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Reaction of platinum(II) derivatives with bis(pyrazolyl)propane. Cleavage of a C(sp^3)-N bond in a bis(pyrazolyl)alkane promoted by platinum(II) derivatives. Crystal structure of *cis*-Pt(pzH)$_2$Cl$_2$ (pzH = pyrazole)

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Abstract

The reactions of bis(pyrazolyl)propane (CH$_3$)$_2$C(pz)$_2$, (pzH = pyrazole), with PtCl$_2$, (RCN)$_2$PtCl$_2$ and K$_2$[PtCl$_4$] have been investigated, and the results compared with those described previously for the corresponding palladium(II) derivatives. In contrast with the behaviour of the palladium analogues, the platinum derivatives promote the rupture of the ligand: simple adducts of pyrazole, *cis*- or *trans*-Pt(pzH)$_2$Cl$_2$, or species containing the ligand [HN=C(R)pz], formally arising from the insertion of a nitrile into the N–H bond of pyrazole, are obtained. For comparison, the reaction of the platinum derivatives with pyrazole itself has been investigated under various conditions. The crystal structure of *cis*-Pt(pzH)$_2$Cl$_2$ has been determined by X-ray diffraction: monoclinic, space group $C2/c$, a 9.180(1), b 15.084(1), c 15.1445(9) Å, β 101.536(7)°, $Z = 8$, $R = 0.039$, $R_W = 0.040$ for 2125 observed reflections.

Introduction

In pursuance of our interest in the interactions of pyrazoles and other pyrazole-containing molecules with d^8 and d^{10} metal ions [1], we recently described the reactions of some bis(pyrazolyl)alkanes, I–III, with palladium(II) and platinum(II)

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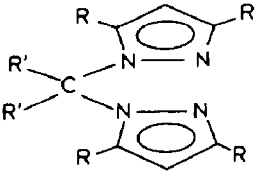


(I : R = H, R′ = H;
II : R = CH_3, R′ = H;
III : R = H, R′ = CH_3)

derivatives [2]. With palladium, both the series (L–L)$PdCl_2$ and $[(L–L)_2Pd]^{2+}$ were obtained for all the ligands I–III.

The X-ray structural study of (L–L)$PdCl_2$ (L–L = III) and $[(L–L)_2Pd]^{2+}$ (L–L = I) showed that the bis(pyrazolyl)alkanes act as chelating ligands. In addition, the structure of the complex (L–L)$PdCl_2$ (L–L = III) showed a peculiar feature, namely an agostic Pd · · · H–C interaction between the metal and one hydrogen of a methyl group.

With platinum, ligands I and II gave the corresponding 1/1 and 1/2 adducts, whereas the ligand III displayed a different and more complex behaviour. Simple adducts were not isolated: the analytical evidence (mainly the C/N ratio) suggested that, inter alia, pyrazole derivatives were formed, implying that a rupture of the ligand had occurred. These preliminary observations indicated that the reaction of this ligand with platinum(II) was unusual and worthy of further investigation. We report here the results obtained from several platinum intermediates under various experimental conditions.

For comparison, reactions with pyrazole itself were carried out, and the structure of *cis*-$Pt(pzH)_2Cl_2$ established by X-ray diffraction. A preliminary report has appeared [3].

Results and discussion

The reactions of bis(pyrazolyl)propane (III) with several platinum(II) derivatives, namely $PtCl_2$, $K_2[PtCl_4]$, $(PhCN)_2PtCl_2$ and $(MeCN)_2PtCl_2$, were examined under a variety of conditions (Scheme 1.) Although more products were identified, none of them contains the unaltered ligand. Only complexes containing pyrazole or moieties arising from pyrazole, were obtained: this implies the cleavage of a C(sp^3)–N bond in bis(pyrazolyl)propane.

