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BULKY PYRAZOLE AS LIGANDS IN RHODIUM(I) COMPLEXES. CRYSTAL STRUCTURE OF CHLORODICARBONYL(3-*p*-METHOXYPHENYLPYRAZOLE)RHODIUM(I)

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Abstract—A new family of complexes containing bulky pyrazoles substituted in the 3 or the 3 and 5 positions, $[RhCl(L_2)(Hpz^{R',R''})]$ (L_2 = NBD, 2CO; R′ = Bu^t, Ph, *p*-$CH_3OC_6H_4$ (An), R″ = H; R′ = Bu^t, Ph, R″ = CH_3; R′ = R″ = H, CH_3), has been obtained. A dynamic behaviour has been observed only in complexes with the less demanding pyrazole ligands, relating with a metallotropic equilibrium when R′ = R″ = H, Me, or a diolefin reorientation when R′ = Bu^t, Ph, An, R″ = H. The X-ray crystal structure of $[RhCl(CO)_2(Hpz^{An})]$ has been solved, showing a molecular stacking with a Rh—Rh separation of 3.398(3) Å along the one-dimensional chain.

The coordination chemistry of pyrazole, $C_3H_4N_2$ (Hpz), the derived anion $C_3H_3N_2^-$ (pz), as well as some related substituted ligands ($C_3H_2N_2R'R''$, $Hpz^{R',R''}$) is well known.[1] In particular rhodium(I) and iridium(I) complexes with these kinds of ligands have been described, but while there are several examples of bimetallic compounds containing pyrazolyl-bridged ligands involving both nitrogen atoms,[2–6] there are only few data on mononuclear species.[7–10]

The potential catalytic activity of bimetallic compounds of rhodium(I) and specially of iridium(I) containing pyrazolyl-bridged ligands has been the reason for which they have largely been investigated.[11–14]

Definitive evidence for the ability of the pyrazolyl group to act as a bridge across a metal–metal bond has been established[15] and the versatility of this η^2-bridging pyrazolyl group which can straddle a wide range of intermetallic separations to hold two adjacent centres in a chemically stable configuration has also been proved.[16]

Related to the metal–metal systems containing pyrazole groups it is remarkable to note that one of the scarce complexes containing a pyrazole group as a neutral two-electron ligand *via* coordination through a nitrogen-atom, $[RhCl(CO)_2(Hpz)]$,[9] has shown in the solid state a one-dimensional chain arrangement of the type which produces anisotropic electrical effects in crystals of third-row transition metal complexes.[17] This columnar chain-structure remains very rare for rhodium or other lighter transition elements although a number of iridium complexes are known.[18]

The interest in the polynuclear transition metal chemistry in terms of electron delocalization between adjacent atoms[19,20] led us to investigate a new family of square-planar rhodium(I) derivatives containing pyrazole groups as neutral ligands.

As the original studies deal with complexes with Hpz or $Hpz^{Me,Me}$ ligands,[7,9] a new class of complexes is prompted by using substituted pyrazole ligands with bulky alkyl and/or aryl groups in the 3 or the 3 and 5 positions of the pyrazole ring. We have recently described some results of rhodium complexes with one of those ligands (Hpz^{Bu^t})[21] and its chemistry appears interesting in order to study the substituent influence in the metal–metal interactions.

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On the other hand, on the basis of the fluxional behaviour noted in [RhCl$(CO)_2$(Hpz)] about which no details have been published,[7] the potential dynamic behaviour of the new complexes offers a new goal for our study. This dynamic character resulting from site exchange of metal between adjacent nitrogen atoms (Fig. 1) has also been observed in palladium(II) derivatives of the type $[PdCl(PEt_3)_2L]^+$ (L = Hpz, $Hpz^{Me,Me}$), but the corresponding platinum(II) complexes were not fluxional.[22, 23]

In addition the coordination of a neutral unsymmetrical pyrazole ($R' \neq R''$) in a related fashion can lead to isomeric forms and the exchange between both will be non-degenerate in contrast to the degenerate exchange represented in Fig. 1 when $R' = R''$. Then an isomeric equilibrium or only the more stable isomer could be expected for complexes with unsymmetrical pyrazoles.

