM(I) COMPLEXES WITH BIS(PYRAZOLYL)METHANE LIGANDS. CRYSTAL STRUCTURE OF $[Rh(COD)(CH_2(Pz)_2)]ClO_4 \cdot \frac{1}{2}\ C_2H_4Cl_2$

L.A. ORO, M. ESTEBAN,

Departamento de Quimica Inorgánica, Universidad de Zaragoza, Zaragoza (Spain)

R.M. CLARAMUNT,

Departamento de Quimica Orgánica, Universidad Nacional de Educación a Distancia, Ciudad Universitaria, Madrid-3 (Spain)

J. ELGUERO,

Instituto de Química Medica, C.S.I.C., Juan de la Cierva 3, Madrid-6 (Spain)

C. FOCES-FOCES and F.H. CANO

Departamento de Rayos-X, Instituto Rocasolano, C.S.I.C., Serrano 119 Madrid-6 (Spain)

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Summary

The synthesis and properties of neutral and cationic complexes of general formulae $[\{RhCl(diolefin)\}_2(CH_2(pz)_2)]$, $[Rh(CO)_2(CH_2(pz)_2)][RhCl_2(CO)_2]$, $[Rh(diolefin)(CH_2(pz)_2)]ClO_4$, $[\{Rh(diolefin)(PPh_3)\}_2(CH_2(pz)_2)](ClO_4)_2$, $[Rh(CO)_2(CH_2(pz)_2)]ClO_4$ and $[Rh(CO)(CH_2(pz)_2)(PPh_3)]ClO_4$ are described. The NMR spectra of $[Rh(COD)(CH_2(pz)_2)]ClO_4$ complexes are discussed. X-ray structural analysis of $[Rh(COD)(CH_2(Pz)_2)]ClO_4 \cdot \frac{1}{2}\ C_2H_4Cl_2$ is presented; the final R factor is 0.061 for 2436 observed data, recorded with Cu-K_α, not corrected for absorption and with the sample inside a capillary. The Rh atom presents a distorted square planar coordination in a mononuclear arrangement. The COD ring has a twisted boat conformation, and the two halves of the $CH_2(Pz)_2$ moiety, which are quite similar to one another, form an angle of 47.2(4)°.

Introduction

Several types of rhodium(I) complexes with pyrazole-type ligands have been described in recent years [1–8]. It seemed of interest to study the coordination behaviour of bis(pyrazolyl)methane derivatives, a class of neutral ligands, little studied in rhodium(I) chemistry [9], and related to the well-known isosteric but uninegative bis(pyrazolyl)borates [10–13]. We thus describe below mononuclear and

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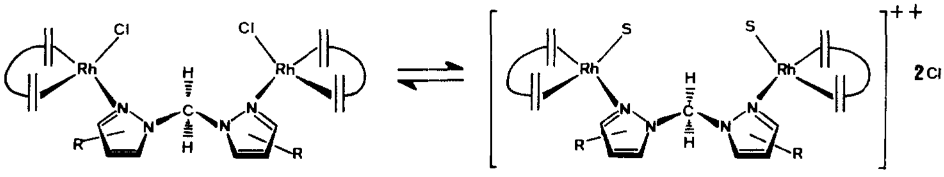
dinuclear rhodium(I) complexes with substituted bis(pyrazolyl)methanes. Throughout the amount a generic bis(pyrazolyl)methane ligand is indicated by $CH_2(pz)_2$, an unsubstituted bis(pyrazolyl)methane by $CH_2(Pz)_2$: the substituted ligands used are bis(3,5-dimethylpyrazolyl)methane ($CH_2(3,5\text{-}Me_2Pz)_2$), bis(3-aminopyrazolyl)methane ($CH_2(3\text{-}NH_2Pz)_2$), 3,5′-diaminobis(pyrazolyl)methane ($CH_2(3/5\text{-}NH_2Pz)_2$), bis(4-bromopyrazolyl)methane ($CH_2(4\text{-}BrPz)_2$) and bis(4-nitropyrazolyl)methane ($CH_2(4\text{-}NO_2Pz)_2$).

Results and discussion

The dinuclear complexes $[RhCl(diolefin)]_2$ (diolefin = tetrafluorobenzobarrelene (TFB) [14], 1,5-cyclooctadiene (COD) [15] or 2,5-norbornadiene (NBD) [16]) react with bis(pyrazolyl)methane type ligands ($CH_2(pz)_2$), in 1/1 molar ratio, to give yellow air-stable microcrystalline solids of formula $[\{RhCl(diolefin)\}_2(CH_2(pz)_2)]$ (diolefin = TFB; pz = Pz (I), 3,5-Me_2Pz (II), 3-NH_2Pz (III), 3/5-NH_2Pz (IV), 4-BrPz (V). diolefin = COD; pz = Pz (VI), 3-NH_2Pz (VII), 3/5-NH_2Pz (VIII), 4-BrPz (IX), 4-NO_2Pz (X). diolefin = NBD; pz = Pz (XI), 3,5-Me_2Pz (XII), 3-NH_2Pz (XIII), 3/5-NH_2Pz (XIV), 4-BrPz (XV)).

Table 1 lists the analytical and other data for the isolated complexes. The molecular weights of the complexes in chloroform point to a dimeric structure, but the observed values of the molecular weight are sometimes somewhat lower than expected, perhaps because of dissociation. In keeping with this conductivity measurements on these complexes in acetone give values of Λ_M in the range 3–60 ohm^{-1} cm^2 mol^{-1}, suggesting the presence of the following equilibrium:



This is consistent with suggestions made by Leung and Peterson for related complexes containing the $PhCH(3,5\text{-}Me_2Pz)_2$ ligand [9].

In these complexes the rhodium atoms are probably in a square planar arrangement, in which the bis(pyrazolyl)methane ligands act as *exo*-bidentate bridges, in contrast with the more general chelating bidentate behaviour [10,17,18]. Some reactions between $CH_2(pz)_2$ and $[RhCl(diolefin)]_2$ in 2/1 molar ratio were carried out in an attempt to prepare $[RhCl(diolefin)(CH_2(pz)_2)]$ or $[Rh(diolefin)(CH_2(pz)_2)]Cl$ compounds, but dinuclear complexes of formula $[\{RhCl(diolefin)\}_2(CH_2(pz)_2)]$ were obtained, along with excess of $CH_2(pz)_2$. However, the reaction of $CH_2(4\text{-}BrPz)_2$ with $[RhCl(COD)]_2$ (2/1 molar ratio) yields the neutral five-coordinated derivative $[RhCl(COD)(CH_2(4\text{-}Brpz)_2)]$ (XVI), identified by elemental analysis and molecular weight measurements. Its low molar conductance (3 ohm^{-1} cm^2 mol^{-1}) support the neutral formulation *. In contrast, if $CH_2(4\text{-}Brpz)_2$ is added to $[RhCl(TFB)]_2$ or $[RhCl(NBD)]_2$, the dinuclear complexes V and XV were obtained.

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* A related ionic derivative of formula $[Rh(COD)(PhCH(3,5\text{-}Me_2pz)_2)]Cl$ has been reported recently [9].