The reaction of the ligand with $(PhCN)_2PtCl_2$, made directly from $PtCl_2$ and benzonitrile, gave a mixture of products. Since it is known that $(PhCN)_2PtCl_2$ prepared in this way contains both the *cis* and *trans* isomers [4], the isomers were separated by flash-chromatography. The *cis*-isomer gave *cis*-$Pt(pzH)_2Cl_2$, an unidentified product, and *trans*-$Pt(pzH)_2Cl_2$, whereas the *trans*-isomer gave *trans*-$Pt(pzH)_2Cl_2$ and a brilliant red, very slightly soluble compound, which was fully characterized by analysis, IR, ^1H, ^{13}C NMR and mass (FAB) spectrometry. Although the analytical data for the red complex fit the formula Pt(PhCN)(pzH)Cl_2, the absence from the IR spectrum of any absorption in the range 2300–2200 cm^{-1}, taken together with the presence of strong and sharp bands at 3300 and 1630 cm^{-1}, suggests a conversion of the nitrile into a HN=C-Ph group.

In the ^1H NMR spectrum (Table 1), three distinct resonances appear for the CH protons of the pyrazole ring, each of them coupled with ^{195}Pt, having the heterocycle coordinated to the metal through a nitrogen atom. Thus it is reasonable to assume that a nucleophilic attack of pyrazole on the *sp* carbon atom of the nitrile has

$$(\mathrm{CH_3})_2\mathrm{C(pz)_2} + \mathrm{K_2[PtCl_4]} \xrightarrow{\mathrm{H_2O/HCl}\ 2N} \textit{cis}\text{-}\mathrm{Pt(pzH)_2Cl_2}$$

$$(\mathrm{CH_3})_2\mathrm{C(pz)_2} + \mathrm{PtCl_2} \xrightarrow{\mathrm{CHCl_3}} \textit{cis}\text{-}\mathrm{Pt(pzH)_2Cl_2}$$

$$(\mathrm{CH_3})_2\mathrm{C(pz)_2} + \textit{cis}\text{-}\mathrm{(PhCN)_2PtCl_2} \xrightarrow{\mathrm{CHCl_3}} \textit{cis}\text{-}\mathrm{Pt(pzH)_2Cl_2} + (\ldots) + \textit{trans}\text{-}\mathrm{Pt(pzH)_2Cl_2}$$

$$(\mathrm{CH_3})_2\mathrm{C(pz)_2} + \textit{trans}\text{-}\mathrm{(PhCN)_2PtCl_2} \xrightarrow{\mathrm{CHCl_3}} \mathrm{Pt[HN{=}C(Ph)pz]Cl_2} + \textit{trans}\text{-}\mathrm{Pt(pzH)_2Cl_2}$$

$$(\mathrm{CH_3})_2\mathrm{C(pz)_2} + \mathrm{(CH_3CN)_2PtCl_2} \xrightarrow{\mathrm{CH_3CN}} \mathrm{Pt[HN{=}C(CH_3)pz]Cl_2}$$

$$2\,\mathrm{pzH} + \mathrm{K_2[PtCl_4]} \xrightarrow{\mathrm{H_2O/HCl}} \textit{cis}\text{-}\mathrm{Pt(pzH)_2Cl_2}$$

$$2\,\mathrm{pzH} + \mathrm{PtCl_2} \xrightarrow{\mathrm{CHCl_3}} \textit{cis}\text{-}\mathrm{Pt(pzH)_2Cl_2}$$

$$2\,\mathrm{pzH} + \textit{cis}\text{-}\mathrm{(PhCN)_2PtCl_2} \xrightarrow{\mathrm{CHCl_3}} \textit{cis}\text{-}\mathrm{Pt(pzH)_2Cl_2} + \textit{trans}\text{-}\mathrm{Pt(pzH)_2Cl_2}$$

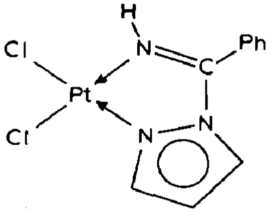
$$\mathrm{pzH} + \textit{trans}\text{-}\mathrm{(PhCN)_2PtCl_2} \xrightarrow{\mathrm{CHCl_3}} \mathrm{Pt[HN{=}C(Ph)pz]Cl_2} + \textit{trans}\text{-}\mathrm{Pt(pzH)_2Cl_2}$$

$$2\,\mathrm{pzH} + \textit{trans}\text{-}\mathrm{(PhCN)_2PtCl_2} \xrightarrow{\mathrm{CHCl_3}} \mathrm{Pt[HN{=}C(Ph)pz]Cl_2} \xrightarrow{\mathrm{CHCl_3}} \textit{trans}\text{-}\mathrm{Pt(pzH)_2Cl_2}$$