In the above contexts we have investigated the chemistry of rhodium(I) complexes of the type [RhCl(NBD)$(Hpz^{R',R''})$] (NBD = bicycle[2.2.1] hepta-2,5-diene, 2,5-norbornadiene) and [RhCl$(CO)_2$$(Hpz^{R',R''})$], where $Hpz^{R',R''}$ ($C_3H_2N_2R'R''$) are pyrazole ligands with two different substituents in the 3 and 5 positions (R' = Ph, Bu^t; R'' = Me) as well as the related 3(5) monosubstituted (R' = Bu^t, Ph, *p*-$CH_3OC_6H_4$(An); R'' = H). For comparative purposes the formation of complexes with Hpz ($R' = R''$ = H) or $Hpz^{Me,Me}$ ($R' = R''$ = Me) has also been examined. The crystalline structure of [RhCl$(CO)_2$$(Hpz^{An})$] has been determined by X-ray diffraction analysis.

RESULTS AND DISCUSSION

[RhCl(NBD)$(Hpz^{R',R''})$] *complexes* (**1–8**)

Reactions of the dimer $[Rh(\mu\text{-}Cl)(NBD)]_2$ with the ligands depicted in Table 1 were performed in a 1 : 2 molar ratio in CH_2Cl_2 or MeOH as solvent (eq. (1)). All the isolated complexes were air-stable orange–yellow solids, characterized as the neutral rhodium(I) compounds [RhCl(NBD)$(Hpz^{R',R''})$], and their purity ascertained by microanalysis (Table 1). These results are in agreement with those obtained in the reactions of $[Rh(\mu\text{-}Cl)(diolefin)]_2$ with monodentate ligands in non-polar or low-polarity solvents.[24] The low molar conductivity of the compounds supports its formulation as neutral species and the structure and rhodium(I) coordination are well characterized by IR and ^1H NMR spectroscopies (Tables 1 and 2). Related to the coordinated pyrazole ligands ($Hpz^{R',R''}$), the compounds have been classified in three groups as follows: **I** (R' = Bu^t, Ph, p-$CH_3OC_6H_4$ (An); R'' = H) (**1**–**3**), **II** (R' = Bu^t, Ph; R'' = Me) (**4**–**5**), **III** ($R' = R''$ = H, Me) (**6**–**7**).

$$[Rh(\mu\text{-}Cl)(NBD)]_2 + 2Hpz^{R',R''} \longrightarrow 2[RhCl(NBD)(Hpz^{R',R''})] \quad (1)$$

In previous works[25,26] we have described that in complexes of the type [Rh(NBD)(NN)] (NN = bis or trisazolylmethane) the methinic protons (H1, H4) of the NBD ligand resonated at higher frequency than the corresponding olefinic protons (H2, H3, H5, H6) when a tetracoordination at rhodium was implied. This behaviour appears to be an intrinsic property of the NBD ligand in rhodium-tetracoordinated species. Related with this fact the NBD proton signals observed in all the studied complexes agree with the presence of the expected tetracoordination at rhodium.

However it is remarkable that those complexes containing pyrazole ligands substituted in the 3-position (type **I**) present one broad signal corresponding to olefinic H2, H3, H5, H6 protons but always maintaining the same field order with respect to that of the methinic protons. The line-width effect could be attributed to the exchange of olefin groups. Although $[Rh(\mu\text{-}OAc)(NBD)]_2$ showed a restricted rotation of NBD groups,[27] a dynamic behaviour for dienes in four-coordinate rhodium(I) complexes was generally observed and attributed to a reorientation of coordinated diene.[28] Therefore, we can consider the presence of an intramolecular exchange of alkene protons between non-equivalent sites in complexes of the type **I**, which is slow on the NMR time-scale.

On the other hand and related to the coordinated pyrazole ligand, the ^1H NMR spectra of each complex consist of one signal corresponding to the H4 proton as well as those related to the protons or substituents at the 3 and 5 positions of the ring (Table 2). Related complexes [RhCl$(CO)_2$(Hpz)] and [RhCl$(CO)_2$$(Hpz^{Me,Me})$] have shown a single resonance for H(3,5) and CH_3(3,5), which was attributed to a metallotropic equilibrium ("shuttling") as represented in Fig. 1.[7,9] By contrast, complexes **6** and **7** (type **III**), containing NBD instead of two CO groups, exhibit two broad H- or CH_3-resonances. This fact suggests that exchange rate seems

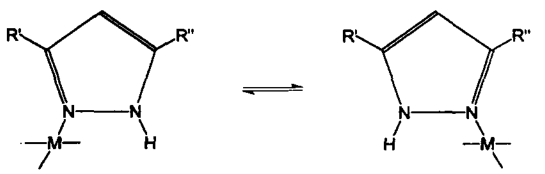

Fig. 1.