TABLE 1. ANALYTICAL DATA FOR THE NEUTRAL COMPLEXES

Complex	Analysis (found (calcd.)(%))			Mol. wt. ($CHCl_3$) (found (calcd.))	Yield (%)
	C	H	N		
$[\{RhCl(TFB)\}_2(CH_2(Pz)_2)]$ (I)	42.85	2.83	6.34	–	71
	(42.44)	(2.30)	(6.38)		
$[\{RhCl(TFB)\}_2(CH_2(3,5\text{-}Me_2Pz)_2)]$ (II)	45.17	3.19	5.13	713	84
	(45.04)	(3.02)	(6.00)	(933)	
$[\{RhCl(TFB)\}_2(CH_2(3\text{-}NH_2Pz)_2)]$ (III)	39.30	2.49	9.18	–	73
	(41.04)	(2.44)	(9.26)		
$[\{RhCl(TFB)\}_2(CH_2(3/5\text{-}NH_2Pz)_2)]$ (IV)	41.46	2.66	9.78	997	80
	(41.04)	(2.44)	(9.26)	(907)	
$[\{RhCl(TFB)\}_2(CH_2(4\text{-}BrPz)_2)]CHCl_3$ (V)	33.21	1.77	4.65	720	76
	(33.29)	(1.66)	(4.85)	(1035)	
$[\{RhCl(COD)\}_2(CH_2(Pz)_2)]$ (VI)	43.25	5.04	8.67	443	67
	(43.08)	(5.03)	(8.74)	(641)	
$[\{RhCl(COD)\}_2(CH_2(3\text{-}NH_2Pz)_2)]$ (VII)	41.96	5.88	12.76	552	62
	(41.15)	(5.10)	(12.52)	(671)	
$[\{RhCl(COD)\}_2(CH_2(3/5\text{-}NH_2Pz)_2)]$ (VIII)	41.63	5.25	12.33	501	77
	(41.15)	(5.10)	(12.52)	(671)	
$[\{RhCl(COD)\}_2(CH_2(4\text{-}BrPz)_2)]$ (IX)	34.22	3.71	6.64	–	55
	(34.57)	(3.78)	(7.01)		
$[\{RhCl(COD)\}_2(CH_2(4\text{-}NO_2Pz)_2)]$ (X)	37.89	4.22	11.04	–	69
	(37.78)	(4.13)	(11.49)		
$[\{RhCl(NBD)\}_2(CH_2(Pz)_2)]$ (XI)	41.42	4.08	9.28	497	82
	(41.41)	(3.97)	(9.20)	(609)	
$[\{RhCl(NBD)\}_2(CH_2(3,5\text{-}Me_2Pz)_2)]$ (XII)	45.34	5.26	8.06	–	60
	(45.13)	(4.84)	(8.42)		
$[\{RhCl(NBD)\}_2(CH_2(3\text{-}NH_2Pz)_2)]$ (XIII)	38.57	3.69	13.78	–	79
	(39.46)	(4.10)	(13.15)		
$[\{RhCl(NBD)\}_2(CH_2(3/5\text{-}NH_2Pz)_2)]$ (XIV)	40.24	4.46	13.56	–	92
	(39.46)	(4.10)	(13.15)		
$[RhCl(NBD)\}_2(CH_2(4\text{-}BrPz)_2)]$ (XV)	33.06	3.12	7.43	–	73
	(32.89)	(2.89)	(7.30)		
$[RhCl(COD)(CH_2(4\text{-}BrPz)_2)]$ (XVI)	32.58	3.43	9.75	450	72
	(32.61)	(3.82)	(10.14)	(552)	

These results suggest that the nuclearity is not determined only by the N-donor ligand, and that the ancillary ligands must also be considered. We suspect that the lower π-aceptor character of the COD ligand compared with that of other diolefins (TFB,NBD) may sometimes favour a lower nuclearity. Thus, whilst [Rh(COD)(2-Menapy)]ClO_4 is mononuclear, the related $[Rh_2(2\text{-Menapy})_2(Y_2)_2](ClO_4)_2$ (Y_2 = TFB, NBD; 2-Menapy = 2-methyl-1,8-naphthyridine) are dinuclear [19].

The IR spectra of these complexes show the presence of ν(Rh–Cl) bands in the 250–300 cm^{-1} range (Nujol mulls) along with the characteristic bands of the coordinated $CH_2(pz)_2$ ligands.

It is noteworthy that no $[\{RhCl(CO)_2\}_2(CH_2(pz)_2)]$ complexes were obtained upon treatment of $[RhCl(CO)_2]_2$ [20] with $CH_2(pz)_2$ in dichloromethane. Instead ionic complexes of formula $[Rh(CO)_2(CH_2(pz)_2)][RhCl_2(CO)_2]$ (pz = Pz (XVII), 3,5-Me_2Pz (XVIII)) were obtained. In these compounds the ligand must act as chelate, probably under the influence of the stability of the $[RhCl_2(CO)_2]^-$ anion [21]. In accord with this formulation, the complexes are 1/1 electrolytes in acetone *, and show four strong ν(C≡O) bands, at ca. 2100 and 2040 cm^{-1}, typical of cationic complexes $[Rh(CO)_2(N{-}N)]^+$, and ca. 2070 and 1985 cm^{-1}, characteristic of the $[RhCl_2(CO)_2]^-$ anion [9,21].

Perchlorate complexes

Cationic complexes of formula [Rh(diolefin)($CH_2(pz)_2$)]ClO_4 can be prepared by addition of the ligand and silver perchlorate to acetone suspensions of $[RhCl(\text{diolefin})]_2$, according to eq. 1

$$\tfrac{1}{2}[RhCl(\text{diolefin})]_2 + CH_2(pz)_2 + AgClO_4 \rightarrow [Rh(\text{diolefin})(CH_2(pz)_2)]ClO_4 + AgCl \qquad (1)$$

(diolefin = TFB; pz = Pz (XIX), 3,5-Me_2Pz (XX), 3-NH_2Pz (XXI), 4-BrPz (XXII), 4-NO_2Pz (XXIII). diolefin = COD; pz = Pz (XXIV), 3,5-Me_2Pz (XXV), 3-NH_2Pz (XXVI), 3/5-NH_2Pz (XXVII), 4-BrPz (XXVIII), 4-NO_2Pz (XXIX). diolefin = NBD; pz = Pz (XXX), 3,5-Me_2Pz (XXXI), 3/5-NH_2Pz (XXXII), 4-BrPz (XXXIII), 4-NO_2Pz (XXXIV)). Complex XXVIII can also be obtained by reaction of the mononuclear neutral complex [RhCl(COD)($CH_2(4\text{-Brpz})_2$)] (XV) with silver perchlorate.

We have also studied the reaction of some [Rh(diolefin)($CH_2(pz)_2$)]ClO_4 compounds (in particular XX and XXVIII) with triphenylphosphine (Rh/PPh_3 1/1), and these give dinuclear complexes of formula $[\{Rh(\text{diolefin})(PPh_3)\}_2(CH_2(pz)_2)](ClO_4)_2$ (diolefin = TFB, pz = 3,5-Me_2Pz (XXXV); diolefin = COD, pz = 4-BrPz (XXXVI)), where the $CH_2(pz)_2$ ligand acts as *exo*-bidentate bridge. Complex XXXVI can also be prepared by treating RhCl(COD)(PPh_3) [15] with silver perchlorate and $CH_2(4\text{-BrPz})_2$.

Bubbling carbon monoxide through dichloromethane solutions of complexes XX and XXIX leads to the displacement of the coordinated olefin and formation of the carbonyl derivatives $[Rh(CO)_2(CH_2(pz)_2)]ClO_4$ (pz = 3,5-Me_2Pz (XXXVII), ν(C≡O)

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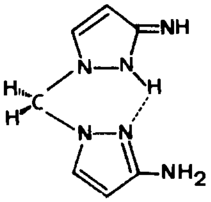
* For complex XVIII the conductivity/concentration plot gives a slope of −293 (Onsager's equation [22]; 1:1 electrolyte in acetone).