Scheme 1

occurred, followed by protonation of the imino-nitrogen atom, to give the amidine HN=C(Ph)-pz. The formation of such an amidine by reaction of a pyrazole with a coordinated nitrile has been reported recently for some ruthenium(II) complexes: in one case, namely $[\mathrm{Ru(CO)H\{HN{=}C(Me)(Me_2pz)\}(PPh_3)_2}]^+$, the X-ray structure determination revealed *endo*-bidentate coordination to the metal through the two nitrogen, imino and pyrazole, atoms [5].

The FAB mass spectra of our species showed the molecular ion, $[M]^+$, m/z 437, corresponding to a mononuclear species, and so we assume that the amidine acts as a chelating ligand, giving a *cis*-derivative:



An analogous, yellow complex was obtained with $\mathrm{(MeCN)_2PtCl_2}$. Although the very low solubility prevented full characterization in solution, the IR and mass spectra (FABMS) suggest a formulation similar to that of the corresponding phenyl species.

The reactions observed for the platinum derivatives seems to be unusual, both on the part of the ligand III, since they are not observed with other bis(pyrazolyl)alkanes (e.g. I and II), and that of the metal itself, as shown by the different reactions of palladium(II) with the same ligand. Moreover, the rupture of the ligand appears to be promoted by platinum, independent of the nature of the starting compound and of the experimental conditions.

We are not aware of other examples of a cleavage of a carbon–nitrogen bond in bis(pyrazolyl)alkanes promoted by metal ions. However the cleavage of a boron-nitrogen bond has been reported in ruthenium(II) chemistry. Thus $[Ru(\eta^6\text{-}C_6H_6)Cl_2]_2$ in acetonitrile reacts with $K[HB(Me_2pz)_3]$ to give $[Ru(\eta^6\text{-}C_6H_6)\{HN{=}C(Me)(Me_2pz)\}(Me_2pzH)]^{2+}$, which contains both a pyrazole and an amidino ligand [6]. In addition, cleavage of a C–N bond has been observed in the reaction of other ruthenium(II) species with 1-hydroxymethyl-3,5-dimethylpyrazole to give 3,5-dimethylpyrazole complexes [7]. As in the ruthenium cases, we do not know how the ligand III is destroyed. Furthermore it is not obvious why the cleavage occurs with platinum and not with palladium.

The observation of a $Pd\cdots H–C$ interaction in the structure of $(L–L)PdCl_2$ (L–L = III) [2] supports the idea of unusual behaviour of the ligand III, with respect to I or II. This observation suggests the possibility of C–H activation, with transfer of hydrogen to the metal, as the first step of the reaction, but we do not have any experimental evidence on this point.

In order to gain further insight into the reactions of platinum species with bis(pyrazolyl)propane, the same reactions were carried out with pyrazole itself. As shown in Scheme 1, the same compounds were obtained under various experimental conditions, proving that pyrazole is the origin of the adducts as well as of the amidino complexes. To throw light on the amidine formation, we also treated the *cis* and *trans*-$Pt(pzH)_2Cl_2$ with PhCN; no reaction occurred and it seems that the attack of the pyrazole proceeds only on a coordinated nitrile.

Pyrazole derivatives, cis- and trans-$Pt(pzH)_2Cl_2$

Both the adducts have been described previously by Reedijk and coworkers: the *cis* isomer was isolated from $K_2[PtCl_4]$, and the *trans* isomer by boiling the $[Pt(pzH)_4)Cl_2 \cdot H_2O$ complex with hydrochloric acid. The latter complex was obtained from *cis*-$Pt(DMSO)_2Cl_2$ and excess ligand in aqueous solution [8].

The complexes $Pt(pzH)_2Cl_2$ were described as insufficiently soluble to give NMR spectra, which were reported only for the corresponding iodides [8]. Although the complexes are indeed only very slightly soluble, we were able to obtain both the ^1H and $^{13}C\{^1H\}$ spectra. The chemical shifts and coupling constants are listed in Tables 1 and 2.