Table 1. IR data, colour and elemental analyses of [RhCl(NBD)(Hpz$^{R',R''}$)] (**1**–**8**)

		IR[a] (cm^{-1})					Calcd (%)			Found (%)		
	Hpz$^{R',R''}$	ν(NH)	ν(RhCl)	β(CH)	Colour	Molecular formula	C	H	N	C	H	N
1	Hpz$^{Bu^t}$	3280	250	1290	orange–yellow	$C_{14}H_{20}N_2ClRh$	47.0	5.3	8.0	47.4	5.6	7.9
2	Hpz^{Ph}	3280	250	1305	orange–yellow	$C_{16}H_{16}N_2ClRh \cdot 1/4CH_2Cl_2$	49.7	4.2	7.2	49.3	4.2	7.1
3	Hpz^{An}	3230	245	1290	orange–yellow	$C_{17}H_{18}N_2OClRh$	50.2	4.2	6.9	50.4	4.4	6.9
4	Hpz$^{Bu^t,Me}$	3200	255	1305	orange–yellow	$C_{15}H_{22}N_2ClRh$	48.5	5.6	7.1	48.8	6.0	7.6
5	Hpz^{Ph,Me}	3090	255	1295	orange–yellow	$C_{17}H_{18}N_2ClRh$	51.5	4.6	7.0	52.5	4.7	7.2
6	Hpz	3260	260	1295	yellow	$C_{10}H_{12}N_2ClRh$	39.4	3.7	9.2	40.3	4.0	9.4
7	Hpz^{Me,Me}	3190	250	1300	yellow	$C_{12}H_{16}N_2ClRh$	43.8	4.7	8.6	44.2	4.9	8.6
8	Mepz		265	1305	orange–yellow	$C_{11}H_{14}N_2ClRh \cdot 1/4CH_2Cl_2$	41.1	4.2	8.3	40.5	4.4	8.4

[a] In KBr discs.

Table 2. ^{1}H-NMR chemical shifts of [RhCl(NBD)(Hpz$^{R',R''}$)] (**1**–**8**) in CDCl$_3$[a]

	NH	H4	H5	H3	CH$_3$(Me)	CH$_3$(Bu^t)	CH$_3$O	Ph[b]	NBD protons
1	11.79	6.02d $J = 1.8$	6.63d			1.27			CH$_2$-7: 1.20 CH-2,3,5,6: 4.19 CH-1,4: 3.81
2	12.26	6.50d $J = 2.1$	6.80d					7.53d (H$_o$) 7.42m (H$_m$, H$_p$) $J = 8.1$	CH$_2$-7: 1.33 CH-2,3,5,6: 4.08 CH-1,4: 3.87
3	12.10	6.40d $J = 2.1$	6.75d				3.83	7.44d (H$_o$) 6.94d (H$_m$) $J = 8.7$	CH$_2$-7: 1.33 CH-2,3,5,6: 4.06 CH-1,4: 3.86
4	11.94	5.74			1.91	1.24			CH$_2$-7: 1.28 CH-2,3,5,6: 4.21 CH-1,4: 3.81
5	11.50	6.20			2.05			7.49dd (H$_o$) 7.40m (H$_m$, H$_p$) $J = 7.8, 1.8$	CH$_2$-7: 1.26 CH-2,3,5,6: 4.15 CH-1,4: 3.81
6	12.04	6.32t $J = 1.8$	6.80br,	7.45br					CH$_2$-7: 1.32 CH-2,3,5,6: 4.05 CH-1,4: 3.84
7	11.75	5.72			2.17br 1.90br				CH$_2$-7: 1.27 CH-2,3,5,6: 4.19 CH-1,4: 3.81
8		6.24t $J = 2.1$	7.42d,	7.36d	4.23(CH$_3$—N)				CH$_2$-7: 1.23 CH-2,3,5,6: 3.95 CH-1,4: 3.84

[a] d = doublet, dd = doublet of doublets, t = triplet, m = multiplet, br = broad. Other signals are singlets.

[b] H$_o$, H$_m$ and H$_p$ indicate *ortho*, *meta* and *para* protons of the phenyl groups.

to be depending on the other coligands and increases in the sequence NBD to 2CO (going from NBD ligand to 2CO ligands).

In order to avoid the metallotropic proposed exchange equilibrium observed in the complexes **6** and **7** we prepared and studied the related compound using *N*-methylpyrazole (Mepz) as ligand. So, the complex [RhCl(NBD)(Mepz)] (**8**) was obtained in a similar way to that described above and characterized by analytical and spectroscopic techniques (Tables 1 and 2). The ^{1}H NMR spectrum confirms the absence of pyrazole exchange showing the signals corresponding to H3 and H5 protons as doublets at 7.42 and 7.36 ppm.