2100, 2035 cm^{-1}; pz = 4-NO_2Pz (XXXIX), ν(C≡O) 2110, 2060 cm^{-1} (Nujol mulls)). These show two strong ν(C≡O) bands typical of *cis*-dicarbonyl derivatives. These complexes, like the analogous 4-BrPz derivative (XXXVIII), (ν(C≡O) 2110, 2040 cm^{-1} in Nujol mulls) can also be, prepared by addition of perchloric acid to Rh(acac)$(CO)_2$ [23] in the presence of the corresponding $CH_2(pz)_2$ ligand.

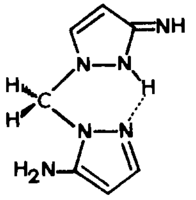
When the carbonylation of complexes XXIV and XXXI, was performed in the presence of triphenylphosphine (Rh/PPh_3 1/1), $[Rh(CO)(CH_2(pz)_2)(PPh_3)]ClO_4$ complexes were obtained (pz = Pz (XL), ν(C≡O) 1990 cm^{-1}; pz = 3,5-Me_2Pz (XLI), ν(C≡O) 1990 cm^{-1}). These complexes are formally related to $[Rh(CO)_2(CH_2(pz)_2)]ClO_4$ by substitution of one carbon monoxide group by triphenylphosphine.

Analytical data and other physical properties for these cationic complexes are listed in Table 2.

The largest modifications in the IR spectra of the ligands compared with those of the complexes are observed in the amino derivatives $CH_2(3\text{-}NH_2Pz)_2$ and $CH_2(3/5\text{-}NH_2Pz)_2$. These ligands in the solid state (KBr pellets or Nujol mulls) show three bands in the N–H stretching region: a very narrow band at 3410 cm^{-1} and two broad bands at 3270 and 3210 cm^{-1}. These last bands correspond, respectively, to the ν_{as} and ν_s vibrations of a NH_2 group (they conform to the Bellamy–Williams' relationship: $\nu_s = 345.5 + 0.875\ \nu_{as}$ [24]). The 3410 cm^{-1} band (shifted to 2550 cm^{-1} by deuteration) probably, belongs to a 3-imino group. Thus, in the solid state the aminated ligands must have following tautomeric structures:



$CH_2(3\text{-}NH_2Pz)_2$



$CH_2(3/5\text{-}NH_2Pz)_2$

In the complexes the imino band disappears and the amino bands are shifted to higher frequencies (for exemple, Table 2, XXI, 3420 and 3360 cm^{-1}; XXVI, 3450 and 3350 cm^{-1}). The first observation corresponds to the fact that the ligand participating in the complexation is the diamino tautomer (both pyrazolic N_2 nitrogens engaged in the coordination with the metal). Since the ν_{as} and $\nu_s(NH_2)$ bands are sensitive to the electronic character of the aromatic ring [25], the observed shifts correspond to a larger electron-withdrawing ability of the complexed pyrazole compared with the free pyrazole ligand.

On the other hand, comparison of the ν(CO) absorption of $[Rh(CO)_2(CH_2(pz)_2)]ClO_4$ complexes with those for analogous derivatives of the type $[Rh(CO)_2L_2]ClO_4$ (L = nitrogen donor ligand) show a shift to higher energies in the sequence: nitrile < diamine < Py < $CH_2(pz)_2$ ~ bipy, suggesting a significant π-acid character of the $CH_2(pz)_2$ ligands.

Finally, we have explored the ability of $[Rh(TFB)(CH_2(Pz)_2)]ClO_4$ to act as a catalyst precursor for the transfer of hydrogen from refluxing isopropanol to

(Continued on p. 86)

TABLE 2

ANALYTICAL DATA FOR THE CATIONIC COMPLEXES

Complex	Analysis (found (calcd.)(%))			A^a	Yield (%)	IR bands (cm^{-1})
	C	H	N			
[Rh(CO)$_2$(CH$_2$(Pz)$_2$)][RhCl$_2$(CO)$_2$] (XVII)	24.08 (24.61)	1.73 (1.50)	10.33 (10.43)	–	60	2100,2070,2040 1995 ν(CO)
[Rh(CO)$_2$(CH$_2$(3,5-Me$_2$Pz)$_2$)][RhCl$_2$(CO)$_2$] (XVIII)	30.09 (30.38)	2.58 (2.38)	9.55 (9.45)	−293	86	2100,2075,2040 1985 ν(CO)
[Rh(TFB)(CH$_2$(Pz)$_2$)]ClO$_4$ (XIX)	38.70 (39.57)	2.75 (2.45)	9.80 (9.71)	−996	82	–
[Rh(TFB)(CH$_2$(3,5-Me$_2$Pz)$_2$)]ClO$_4$ · Me$_2$CO (XX)	45.27 (45.20)	4.26 (4.08)	8.11 (8.30)	–	95	1555 ν(CN) 1710 ν(CO)
[Rh(TFB)(CH$_2$(3-NH$_2$Pz)$_2$)]ClO$_4$ (XXI)	37.62 (37.61)	3.03 (2.66)	13.21 (13.85)	−1469	71	3420,3360 ν(NH) 1620 δ(NH) 1555 ν(CN)
[Rh(TFB)(CH$_2$(4-BrPz)$_2$)]ClO$_4$ (XXII)	31.20 (31.07)	1.61 (1.65)	7.51 (7.63)	−1114	74	–
[Rh(TFB)(CH$_2$(4-NO$_2$Pz)$_2$)]ClO$_4$ (XXIII)	34.14 (34.23)	1.91 (1.81)	12.23 (12.61)	−1381	81	1540,1530 ν(CN)+ ν(NO)
[Rh(COD)(CH$_2$(Pz)$_2$)]ClO$_4$ (XXIV)	39.12 (39.28)	4.47 (4.39)	12.03 (12.21)	−1217	93	1540 ν(CN)
[Rh(COD)(CH$_2$(3,5-Me$_2$Pz)$_2$)]ClO$_4$ (XXV)	43 67 (44.53)	5.42 (5.48)	10.95 (10.88)	−840	81	1565 ν(CN)
[Rh(COD)(CH$_2$(3-NH$_2$Pz)$_2$)]ClO$_4$ (XXVI)	37 14 (36.86)	4.64 (4.54)	16.21 (17.19)	–	84	3450,3350 ν(NH) 1630 δ(NH) 1560 ν(CN)
[Rh(COD)(CH$_2$(3/5-NH$_2$Pz)$_2$)]ClO$_4$ (XXVII)	36.70 (36.86)	4.67 (4.54)	16.57 (17.19)	−969	93	3420,3360,3330 ν(NH) 1610 δ(NH) 1550 ν(CN)