In the ^1H spectra only one set of signals is observed for the two pyrazole ligands. The assignment of the upfield resonance to the (4) protons was made by analogy with the spectra of pyrazole and other pyrazole derivatives, as well as on the basis of multiplicity: indeed the resonance appears, in most cases, as a pseudo-triplet. The assignment of the protons (3) and (5) is based on the value of the observed $^{195}Pt\text{-}^1H$ coupling constants, i.e. on the assumption of $^3J(Pt–H(3)) > {}^4J(Pt–H(5))$. The assumption leads to an assignment which is in agreement also with Elguero's rule that in pyrazoles $J(H(4),H(5))$ is larger than $J(H(3),H(4))$ [9].

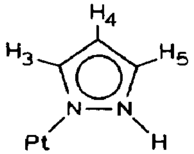
For the *trans*-isomer the spectrum was recorded in $(CD_3)_2CO$ and $CDCl_3$: as for the resonances of the (3) and (5) protons, it is strongly dependent on the solvent. The H(4) resonance seems to be only slightly affected by the nature of the solvent or by complexation. In acetone solution the H(3) and H(5) resonances of the two isomers seem to be affected by complexation in different ways. In the *trans*-isomer,

Table 1

s^{1}H NMR data (δ)

Compound	H(1)	H(3) (^3J(Pt–H))	H(4) (^4J(Pt–H))	H(5) (^4J(Pt–H))	$J_{3,4}$	$J_{4,5}$	$J_{3,5}$	Ref.
pzH [a]		7.58	6.30	7.58				
pzH [b]		7.64	6.31	7.64				
pzH [c]	13.3	7.74	6.38	7.74				
cis-Pt(pzH)$_2$I$_2$ [b]		7.75 (17)	6.50 (10)	8.03 (10)				8
trans-Pt(pzH)$_2$I$_2$ [b]		7.85 (19)	6.45 (10)	7.98 (10)				8
cis-Pt(pzH)$_2$Cl$_2$ [c]	12.8	7.43dd (17)	6.51 [d] (8.5)	8.02dd (10)	2.3	2.7	0.7	this work
trans-Pt(pzH)$_2$Cl$_2$ [c]	12.5	8.12dd (17)	6.53 [d] (8)	8.0dd (10)	2.3	2.7	0.8	this work
trans-Pt(pzH)$_2$Cl$_2$ [a]	11.9	8.14dd (17)	6.38 [d] (8)	7.57dd (9)	2.5	2.9	0.6	this work
Pt[HN=C(Ph)pz]Cl$_2$ [c,e]	11.5	8.34dd (15.3)	7.05 (8.7)	8.54dd (10.2)	2.2	3.3	0.5	this work
Pt[HN=C(CH$_3$)pz]Cl$_2$ [c]		8.2d (15)	7.01 (8.5)	8.8dd (10)	2.1	3.3	0.5	this work

[a] CDCl$_3$. [b] DMF-d_7. [c] (CD$_3$)$_2$CO. [d] Pseudotriplet. [e] Ph-protons: 7.6–8.1 ppm.



both the signals shift downfield, as previously reported for the corresponding iodide [8], whereas in the *cis*-isomer the H(5) and H(3) resonances shift to lower and higher field, respectively, with a large splitting between the two signals.

In the ^{13}C{^{1}H} spectra {(CD$_3$)$_2$CO} the observed resonances were assigned to the three carbon atoms of the pyrazole rings through a 2D heteronuclear chemical shift correlation experiment. The assignments are in agreement also with the assumption ^2J(Pt–C) > ^3J(Pt–C).

Table 2

^{13}C NMR data

Compound	C(3)	J(Pt–C(3))	C(4)	J(Pt–C(4))	C(5)	J(Pt–C(5))
pzH [a]	133.3		104.4		133.3	
pzH [b]	133.3		104.5		133.3	
cis-Pt(pzH)$_2$Cl$_2$ [a]	141.0	46.4	107.5	39.2	132.0	30
trans-Pt(pzH)$_2$Cl$_2$ [a]	141.1	43.8	107.0	34.7	132.1	29.3
trans-Pt(pzH)$_2$Cl$_2$ [b]	140.8	[c]	106.8	35.7	130.1	29
Pt[NH=C(Ph)pz]Cl$_2$ [a]	143.6	[c]	111.3	[c]	133.9	[c]

[a] In (CD$_3$)$_2$CO. [b] In CDCl$_3$. [c] Not resolved.