The other groups of complexes (**I** and **II**) show the expected signals corresponding to the substituents in the 3 or the 3 and 5 positions (Table 2). The absence of any line-width effect suggests that pyrazole exchange does not occur in these examples or is still very rapid on the NMR time-scale.

In the complexes containing asymmetric pyrazole ligands, the tautomeric exchange does not appear to have been established by NMR. All the resonances in ^{1}H NMR spectra show no broadening and unaccountable signals. The present NMR data suggest that if an equilibrium exists in solution one isomer should predominate or exchange is very rapid.

At this point we took into account the literature data related to the tautomeric equilibrium of some asymmetric pyrazoles, which indicate that for 3(5)-phenylpyrazole the major tautomer in solution and solid state was the 3-phenyl one and for 3(5)-methyl-3(5)-phenylpyrazole both tautomers are present in the solid state while 5-methyl-3-phenylpyrazole was the major one in solution.[29]

Then, we tentatively propose that the isomer produced in complexes **I** and **II** should be that containing the more demanding substituent in the 3-position of the pyrazole ring and the less one (H or CH_3) in the 5-position close to the rhodium atom.

$[RhCl(CO)_2(Hpz^{R',R''})]$ *complexes* (**1a–5a**)

The dicarbonyl derivatives $[RhCl(CO)_2(Hpz^{R',R''})]$ ($R' = Bu^t$, Ph, p-$CH_3OC_6H_4$ (An), $R'' = H$, **1a–3a**. $R' = Bu^t$, Ph, $R'' = Me$, **4a–5a**) were obtained readily by carbonylation reactions of $[RhCl(NBD)(Hpz^{R',R''})]$ according the eq. (2). The related complexes containing Hpz and $Hpz^{Me,Me}$ had already been described and prepared by an alternative route.[7,9]

$$[RhCl(NBD)(Hpz^{R',R''})]+2CO \longrightarrow [RhCl(CO)_2(Hpz^{R',R''})]+NBD \quad (2)$$

Complexes **1a–5a** were air-stable, orange–yellow in solution but dark violet–blue and dichroic in the solid state which should be a consequence of metal–metal interaction. This fact was proved in the compound **3a** by the resolution of its crystalline structure as described below which indicated a Rh—Rh distance of 3.398 Å.

The analytical data, IR and ^{1}H NMR spectra are in agreement with the proposed formulation (Tables 3 and 4).

The IR spectra in solid state present four or two split absorptions of similar intensity at *ca* 2080 and 2000 cm^{-1}. The splitting disappears in dichloromethane solution and therefore it could be attributed to solid-state effects. The presence of two different molecular arrangements in the complexes as observed in the crystalline structure of **3a** agrees with the above result. In the lower frequency region an absorption at *ca* 300 cm^{-1} was consistent with the presence of a Rh—Cl bond.

The ^{1}H NMR spectra in $CDCl_3$ solution show the signals required by the pyrazole ligands (Table 4). All the resonances show no discernible broadening and contain no unaccountable signals suggesting the presence of a unique isomer for each compound. For this isomer we can assume that the more sterically demanding group should occupy the 3-position in the coordinated pyrazole ring in order to minimize the crowding near the metal. The resolution of the X-ray structure of $[RhCl(CO)_2(Hpz^{An})]$ (**3a**) agrees with the above proposal.

We have started to study the electrical conductivity properties of these complexes. So, the conductivity of $[RhCl(CO)_2(Hpz^{Ph})]$ was determined to be 10^{-9} ohm^{-1} cm^{-1} at room temperature in powder pellet. Further work will be carried out to substantiate these properties.

Crystal structure of $[RhCl(CO)_2(Hpz^{An})]$ (**3a**)

An X-ray diffraction study of the compound $[RhCl(CO)_2(Hpz^{An})]$ indicates that the crystalline structure has molecular stacking along a one-dimensional chain. Table 5 lists the bond lengths and bond angles.

Figure 2 depicts the interaction between three molecules of the chain, showing the molecular geometry and the atom labelling.[30] The square-planar environment about the rhodium atom is defined by two carbonyl groups, a nitrogen-bonded pyrazole and a chlorine ligand. The rhodium atom is displaced by 0.021(2) Å from the best square-plane through N(1)C(1)C(2)Cl.[31]

The pyrazole heterocycle is rotated 7(1)° only away from coincidence with the metal coordination plane and the phenyl ring deviates 7(1)° from the pyrazole plane (Table 6).[31]