$[Rh(COD)(CH_2(4\text{-}BrPz)_2)]ClO_4$ (XXVIII)	29.59	3.07	8.97	−911	73	–
	(29.22)	(2.94)	(9.08)			
$[Rh(COD)(CH_2(4\text{-}NO_2Pz)_2)]ClO_4$ (XXIX)	32.24	3.52	15.09	–	87	1530 ν(CN) + ν(NO)
	(32.83)	(3.31)	(15.32)			
$[Rh(NBD)(CH_2(Pz)_2)]ClO_4$ (XXX)	36.81	3.54	12.26	–	68	1530 ν(CN)
	(37.99)	(3.64)	(12.66)			
$[Rh(NBD)(CH_2(3,5\text{-}Me_2Pz)_2)]ClO_4$ (XXXI)	43.45	5.14	11.00	–	71	1555 ν(CN)
	(43.35)	(4.85)	(11.23)			
$[Rh(NBD)(CH_2(3/5\text{-}NH_2Pz)_2)]ClO_4$ (XXXII)	35.36	4.36	18.60	–	65	
	(35.57)	(3.84)	(17.78)			
$[Rh(NBD)(CH_2(4\text{-}BrPz)_2)]ClO_4$ (XXXIII)	28.19	2.36	9.69	−1040	73	
	(28.00)	(2.35)	(9.33)			
$[Rh(NBD)(CH_2(4\text{-}NO_2Pz)_2)]ClO_4$ (XXXIV)	30.38	2.69	15.26	–	83	
	(31.57)	(2.65)	(15.78)			
$[\{Rh(TFB)(PPh_3)\}_2(CH_2(3,5\text{-}Me_2Pz)_2)](ClO_4)_2$ (XXXV)	53.49	3.72	2.90	–	80	1560 ν(CN)
	(53.77)	(3.68)	(2.53)			
$[\{Rh(COD)(PPh_3)\}_2(CH_2(4\text{-}BrPz)_2)](ClO_4)_2$ (XXXVI)	49.35	5.27	3.16	–	82	–
	(48.82)	(4.17)	(3.86)			
$[Rh(CO)_2(CH_2(3,5\text{-}Me_2Pz)_2)]ClO_4$ (XXXVII)	33.44	3.27	12.41	–	54	2100,2035 ν(CO)
	(33.75)	(3.05)	(12.11)			
$[Rh(CO)_2(CH_2(4\text{-}BrPz)_2)]ClO_4$ (XXXVIII)	18.69	0.91	9.54	−1437	73	2110,2040 ν(CO)
	(19.15)	(1.07)	(9.93)			
$[Rh(CO)_2(CH_2(4\text{-}NO_2Pz)_2)]ClO_4$ (XXXIX)	21.76	1.51	16.28	−1096	61	2110,2060 ν(NO)
	(21.77)	(1.22)	(16.92)			
$[Rh(CO)(CH_2(Pz)_2)(PPh)_3)]ClO_4$ (XL)	49.33	4.01	8.60	−752	84	1990 ν(CO)
	(48.73)	(3.62)	(8.74)			
$[Rh(CO)(CH_2(3,5\text{-}Me_2Pz)_2)(PPh_3)]ClO_4$ (XLI)	52.23	4.99	7.43	–	65	1990 ν(CO)
	(51.70)	(4.48)	(8.04)			1555 ν(CN)

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[a] From $\Lambda_c = \Lambda_0 - A\sqrt{c}$ (in acetone).

cyclohexene or acetophenone in the presence of potassium hydroxide. After 2 h only 6.5% of cyclohexene or 1% of acetophenone were reduced.

Solution studies on perchlorate complexes

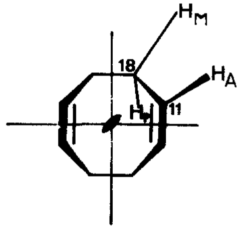
Conductivity measurements in acetone at various concentrations for [Rh(diolefin)($CH_2(pz)_2$)]ClO_4 complexes, give values for A in Onsager's equation ($\Lambda_e = \Lambda_0 - A\sqrt{c}$) [22] in the range 840–1470 [26]. These values point to an association in dilute solution (10^{-3}–10^{-5} *N*). Similar results are obtained for the related carbonyl derivatives, $[Rh(CO)_2(CH_2(4\text{-}BrPz)_2)]ClO_4$ (XXXVIII), $[Rh(CO)_2(CH_2(4\text{-}NO_2Pz)_2)]ClO_4$ (XXXIX) and $[Rh(CO)(CH_2(Pz)_2)(PPh_3)]ClO_4$ (XL) (See Table 2). These observations suggest that in these dilute acetone solutions the complexes must be considered as dimers of formula $[Rh_2(\text{diolefin})_2(CH_2(pz)_2)_2](ClO_4)_2$, $[Rh_2(CO)_4(CH_2(pz)_2)_2](ClO_4)_2$ and $[Rh_2(CO)_2(CH_2(pz)_2)_2(PPh_3)_2](ClO_4)_2$.

Further support for the presence of an association process involving the following equilibrium:

$$[Rh(\text{diolefin})(CH_2(pz)_2)]ClO_4 \rightleftarrows [Rh_2(\text{diolefin})_2(CH_2(pz)_2)_2](ClO_4)_2$$

comes from ^1H NMR measurements on some selected diolefin complexes (XXIV, XXV and XXVI, Table 3; the ^1H NMR spectra of the ligands in $CDCl_3$ and DMSO-d_6 have already been published [27,28]). The complexation shifts all the ligand signals to lower fields (higher frequencies), the longest shifts being those for the methylene bridge and the amino substituent (XXVI). The $^3J_{34}$ coupling constant increases (from 1.7 to 2.4 Hz) and the signal of the H(3) proton narrows (in XXIV is a well resolved quartet). All these observations are similar to those noted for quaternisation [29], although the effects on the shifts are larger when N_2 bears a real positive charge. But the most characteristic feature is the suppression of the quadrupolar effect of N(2) on H(3) (broadening) which occurs on ^{14}N irradiation, protonation, quaternisation and rhodium complexation.

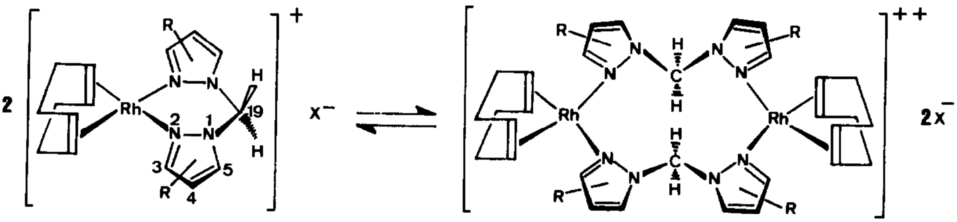
In all the studied complexes, the olefin is 1,5-cyclooctadiene (COD). The 400 MHz spectra of XXIV in acetone was investigated carefully (proton–proton selective decoupling experiments). Only three different protons were observed, one olefinic H_A (broadened by coupling with ^{103}Rh) and two aliphatic, H_M and H_P. This proves beyond doubt than in XXIV the COD ligand has two perpendicular planes of symmetry.



δ_A 4.63 ppm, $^3J_{AM}$ 3.0 Hz;
δ_M 2.60 ppm, $^3J_{AP}$ 0 Hz;
δ_P 2.08 ppm, $^2J_{MP}$ 8.6 Hz (J_{gem})

The fact that $J_{AM} \gg J_{AP}$ suggests that protons H_A and H_M are nearly eclipsed, whereas H_A and H_P are nearly gauche.

The most interesting aspect of the ^1H NMR spectra of the perchlorates XXIV–XXVI is the appearance of the CH_2 signal. It ranges from a narrow singlet (XXIV in acetone) to a well resolved AB system (J_{gem} 15.6 Hz, XXV in acetone) through broad signals (intermediate exchange rates). The singlet corresponds to a planar monomer and the AB system to a folded dimer (diastereotopic protons).

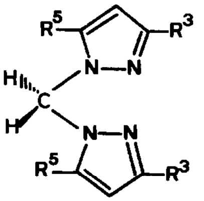


The rate and position of the above equilibrium depends on the nature of R and on the solvent.