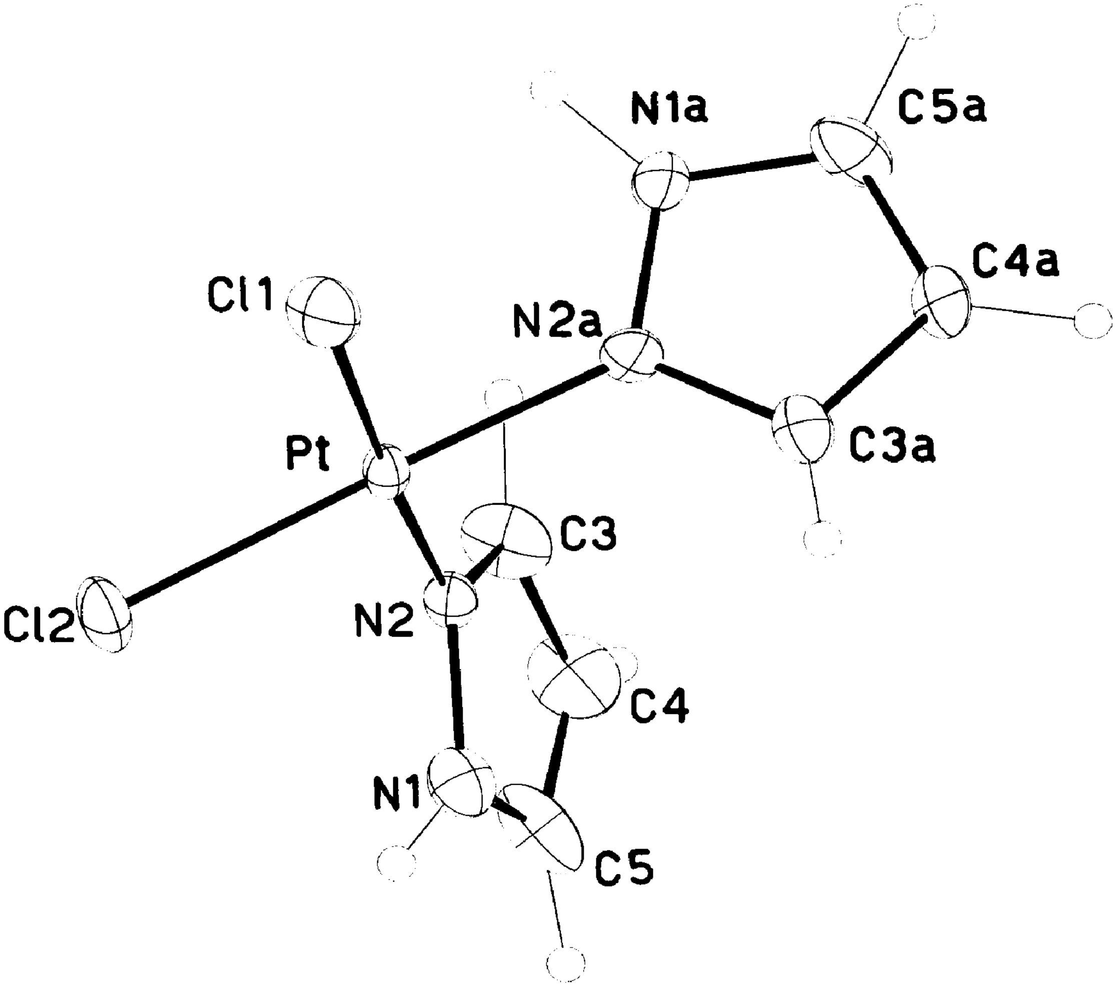


Fig. 1. ORTEP plot and numbering scheme. Thermal ellipsoids enclose 30% of the electron density.

No explanation can be given, at present for the behaviour of these species in solution as indicated by the ^1H and ^{13}C spectra. It is likely that the influence of one pyrazole ring on the other is quite different in the two isomers as a consequence of the different geometry (*cis* or *trans*), leading to different shielding or deshielding effects on the hydrogen atoms. In addition, it is possible that in solution the two isomers are associated in a different way as a result of hydrogen bonds involving the N–H groups, as suggested by the strong influence of the solvent on the NMR spectra.