The molecular packing within the crystals is dominated by stacking of square metal-centred units along one axis, forming slightly zig-zag metal chains [171.6(1)°]. This arrangement has already been observed in $[RhCl(CO)_2(Hpz)]$,[9] but some differences have been noted between the structures of both compounds. So, the Rh—Rh distance in **3a** [3.398(3) Å] is slightly shorter than that found in $[RhCl(CO)_2(Hpz)]$ [3.4522(4) Å].[9] On the other hand, the Rh—Rh distance in **3a** is 0.13 Å longer than in $[Rh(acac)(CO)_2]$[32] which has been considered as an intrinsic semiconductor.[18]

In addition the complex **3a** has all the pyrazole planes consecutively stacking in an arrangement alternatively staggered (Fig. 3). Consequently the phenyl planes have a similar disposition with the

Table 3. IR data, colour and elemental analyses of [RhCl(CO)$_2$(Hpz$^{R',R''}$)] (**1a**–**5a**)

		IR[a] (cm^{-1})					Calcd (%)			Found (%)		
	Hpz$^{R',R''}$	ν(CO)	ν(NH)	ν(RhCl)	Colour	Molecular formula	C	H	N	C	H	N
1a	Hpz$^{Bu^t}$	2080 2060 1995 1990	3260	290	blue–black	$C_9H_{12}N_2O_2ClRh$	33.7	3.7	8.7	33.9	3.8	8.8
2a	Hpz^{Ph}	2080 2060 2000 1990	3280	300	green–violet	$C_{11}H_8N_2O_2ClRh$	39.8	2.7	7.7	39.0	2.4	8.3
3a	Hpz^{An}	2085 2065 2010 2000	3300	305	green–violet	$C_{12}H_{10}N_2O_3ClRh \cdot 1/3C_6H_{14}$	42.4	3.4	7.1	42.3	3.7	7.1
4a	Hpz$^{Bu^t,Me}$	2080 2060 2000	3230	290	violet	$C_{10}H_{14}N_2O_2ClRh$	36.1	4.3	8.8	36.1	4.3	8.4
5a	Hpz^{Ph,Me}	2080 2000	3080	310	violet	$C_{12}H_{10}N_2O_2ClRh$	40.6	2.8	7.8	40.9	2.9	7.9

[a] In KBr discs.

Table 4. ^{1}H-NMR chemical shifts of [RhCl(CO)$_2$(Hpz$^{R',R''}$)] (**1a**–**5a**) in CDCl$_3$[a]

	NH	H4	H5	CH$_3$(Me)	CH$_3$(Bu^t)	CH$_3$O	Ph[b]
1a	11.92	6.22d $J = 1.8$	7.49d		1.34		
2a	12.36	6.68d $J = 2.1$	7.66d				7.57d (H$_o$) 7.48m (H$_m$, H$_p$) $J = 8.1$
3a	12.21	6.58d $J = 2.1$	7.61d			3.86	7.50d (H$_o$) 6.99d (H$_m$) $J = 8.7$
4a	11.33	5.99		2.40	1.30		
5a	11.90	6.36		2.40			7.55d (H$_o$) 7.45m (H$_m$, H$_p$) $J = 7.8$

[a] d = doublet, t = triplet, m = multiplet. Other signals are singlets.

[b] H$_o$, H$_m$ and H$_p$ indicate *ortho*, *meta* and *para* protons of the phenyl groups.

MeO groups located in the opposite direction to minimize the steric congestion. The two CO and Cl groups around the metal are also stacked in the same arrangement alternatively staggered.

It is remarkable to note that in the molecular columnar stacking all the phenyl groups are parallel as well as the coordination planes. However, consecutive pyrazole planes have a dihedral angle of 13(1)° (Table 6).

The close Rh—Rh intermolecular distance of 3.398(3) Å is comparable to that found in a number of rhodium(I) complexes involving metal–metal interactions which are stacked along an axis in a linear fashion (Table 7). From some of the above data it was proposed that the choice of the ligand can affect not only the magnitude of the metal–metal interaction but also profoundly influence the stacking arrangement which also affect the metallic behaviour.[33] The structure data of [RhCl(CO)$_2$(Hpz^{An})] compared with those of [RhCl(CO)$_2$(Hpz)] agree with this suggestion.