A parallel study was carried out by ^{13}C NMR spectroscopy (Table 4). The comparison ligand-complex shows a deshielding of the pyrazole carbons C(3), C(4) and C(5). The effect on C(4) and C(5) is similar to that produced by quaternisation [30], but the C(3) shift (+8.2 ppm for the pair $CH_2(Pz)_2$–XXIV) is very different from the quaternisation effect (−0.8 ppm [30]). Probably, the explanation is a

TABLE 3

^1H NMR CHEMICAL SHIFTS AND COUPLING CONSTANTS FOR SOME LIGANDS AND ITS DIOLEFIN (COD) COMPLEXES

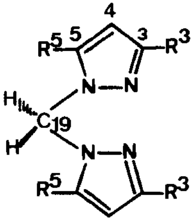


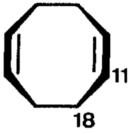
Ligand	R^3	R^5	Solvent	H(3)	H(4)	H(5)	CH_2	Coupling constants (Hz)
$CH_2(Pz)_2$	H	H	Acetone[a]	7.43[c]	6.20	7.70	6.36	J_{34} 1.7; J_{45} 2.5; J_{35} 0.4
$CH_2(3,5\text{-}MePz)_2$	CH_3	CH_3	Acetone[a]	2.08	5.75	2.44	6.03	J_{45} 0.75
$CH_2(3\text{-}NH_2Pz)_2$	NH_2	H	Actone[a]	4.19	5.49	7.37	5.77	J_{45} 2.4
Complex								
XXIV	H	H	Actone[b]	7.86[d]	6.55	8.24	7.12[e]	J_{34} 2.4; J_{45} 2.6; J_{35} 0.3
XXIV	H	H	DMSO[a]	7.85[d]	6.53	8.17[c]	6.90[e]	$J_{34} = J_{45} = 2.5$
XXV	CH_3	CH_3	Acetone[a]	2.34[c]	6.05	2.49	6.77,7.80[g]	J_{45} 0.75
XXV	CH_3	CH_3	DMSO[a]	2.27	6.07	2.41	7.00[f]	J_{45} 0.75
XXVI	NH_2	H	Acetone[a]	5.15	5.67	7.72	6.77[f]	J_{45} 2.8
XXVI	NH_2	H	DMSO[a]	5.36	5.55	7.63	6.66[h]	J_{45} 2.7

[a] At 90 MHz. [b] At 400 MHz. [c] Slightly broadened. [d] Well resolved quartet. [e] Narrow singlet. [f] Very broad singlet ($\Delta\nu 1/2 \sim 50$ Hz). [g] Well resolved AB system (J_{AB} 15.6 Hz). [h] Slightly broad singlet.

TABLE 4

^{13}C NMR CHEMICAL SHIFTS AND ^{13}C–^{103}Rh COUPLING CONSTANTS OF SOME LIGANDS AND ITS DIOLEFIN (COD) COMPLEXES





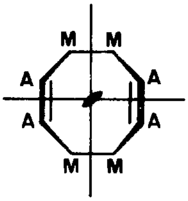
Ligand	R^3	R^5	Solvent	C(3)	C(4)	C(5)	C(19)	C(11)	$^1J(^{13}C-^{103}Rh)$ (Hz)	C(18)	R^3	R^5
$CH_2(Pz)_2$	H	H	DMSO [a]	140.1	106.3	130.5	64.4		–		–	–
$CH_2(3,5\text{-}MePz)_2$	CH_3	CH_3	$CDCl_3$ [a]	148.3	106.4	140.5	60.5		–		13.5	11.1
$CH_2(3\text{-}NH_2Pz)_2$	NH_2	H	DMSO [a]	155.6	93.2	130.7	63.6		–		–	–
Complex												
XXIV	H	H	Acetone [b]	148.3	108.9	135.5	64.7	85.3	12.3	31.2	–	–
XXV	CH_3	CH_3	Acetone [a]	155.4 [c]	109.5	145.7 [d]	60.0	83.5	12.4	31.0	14.2	11.1
XXVI	NH_2	H	DMSO [a]	157.8	94.5	134.0	63.2	81.1	12.3	30.0	–	–

[a] At 20 MHz. [b] At 100 MHz. [c] Broad. [d] Slightly broadened.

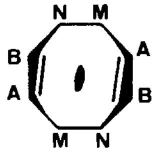
contact shift on C(3) due to the metal bonded to N_2.

It is noteworthy that the COD ligand shows only two signals: one corresponding to the four methylenic carbons, and the other (splitted by a $^1J(^{13}C-^{109}Rh)$ coupling) to the four olefinic carbons. From a symmetry point of view the situation is similar to that observed by ^{1}H NMR. This behaviour has already been described [9] for a complex similar to XXV but with a phenyl group on the C(19) ligand bis(pyrazolyl)phenylmethane, but it is necessary to regard the published ^{13}C chemical shift data (Table 3, ref [9]) with caution: most of them are erroneous. For instance, the shifts for 3,5-dimethylpyrazole (3,5-Me_2Pz) and 1-phenyl-3,5-dimethylpyrazole (Ph-3,5-Me_2Pz) in $CDCl_3$ are as follows (the values from ref. 9 are shown in parentheses): 3,5-Me_2Pz, C_3, 144.2 (156.2), C(4), 104.0 (103.4), Me, 12.1 (65.3); Ph-3,5-Me_2Pz, C(3), 148.8 (127.6), C(4), 106.9 (96.1), C(5), 139.3 (129.2), Me(3), 12.3 (2.18), Me(5), 13.5 (0.91), C_i, 139.9 (137.1), C_o, 124.6 (117.6), C_m. 128.9 (112.8), C_p, 127.1 (115.4). The shifts reported for the ligands are correct but incorrectly assigned (inversion of positions 3 and 5 and *ortho* and *meta*). Finally for complex III they reported incorrect chemical shifts for the methyl groups (their values were about 20 ppm downfield).

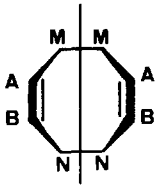
In order to verify the formulation and to ascertain the nuclearity of complex XXIV in the solid state, an X-ray structural determination (see below) was undertaken. The X-ray structure confirms the monomeric formula but seems to be in contradiction with the NMR conclusions in two aspects: (a) the protons on C(19), H(19a) and H(19b), are diastereotopic and should appear as an AB system and (b) the COD ligand has a pseudoaxis of symmetry of order two and should show two olefinic carbons and two methylene carbons (and similarly in ^{1}H NMR). In other studies [31] we have observed a situation in which the COD ligand has only a plane of symmetry, and this was immediately evident from ^{1}H and ^{13}C NMR studies. Thus, three different situations are possible:



C_{2v} symmetry
This work, ^{1}H and
^{13}C NMR, XXIX-XXVI



ψ-C_2 symmetry
This work,
X-ray, XXIV



C_s symmetry
Ref. 31,
^{1}H and ^{13}C NMR

To reconcile the X-ray structure and the NMR observations it is necessary to assume a boat–boat inversion of the metallocycle, Rh(N–N)$_2$C, which gives rise to an enantiomer (also present in the crystal) which permutes H(19a) and H(19b) and the diastereotopic carbons in COD. If the inversion is rapid enough on the NMR time scale, only an averaged signal is observed for H(19a) and H(19b) and the COD seems to have a C_{2v} symmetry. The proton–proton coupling constants between H_A and H_M and H_A and H_P are also consistent with this explanation. The dihedral angles in XXIV are (mean values): between H_A and H_M, 8°, and between H_A and H_P, 97°.

Finally, we refer again to the anisochrony of the H(19) protons in XXV. Although conductivity measurements pointed to a monomer–dimer equilibrium, the possibility of a monomer with high boat–boat inversion barrier cannot be excluded.

Crystal structure of $[Rh(COD)(CH_2(Pz)_2)]ClO_4 \cdot \frac{1}{2}C_2H_4Cl_2$

The rhodium atom is in the usual square planar arrangement, and is bonded to two N atoms of the $CH_2(Pz)_2$ group and to the olefinic bonds of the COD ligand (Fig. 1 and 2).