In the solid state, the structure of only one of the two isomers has so far been established, namely that of the *cis*-complex, for which it was possible to obtain crystals suitable for an X-ray analysis.

Structure in the solid state of cis-Pt(pzH)$_2$Cl$_2$

The crystal structure of the title compound consists of discrete molecules. The ORTEP [10] drawing of the molecule with the numbering scheme, is showed in Fig. 1, the crystal data are listed in Table 3. Although a virtual *Cs* symmetry could be

Table 3

Crystal data, data collection, and refinement of the structure

Formula	$C_6H_8Cl_2N_4Pt$
fw	402.2
space group	*C*2/*c*
a, Å	9.180(1)
b, Å	15.084(1)
c, Å	15.1445(9)
β, deg	101.536(7)
v_c, Å^3	2054.7(3)
Z	8
D_{calcd}, g cm^{-3}	2.60
cryst. size, mm	0.32×0.56×0.64
μ(Mo-K_α) cm^{-1}	148.4
Data coll. instrument	Philips PW 1100
Radiation (monochromated)	Mo-K_α (λ = 0.7107 Å)
T of data collection, K	293
Scan mode	$\omega/2\theta$
Scan speed, deg s^{-1}	0.100
Scan width, deg (in ω)	2.10
Data coll. range (2ϑ)	$4 < 2\vartheta < 60$
Stds (measd every 300 min)	4 0 0, 0 6 0, 0 0 6
No. of unique reflcns measd	2970($\pm h, k, l$)
No. of data with $F_0^2 > 3\sigma(F_0^2)$	2125
No. of param. refined	142
Transmission factors: max; min	0.999; 0.318
R^a and $R_w{}^b$	0.039, 0.040
Quality-of-fit indicator ^{c}	2.35

[a] $R = (\Sigma \| F_0 | - k | F_c \|)/\Sigma | F_0 |)$. [b] $R_w = [\Sigma w(| F_0 | - k | F_c |)^2/\Sigma w | F_0 |^2]^{1/2}$. [c] Quality-of-fit = $[\Sigma w(| F_0 | - k | F_c |)^2/(N_{observns} - N_{params})]^{1/2}$.

Table 4

Bond lengths (Å) and angles (deg) for non-hydrogen atoms

In the coordination sphere			
Pt–Cl(1)	2.276(3)	Cl(1)–Pt–N(2)	177.0(2)
Pt–Cl(2)	2.291(3)	Cl(1)–Pt–N(2a)	89.7(3)
Pt–N(2)	1.934(8)	Cl(2)–Pt–N(2)	92.1(2)
Pt–N(2a)	1.966(8)	Cl(2)–Pt–N(2a)	178.4(3)
Cl(1)–Pt–Cl(2)	90.9(1)	N(2)–Pt–N(2a)	87.4(3)
In the pyrazole ligands			
N(1)–N(2)	1.38(1)	N(1a)–N(2a)	1.37(1)
N(1)–C(5)	1.38(2)	N(1a)–C(5a)	1.38(1)
N(2)–C(3)	1.36(2)	N(1a)–C(3a)	1.36(1)
C(3)–C(4)	1.40(2)	C(3a)–C(4a)	1.40(2)
C(4)–C(5)	1.35(2)	C(4a)–C(5a)	1.35(2)
N(2)–N(1)–C(5)	110.8(1.0)	N(2a)–N(1a)–C(5a)	108.6(9)
N(1)–N(2)–C(3)	102.6(9)	N(1a)–N(2a)–C(3a)	106.5(8)
Pt–N(2)–N(1)	126.0(7)	Pt–N(2a)–N(1a)	125.5(6)
Pt–N(2)–C(3)	131.4(8)	Pt–N(2a)–C(3a)	128.0(7)
N(2)–C(3)–C(4)	113.5(1.2)	N(2a)–C(3a)–C(4a)	109.8(1.0)
C(3)–C(4)–C(5)	104.0(1.2)	C(3a)–C(4a)–C(5a)	106.3(9)
C(4)–C(5)–N(1)	108.6(1.1)	C(4a)–C(5a)–N(1a)	108.8(1.0)