In addition we deduce that the propensity to pro-

Table 5. Bond lengths (Å) and bond angles (°) of $[RhCl(CO)_2(Hpz^{An})]$ (with esd values)

Bond lengths			
Rh—Cl	2.342(7)	C(4)—C(5)	1.38(4)
Rh—N(1)	2.05(2)	C(6)—C(7)	1.38(4)
Rh—C(1)	1.80(3)	C(6)—C(11)	1.37(3)
Rh—C(2)	1.82(3)	C(7)—C(8)	1.37(4)
N(1)—N(2)	1.36(3)	C(8)—C(9)	1.32(5)
N(1)—C(5)	1.37(3)	C(9)—C(10)	1.35(5)
N(2)—C(3)	1.33(3)	C(9)—O(3)	1.36(4)
C(1)—O(1)	1.13(4)	C(10)—C(11)	1.40(5)
C(2)—O(2)	1.11(4)	C(12)—O(3)	1.12(5)
C(3)—C(4)	1.41(3)	Rh-Rh′	3.398(3)
C(3)—C(6)	1.48(3)	Rh-Rh″	3.398(3)

Bond angles			
Rh′—Rh—Rh″	171.6(1)	C(4)—C(3)—C(6)	132(2)
C(1)—Rh—C(2)	89(1)	C(3)—C(4)—C(5)	107(2)
N(1)—Rh—C(2)	178(2)	N(1)—C(5)—C(4)	111(2)
N(1)—Rh—C(1)	91(1)	C(3)—C(6)—C(11)	123(2)
Cl—Rh—C(2)	90(1)	C(3)—C(6)—C(7)	118(2)
Cl—Rh—C(1)	179(1)	C(7)—C(6)—C(11)	118(2)
Cl—Rh—N(1)	90(1)	C(6)—C(7)—C(8)	120(3)
Rh—N(1)—C(5)	133(2)	C(7)—C(8)—C(9)	122(3)
Rh—N(1)—N(2)	124(1)	C(8)—C(9)—O(3)	115(3)
N(2)—N(1)—C(5)	103(2)	C(8)—C(9)—C(10)	120(3)
N(1)—N(2)—C(3)	116(2)	C(10)—C(9)—O(3)	125(3)
Rh—C(1)—O(1)	177(3)	C(9)—C(10)—C(11)	120(3)
Rh—C(2)—O(2)	175(3)	C(6)—C(11)—C(10)	120(2)
N(2)—C(3)—C(6)	125(2)	C(9)—O(3)—C(12)	118(4)
N(2)—C(3)—C(4)	104(2)		

Prime: *x*, 1/2−*y*, 1/2+*z*. Double prime: *x*, 1/2−*y*, *z*−1/2.

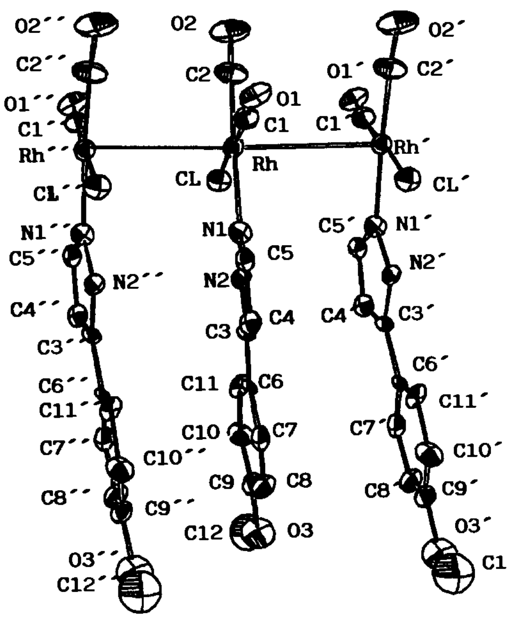

Fig. 2. Perspective ORTEP[30] view of three molecules of $[RhCl(CO)_2(Hpz^{An})]$ with atomic numbering scheme. Hydrogen atoms are omitted, and thermal ellipsoids are at 20% probability level.

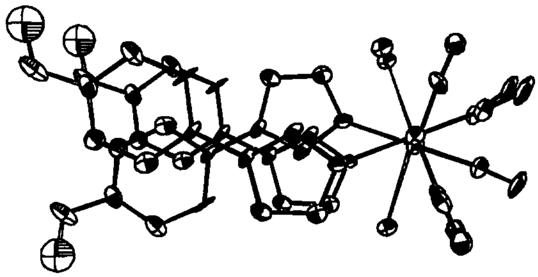

Fig. 3. Perspective ORTEP[30] view of three molecules of $[RhCl(CO)_2(Hpz^{An})]$ along the *c* axis, showing the alternate staggering.

duce extended rhodium–rhodium interactions appeared to increase with the presence of aryl substituents in the pyrazole ring. This fact is also supported by comparing the chain metal–metal distances observed in the dimers $[Rh(C_5H_{10}N_2)(CO)_2]BF_4$ [3.271(3), 3.418(3) Å][33] and $[Rh_2(C_{22}H_{23}N_4)(CO)_4]^+$ [3.057(3), 3.268(4) Å].[34]