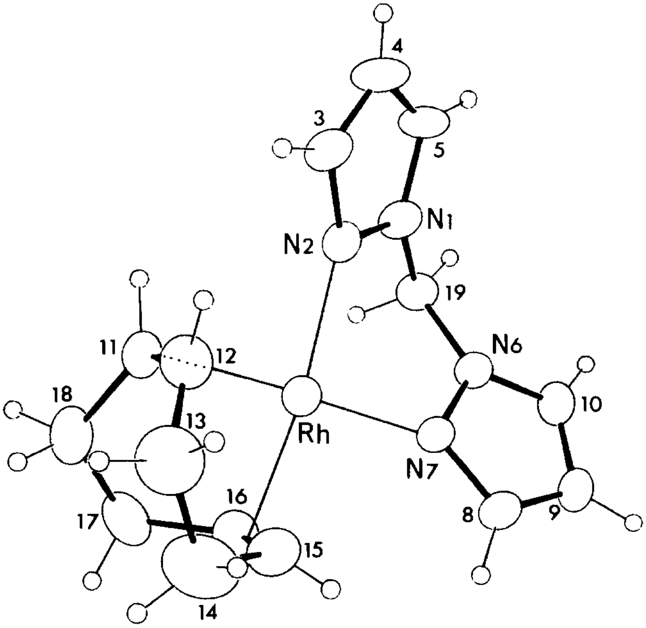


Fig. 1. An ORTEP view of complex XXIV showing the Rh coordination and the atomic numbering.

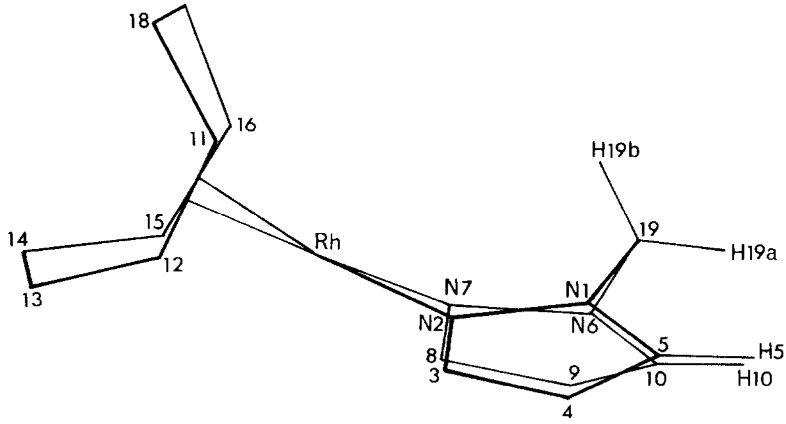


Fig. 2. Lateral view of the complex showing the coordination and the bending of the $CH_2(Pz)_2$ moiety and the situation of the CH_2 hydrogen atoms. The others H atoms have been omitted for sake of clarity.

The Rh distances (see Table 5) to the coordinated N atoms, are in agreement with literature data (2.119(5)–2.140(4) Å) for related, cyclooctadienerhodium complexes [32,33]. The Rh–C(102) and Rh–C(506) distances (C(102) and C(506) are the mid-points of the olefinic bonds) show values in agreement with those found for Rh-COD square planar coordination [34–38].

The coordination is distorted from the theoretical planar form, the angle between the planes C(102), C(506), Rh and N(2), N(7), Rh being 6.5(2)°, within the range of the observed values for related complexes [34–38]. Thus the four atoms in the coordination set depart significantly from co-planarity, the χ^2 value is 267.8 compared with the theoretical value of 3.84. The six-membered ring, Rh, N(2), N(1),

TABLE 5

BOND DISTANCES (Å)[a] AND ANGLES (°)

Rh–N(2)	2.111(8)	N(1)–N(2)	1.356(10)
Rh–N(7)	2.097(7)	N(2)–C(3)	1.340(13)
Rh–C(11)	2.128(10)	C(3)–C(4)	1.374(16)
Rh–C(12)	2.134(11)	C(4)–C(5)	1.370(18)
Rh–C(15)	2.125(12)	C(5)–N(1)	1.362(13)
Rh–C(16)	2.112(11)	N(6)–N(7)	1.372(10)
Rh–C(102)	2.015(8)	N(7)–C(8)	1.336(12)
Rh–C(506)	2.007(8)	C(8)–C(9)	1.393(14)
C(11)–C(12)	1.386(16)	C(9)–C(10)	1.347(16)
C(12)–C(13)	1.506(21)	C(10)–N(6)	1.341(12)
C(13)–C(14)	1.456(24)	Cl(1)–O(1)	1.410(8)
C(14)–C(15)	1.535(24)	Cl(1)–O(2)	1.411(10)
C(15)–C(16)	1.361(16)	Cl(1)–O(3)	1.418(10)
C(16)–C(17)	1.517(18)	Cl(1)–O(4)	1.417(9)
C(17)–C(18)	1.503(21)	Cl(2)–C(20)	1.831(25)
C(18)–C(11)	1.509(16)	C(20)–C(20′)[b]	1.420(37)
N(1)–C(19)	1.444(12)		
C(19)–N(6)	1.444(12)		
C(102)–Rh–C(506)	87.4(3)	C(4)–C(5)–N(1)	105.2(10)
N(2)–Rh–N(7)	88.4(3)	C(5)–N(1)–N(2)	112.0(8)
N(2)–Rh–C(102)	92.1(3)	C(19)–N(1)–C(5)	127.0(8)
N(7)–Rh–C(506)	92.1(3)	C(19)–N(1)–N(2)	120.5(7)
Rh–N(2)–C(3)	134.9(7)	C(19)–N(6)–C(10)	128.6(8)
Rh–N(2)–N(1)	119.9(6)	C(19)–N(6)–N(7)	119.7(7)
Rh–N(7)–N(6)	120.2(5)	N(6)–N(7)–C(8)	105.5(7)
Rh–N(7)–C(8)	134.2(6)	N(7)–C(8)–C(9)	109.1(9)
C(11)–C(12)–C(13)	124.6(11)	C(8)–C(9)–C(10)	107.5(9)
C(12)–C(13)–C(14)	116.6(14)	C(9)–C(10)–N(6)	106.8(8)
C(13)–C(14)–C(15)	113.2(14)	C(10)–N(6)–C(7)	111.0(7)
C(14)–C(15)–C(16)	123.7(13)	O(1)–Cl(1)–O(2)	112.3(6)
C(15)–C(16)–C(17)	126.0(11)	O(1)–Cl(1)–O(3)	108.7(6)
C(16)–C(17)–C(18)	113.6(11)	O(1)–Cl(1)–O(4)	109.0(6)
C(17)–C(18)–C(11)	114.7(10)	O(2)–Cl(1)–O(3)	106.6(6)
C(18)–C(11)–C(12)	122.5(11)	O(2)–Cl(1)–O(4)	111.0(6)
N(1)–N(2)–C(3)	104.9(8)	O(3)–Cl(1)–O(4)	109.4(7)
N(2)–C(3)–C(4)	110.5(10)	Cl(2)–C(20)–C(20′)	104.9(17
C(3)–C(4)–C(5)	107.3(11)		

[a] C(102) and C(506) are the midpoints of C(11), C(12) and of C(15), C(16), respectively. [b] The Cl_2Et is situated at a crystallographic symmetry center; C(20′) being related to C(20) through this symmetry.