On the other hand, the minimum distances between individual stacks in **3a** are 3.59(4) Å (O1—C12) and 3.63(5) Å (C12—C12), so that the

Table 6. Selected angles (°) between the least-squares sets defined by the specified atoms for [RhCl(CO)$_2$(Hpz^{An})]

1—Cl,C(2),C(1),N(1)
2—N(1),N(2),C(3),C(4),C(5)
3—C(6),C(7),C(8),C(9),C(10),C(11)
4—Cl′,C(2′),C(1′),N(1′)
5—N(1′),N(2′),C(3′),C(4′),C(5′)
6—C(6′),C(7′),C(8′),C(9′),C(10′),C(11′)
7—Cl″,C(2″),C(1″),N(1″)
8—N(1″),N(2″),C(3″),C(4″),C(5″)
9—C(6″),C(7″),C(8″),C(9″),C(10″),C(11″)

1-2	7(1)	2-5	13(1)
1-3	7(1)	2-8	13(1)
2-3	7(1)	5-8	0(1)
1-4	0.7(6)	3-6	0(1)
1-7	0.7(6)	3-9	0(1)
4-7	0(1)	6-9	0(1)

Prime: x, $1/2-y$, $1/2+z$. Double prime: x, $1/2-y$, $z-1/2$.

Table 7. Rhodium(I)–rhodium(I) distances in complexes stacked in a columnar fashion

Complex	Rhodium–rhodium (Å)	Ref.
$[Rh(acac)(CO)_2]_n$	3.26(1), 3.27(1)	32
$[Rh(CO)_2(CF_3CO)_2CH]_n$	3.34(1)	32
$[RhCl(CO)_2(Hpz)]_n$	3.4522(4)	9
$[RhCl(CO)_2(Hpz^{An})]_n$	3.398(3)	This work

minimum Rh···Rh distance is 8.310(4) Å, indicating that no intermetallic interactions should occur between the columnar stacks (Fig. 4).

CONCLUDING REMARKS

A new family of square-planar complexes of the type [RhCl(L$_2$)(Hpz$^{R',R''}$)] (L$_2$ = NBD, 2CO) has been obtained. Interchange metallotropic equilibrium was observed for complexes containing symmetric pyrazole ligands, while for those with asymmetric pyrazole non-isomeric equilibrium was detected and only the isomer contained the bulkiest substituent in the 3-position was obtained. However, a dynamic behaviour of the NBD ligand was only observed for those complexes containing 3-substituted pyrazole ligands.

The physical properties (colour and dichroism) of the complexes [RhCl(CO)$_2$(Hpz$^{R',R''}$)] indicated the presence of metal–metal interactions. So, one-dimensional structure with extended rhodium–rhodium interactions has been proved in [RhCl(CO)$_2$

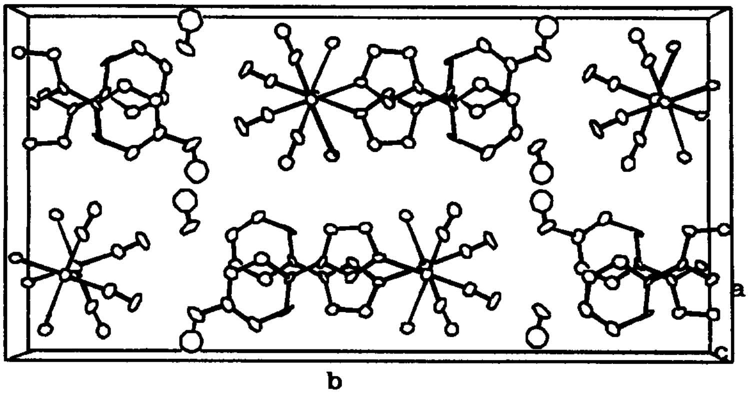

Fig. 4. View of [RhCl(CO)$_2$(Hpz^{An})] cell down the c axis.

(Hpz$^{\mathrm{An}}$)]. The observed Rh—Rh distance (3.398 Å) suggests the possibility of conductivity properties in these complexes.

EXPERIMENTAL

In spite of the use of the Schlenck technique in previous works, we have found that it is not necessary to carry out the reactions in an inert atmosphere, except that for the complex containing Mepz as ligand. However, commercial solvents were dried prior to use. Syntheses of the starting rhodium-complex and the ligands have been described previously: [Rh(μ-Cl)(NBD)]$_2$,[35] Hpz$^{\mathrm{But}}$,[36] Hpz$^{\mathrm{Ph}}$,[36] Hpz$^{\mathrm{An}}$,[37] Hpz$^{\mathrm{Ph,Me}}$,[38] Hpz$^{\mathrm{But,Me}}$,[37] and Mepz.[39] The ligands Hpz and Hpz$^{\mathrm{Me,Me}}$ are commercial and they were used without purification.

IR spectra were recorded on a Perkin–Elmer 1300 spectrometer in KBr discs. ^{1}H NMR spectra were performed on a Varian XL-300 spectrometer working at 299.95 MHz. Chemical shifts are listed in parts per million relative to tetramethylsilane and coupling constants are in Hertz. The chemical shifts and coupling constants are accurate to 0.01 ppm and 0.2 Hz respectively.

Preparation of [RhCl(NBD)(Hpz$^{\mathrm{R',R''}}$)] (**1–8**)

To a yellow solution of [Rh(μ-Cl)(NBD)]$_2$ (0.1 mmol) in dichloromethane (15 cm^3) or suspension in methanol (15 cm^3) was added the corresponding pyrazole (0.2 mmol). The clear orange–yellow solution that formed immediately after the addition was stirred at room temperature for 2 h. Then the volume was reduced *in vacuo* to approx. 2 cm^3. Addition of hexane caused the precipitation of an orange–yellow solid, which was filtered off, washed with small portions of hexane and dried *in vacuo*. Yields are practically quantitative.

Preparation of [RhCl(CO)$_2$(Hpz$^{\mathrm{R',R''}}$)] (**1a–5a**)

Carbon monoxide was bubbled for 10–15 min through a solution of [RhCl(NBD)(Hpz$^{\mathrm{R',R''}}$)] in dichloromethane at room temperature and atmospheric pressure. The initial orange–yellow colour of the solution changed to lighter yellow. The blue–violet residue obtained by evaporation was recrystallized by dissolving it in dichloromethane and adding hexane. The blue–violet crystals obtained were filtered off and dried *in vacuo*. Yields are quantitative.

X-ray structure determination of [RhCl(CO)$_2$(Hpz$^{\mathrm{An}}$)] (**3a**)

Single green–violet crystals of [RhCl(CO)$_2$(Hpz$^{\mathrm{An}}$)] were obtained as needles from dichloromethane solution at −5°C.

A crystal was coated with epoxy resin and mounted in a kappa diffractometer. The cell dimensions were refined by least-squares fitting of the θ values of 25 reflections. A summary of the fundamental crystal data are given in Table 8.

The intensities were corrected for Lorentz and polarization effects. Scattering factors for neutral atoms and anomalous dispersion correction for rhodium and chlorine were taken from *International Tables for X-ray Crystallography*.[40] The structure was solved by Patterson and Fourier methods. An empirical absorption correction[41] was applied at the end of the isotropic refinement. The maximum and minimum absorption correction factors were 1.434 and 0.462 respectively. The positions of the hydrogen atoms were calculated and included.

A final refinement with unit weights with fixed coordinates and isotropic thermal factors for the

Table 8. Crystal and refinement data for [RhCl(CO)$_2$(Hpz$^{\mathrm{An}}$)] (**3a**)

Formula	$RhClO_3N_2C_{12}H_{10}$
Molecular weight	368.58
Crystal system	orthorhombic
Space group	*Pbca*
a (Å)	28.300(6)
b (Å)	14.168(7)
c (Å)	6.778(3)
V (Å^3)	2717(2)
Z	8
F(000)	1456
ρ (calcd) (g cm^{-3})	1.80
Temperature (K)	294
μ (cm^{-1})	14.38
Crystal dimensions (mm)	0.15 × 0.05 × 0.06
Diffractometer	Enraf–Nonius CAD4
Radiation	graphite-monochromated Mo-K_α (λ = 0.71069 Å)
Scan technique	$\omega/2\theta$
Data collected	(0,0,0) to (39,19,9)
θ	$1 < \theta < 30$
Unique data	3865
Unique data (I) $\geqslant 2\sigma(I)$	783
Standard reflexions	3/64
R_F (%)	6.4
R_{wF} (%)	7.1
Average shift/error	0.085

hydrogen atoms and the isotropic temperature factors for C(12) led to $R_F = 0.064$ and $R_{wF} = 0.071$. Calculations were performed using the X-Ray 80 system.[42] No trends in ΔF *vs* F_0 or $(\sin\theta)/\lambda$ were observed.

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Supplementary material available—Tables giving fractional coordinates, thermal parameters, and bond distances and angles for $[RhCl(CO)_2(Hpz^{An})]$ (7 pages). Tables of observed and calculated structure factors (26 pages) can be obtained from the authors.

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