C(19), N(6), N(7), has a boat conformation at Rh and C(19) but distorted towards an envelope because the Rh flap is lower than that at C(19) (see Table 6). This may be due to the fact that coordination is on only one side of the ring [39]. For the N-atoms the coordination shows the normal asymmetry in repect to the values of the angles (see Table 5).

The COD ring presents the usual conformation, that of a twisted boat [40], with only an approximate two fold axis of pseudosymmetry normal to its least-squares plane (see Table 6). The olefinic bonds have lengths within the range in the literature (1.357(9)–1.425(23) Å) [34–38,40], and are longer than in the free molecule (1.341 Å) [41]. The formally C_{sp^2}–C_{sp^3} and the C_{sp^3}–C_{sp^3} bond lengths [42] are similar, but there is a clear distinction between the higher value of the C_{sp^2}–C_{sp^3} angles from the others (see Table 5).

The $CH_2(Pz)_2$ moiety presents quite regular values [18], both halves being quite similar (see Table 5), and again there is angular asymmetry at the C(19)–N junction. The relative positions of the two halves can be seen in Fig. 2; the angle between the two pyrazolyl rings is 47.1(4)° and these moieties are bent about a notional line through Rh and C(19); both five-membered rings lie at about 62° (see Table 6) to the N(1), C(19), N(6) plane, and the conformation around C(19)–N(1) and

TABLE 6

MAIN TORSION ANGLES AND ANGLES BETWEEN THE LEAST-SQUARES SETS DEFINED BY THE SPECIFIED ATOMS (°)

C(11)–C(12)–C(13)–C(14)		56.5(21)
C(12)–C(13)–C(14)–C(15)		18.1(22)
C(13)–C(14)–C(15)–C(16)		−85.2(19)
C(14)–C(15)–C(16)–C(17)		3.0(21)
C(15)–C(16)–C(17)–C(18)		54.5(18)
C(16)–C(17)–C(18)–C(11)		21.3(17)
C(17)–C(18)–C(11)–C(12)		−85.9(15)
C(18)–C(11)–C(12)–C(13)		2.3(19)
N(7)–Rh–N(2)–N(1)		26.8(6)
Rh–N(2)–N(1)–C(19)		12.4(10)
N(2)–N(1)–C(19)–N(6)		−65.2(10)
N(1)–C(19)–N(6)–N(7)		65.7(10)
C(19)–N(6)–N(7)–Rh		−13.6(10)
N(6)–N(7)–Rh–N(2)		−26.1(6)
N(2)–N(1)–C(19)–H(19a)		175(6)
N(2)–N(1)–C(19)–H(19b)		50(5)
N(7)–N(6)–C(19)–H(19a)		180(6)
N(7)–N(6)–C(19)–H(19b)		−47(5)
N(1)–C(19)–N(6)–C(10)		−124.5(10)
N(6)–C(19)–N(1)–C(5)		123.4(10)
Rh,C(102),C(506)	Rh,N(2),N(7)	6.5(2)
N(1),N(2),C(3),C(4),C(5)	N(1),C(19),N(6)	61.5(5)
N(6),N(7),C(8),C(9),C(10)	N(1),C(19),N(6)	61.8(7)
N(1),N(2),C(3),C(4),C(5)	N(6),N(7),C(8),C(9),C(10)	47.1(4)
Rh,N(2),N(1),C(19)	Rh,N(7),N(6),C(19)	50.0(3)
N(1),N(2),C(3),C(4),C(5)	Rh,N(1),N(2),C(19)	4.7(3)
N(6),N(7),C(8),C(9),C(10)	Rh,N(7),N(6),C(19)	5.6(4)

C(19)–N(6) is such that C(5) and C(10) are eclipsing the H(19a), which is equatorial with respect to the Rh, N(2), N(1), C(19), N(6), N(7) boat ring.

The ClO_4^- anion and the dichloroethane of crystallization present no unusual features.

Experimental

C, H and N analyses were carried out with a Perkin–Elmer 240B microanalyser. IR spectra were recorded on a Perkin–Elmer 577 spectrophotometer. ^1H NMR and ^{13}C NMR were recorded on a Varian EM 390 (90 MHz) and a Bruker WP80SY (20 MHz) spectrometers, respectively. The spectra of compound XXIV in acetone-d_6, both ^1H (400 MHz) and ^{13}C (100 MHz), were obtained at Simon Fraser University (Canada) by Prof. Y.L. Chow on a Bruker WM 400 spectrometer. Chemical shifts are given in ppm (δ scale) relative to internal TMS. Molecular weights were determined osmometrically with a Perkin–Elmer 115 instrument. Conductivities were measured in acetone solution with a Philips 9501/01 conductimeter.

The six ligands $CH_2(pz)_2$ have been described previously [27,28].

Preparation of complexes of the type $[\{RhCl(diolefin)\}_2(CH_2(pz)_2)]$ *(I–XV)*

These complexes were prepared as is described below for $[\{RhCl(TFB)\}_2(CH_2(3/5\text{-}NH_2Pz)_2)]$.

To a suspension of 52 mg (0.071 mmol) of $[RhCl(TFB)]_2$ in acetone were added 14.1 mg (0.079 mmol) of $CH_2(3/5\text{-}NH_2Pz)_2$. The resulting yellow solution was stirred for 15 min and vacuum-concentrated to ca. 2 ml. Addition of diethyl ether gave a yellow solid, which was filtered off, washed with diethyl ether and air-dried.

Preparation of $[RhCl(COD)(CH_2(4\text{-}BrPz)_2)]$ *(XVI)*

Addition of a solution of 63.4 mg (0.207 mmol) of $CH_2(4\text{-}BrPz)_2$ in acetone to a solution of 50.9 mg (0.103 mmol) of $[RhCl(COD)]_2$ in the same solvent gave an intense-yellow solution, which was stirred for 40 min and vacuum-concentrated to dryness. The residue was extracted with diethyl ether and the extract was evaporated to give a yellow microcrystalline solid, which was kept under vacuum for a long time.

Preparation of complexes of the type $[Rh(CO)_2(CH_2(pz)_2)][RhCl_2(CO)_2]$ *(XVII–XVIII)*

These two complexes were prepared as described below for $[Rh(CO)_2(CH_2(3,5\text{-}Me_2Pz)_2)][RhCl_2(CO)_2]$.

To a dichloromethane solution of 35.7 mg (0.092 mmol) of $[RhCl(CO)_2]_2$ were added 18.9 mg (0.092 mmol) of $CH_2(3,5\text{-}Me_2Pz)_2$. After 2 h stirring the solution was vacuum-concentrated to ca. 2 ml and slow addition of diethyl ether gave a yellow solid, which was filtered off, washed with diethyl ether, and air-dried.

Preparation of complexes of the type $[Rh(diolefin)(CH_2(pz)_2)]ClO_4$ *(XIX–XXXIV)*

The preparation of $[Rh(COD)(CH_2(Pz)_2)]ClO_4$ is described as an example.

Addition of 46.9 mg (0.226 mmol) of silver perchlorate in 5 ml of acetone to a suspension of 53.4 mg (0.108 mmol) of $[RhCl(COD)]_2$ in 10 ml of acetone, gave an immediate precipitate of silver chloride. The suspension was stirred for 30 min, then the precipitate was filtered off and the filtrate was added to 33.5 mg (0.226 mmol) of $CH_2(Pz)_2$ in acetone. The resulting yellow solution was stirred for 20 min and vacuum-concentrated to ca. 2 ml. The complex was precipitated as a yellow solid by addition of diethyl ether. This solid was filtered off, washed with diethyl ether, and air-dried.

Preparation of complexes of the type $[\{Rh(diolefin)(PPh_3)\}_2(CH_2(pz)_2)](ClO_4)_2$ *(XXXV–XXXVI)*

The preparation of $[\{Rh(COD)(PPh_3)\}_2(CH_2(pz)_2)](ClO_4)_2$ is described as an example.

TABLE 7

CRYSTAL ANALYSIS PARAMETERS AT ROOM TEMPERATURE

Crystal data	
Formula	$[Rh(COD)(CH_2(Pz)_2)]ClO_4 \cdot \frac{1}{2}C_2H_4Cl_2$
Crystal habit	Yellow, prismatic
Crystal size (mm)	0.08 × 0.08 × 0.33 (see text)
Symmetry	$2/m$. Monoclinic. $P2_1/c$
Unit cell determination: least-squares fit to $\theta(Cu) < 45$ deg.	50 reflexions
Unit cell dimension (Å)	9.5602(2), 20.7383(7), 10.0692(1) β 92.130(2)°
Packing: $V(Å^3)$, Z	1988.82(7), 4
$D(\text{g cm}^{-3})$, M, $F(000)$, μ	1.697, 508.19, 1028, 98.51 cm^{-1}
Experimental data	
Radiation and technique	Cu-K_α PW1100 Philips Diffractometer Bisecting geometry
Monochromator	Graphite oriented
Collection mode	$\omega/2\theta$, 1 × 1 deg. det. apertures, $\theta < 60°$ 1 min/refl/scan width of 1.4 deg.
Total independent data	2931
Observed data $I > 3\sigma(I)$	2436
Stability	Two reflexions every 90 min. no variation
Solution and refinement	
Solution mode	Patterson. X-Ray 76 System [43] Vax 11/750
Refinement mode	Least-squares on F's, observed reflexions only. 1 blocks in the final cycles.
Final shift/error	0.17
Parameters:	
no. of variables	332
degrees of freedom	2104
ratio of freedom	7.3
Weighting scheme	Empirical as to give no trend in $\langle w\Delta^2F \rangle$ vs. $\langle F_0 \rangle$ or $\langle \sin\theta/\lambda \rangle$.
Max. thermal values ($Å^2$)	$U_{22}(O4) = 0.22(1)$
Final F-peaks	1.3 eA^{-3} near the Rh atom
Final R, R_w	0.061, 0.067
Atomic factors	International Tables for X-Ray Crystallography [44]. Neutral atoms. Real part of anomalous dispersion applied for Rh and Cl.

Addition of 16.6 mg (0.063 mmol) of triphenylphosphine to a solution of 37.5 mg (0.061 mmol) of $[Rh(COD)(CH_2(4\text{-}BrPz)_2)]ClO_4$ in 10 ml of dichloromethane caused a change in colour from yellow to orange-yellow. After 10 min stirring, the solution was vacuum-concentrated to ca. 1 ml. Addition of diethyl ether gave an orange-yellow solid, which was filtered off, washed with diethyl ether, and air-dried.

Preparation of complexes of the type $[Rh(CO)_2(CH_2(pz)_2)]ClO_4$ *(XXXVII–XXXIX)*

These complexes were prepared by two routes, which are ilustrated below.

(i) Preparation of $[Rh(CO)_2(CH_2(3,5\text{-}Me_2Pz)_2)]ClO_4$. Carbon monoxide at normal pressure was bubbled through a solution of 32.9 mg (0.052 mmol) of $[Rh(TFB)(CH_2(3,5\text{-}Me_2Pz)_2)]ClO_4$ in dichloromethane for 20 min, causing a change in colour from yellow to pale yellow. After vacuum-concentration to ca. 1 ml, diethyl ether was added and a pale yellow solid separated. This was filtered off, washed with diethyl ether, and air-dried.

(ii) Preparation of $[Rh(CO)_2(CH_2(4\text{-}NO_2Pz)_2)]ClO_4$. Addition of 29.5 mg (0.124 mmol) of $CH_2(4\text{-}NO_2Pz)_2$ and 14 μl (0.129 mmol) of perchloric acid (60%) to a suspension of 30.8 mg (0.119 mmol) of $Rh(acac)(CO)_2$ in methanol caused a change in colour from yellow to pale yellow and formation of a precipitate. After 20 min stirring, the suspension was vacuum-concentrated to half its volume. Addition of

TABLE 8

FINAL ATOMIC COORDINATES

ATOM	x/a	y/b	z/c
Cl(1)	0.7047(2)	0.0773(1)	0.6904(2)
O(1)	0.5624(8)	0.0832(6)	0.7203(10)
O(2)	0.7679(12)	0.0226(4)	0.7508(12)
O(3)	0.7779(11)	0.1318(5)	0.7423(13)
O(4)	0.7161(10)	0.0755(7)	0.5501(9)
Rh	0.14783(7)	0.16466(3)	0.23720(6)
N(1)	0.4308(8)	0.1692(4)	0.3820(8)
N(2)	0.3443(8)	0.2032(4)	0.2982(7)
C(3)	0.4080(11)	0.2602(5)	0.2838(11)
C(4)	0.5327(13)	0.2617(6)	0.3565(14)
C(5)	0.5475(11)	0.2033(6)	0.4194(12)
N(6)	0.2744(7)	0.0953(3)	0.4783(7)
N(7)	0.1497(7)	0.1116(3)	0.4151(7)
C(8)	0.0506(10)	0.0913(4)	0.4956(10)
C(9)	0.1138(12)	0.0631(5)	0.6084(10)
C(10)	0.2534(12)	0.0662(5)	0.5952(9)
C(11)	0.1815(12)	0.1915(5)	0.0363(10)
C(12)	0.1061(14)	0.2399(5)	0.0963(12)
C(13)	−0.0490(18)	0.2504(8)	0.0749(21)
C(14)	−0.1394(19)	0.1961(8)	0.1039(26)
C(15)	−0.0667(12)	0.1447(5)	0.1919(13)
C(16)	0.0132(12)	0.0963(5)	0.1434(11)
C(17)	0.0491(19)	0.0868(8)	−0.0011(13)
C(18)	0.1151(15)	0.1449(6)	−0.0625(11)
C(19)	0.4033(10)	0.1021(5)	0.4089(11)
Cl(2)	0.6252(5)	0.0595(3)	0.1294(4)
C(20)	0.4788(26)	0.0308(13)	0.0224(25)

diethyl ether completed the precipitation of the complex, which was filtered off, washed with diethyl ether and air-dried.

Preparation of complexes of the type $[Rh(CO)(CH_2(pz)_2)(PPh_3)]ClO_4$ *(XL–XLI)*

These two complexes were prepared as described for $[Rh(CO)(CH_2(3,5\text{-}Me_2Pz)_2)(PPh_3)]ClO_4$.

Carbon monoxide at normal pressure was bubbled through a dichloromethane solution of 24.7 mg (0.050 mmol) of $[Rh(NBD)(CH_2(3,5\text{-}Me_2Pz)_2)]ClO_4$ and 13 mg (0.050 mmol) of triphenylphosphine, for 90 min. This pale yellow solution was vacuum-concentrated to ca. 2 ml, and addition of diethyl ether gave a yellow solid. This was filtered off, washed with diethyl ether, and air-dried.

X-Ray analysis

Crystal analysis parameters are given in Table 7. The single crystal used was grown by slow diffusion of diethyl ether into a dichloroethane solution, and it was sealed into a Lindemann capillary, which also contained solvent to avoid sample deterioration. This prevent us from making any absorption correction. The weighting scheme was tested through normal probability plots [45]. The final non-hydrogen atomic coordinates are listed in Table 8, with the atomic numbering corresponding to that in Fig. 1. A list of structure factors, thermal parameters and hydrogen atomic positions can be obtained from the authors on request.

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