Table 5

Planarity of molecular regions

Plane	Equation [a], χ^2, P	Atoms [b]	Displacements (Å)
I	$0.7020X' - 0.6177Y - 0.3545Z' + 2.3280 = 0$	Pt*	−0.0001(4)
		Cl(1)*	−0.001(3)
		Cl(2)*	0.005(3)
	$\chi^2 = 31.97 (n = 2) P > 99\%$	N(2)*	−0.007(8)
		N(2a)*	0.047(9)
		N(1)	0.932(11)
		N(1a)	−1.005(11)
		C(3)	−0.825(14)
		C(3a)	1.087(13)
II	$0.4561X' + 0.1045Y - 0.8838Z' + 5.5318 = 0$	N(1)*	−0.028(10)
		N(2)*	0.022(8)
		C(3)*	−0.052(13)
	$\chi^2 = 36.88 (n = 2) P > 99\%$	C(4)*	0.024(13)
		C(5)*	0.011(11)
		Pt	0.2613(3)
III	$-0.8808X - 0.4534Y - 0.1365Z' + 3.4284 = 0$	N(1a)*	−0.001(11)
		N(2a)*	0.001(9)
		C(3a)*	−0.003(14)
	$\chi^2 = 0.11 (n = 2) P = 5.3\%$	C(4a)*	0.002(13)
		C(5a)*	0.000(14)
		Pt	0.0439(4)

Dihedral angles (deg)

I/II 55.3(6) I/III 106.8(5) II/III 109.2(7)

[a] Transformation matrix from monoclinic X, Y, Z to orthogonal X', Y, Z' coordinates:

$$\begin{pmatrix} 1 & 0 & -\cos\beta^{\star} \\ 0 & 1 & 0 \\ 0 & 0 & \sin\beta^{\star} \end{pmatrix}$$

[b] Starred (*) atoms were included in the calculation of the plane.

Table 6

Comparison of bond distances (Å) and angles (deg) of pyrazole rings

Atoms	Ring 1	Ring 1a	Av. values calculated ref. 13
N(1)–N(2)	1.38(1)	1.37(1)	1.354
N(1)–C(5)	1.38(2)	1.38(2)	1.346
N(2)–C(3)	1.36(2)	1.36(1)	1.333
C(3)–C(4)	1.40(2)	1.40(2)	1.386
C(4)–C(5)	1.35(2)	1.35(2)	1.362
N(2)–N(1)–C(5)	110.8(1.0)	108.6(9)	111.5
N(1)–N(2)–C(3)	102.6(9)	106.5(8)	105.3
N(2)–C(3)–C(4)	113.5(1.2)	109.8(1.0)	110.2
C(3)–C(4)–C(5)	104.0(1.2)	106.3(9)	106.3
C(4)–C(5)–N(1)	108.6(1.1)	108.8(1.0)	106.7
M–N(2)–N(1)	126.0(7)	125.5(6)	121.6
M–N(2)–C(3)	131.4(8)	128.0(7)	132.5

assumed, the molecule has no real symmetry and all the atoms occupy general positions. The interatomic distances and angles are shown in Table 4. The least-square planes of the regions in the compound, the displacements of atoms from them, and the χ^2 values with the corresponding probability P that the regions are non-planar, are shown in Table 5.

The coordination around the platinum(II) is slightly distorted from the ideal square-planar geometry in the direction of a tetrahedron. The distortion is indicated by the Cl(1)–Pt–N(2)(177.0(2)°) and Cl(2)–Pt–N(2a)(178.4(3)°) angles, which depart significantly from 180°, and by the displacements of atoms from the best coordination plane: the displacements of Pt, Cl(1) and N(2) are not significant, since they are smaller than their respective e.s.d.'s, whereas the displacements of Cl(2) and N(2a) above the plane are significant.

In addition, although the angle Cl(2)–Pt–N(2a) is 178.4(3)°, there is a significant difference between the value of the Cl(2)–Pt–N(2) angle, 92.1(2)°, and that of the N(2)–Pt–N(2a) angle, 87.4(3)°. The two Pt–N distances, 1.934(8) and 1.966(8) Å

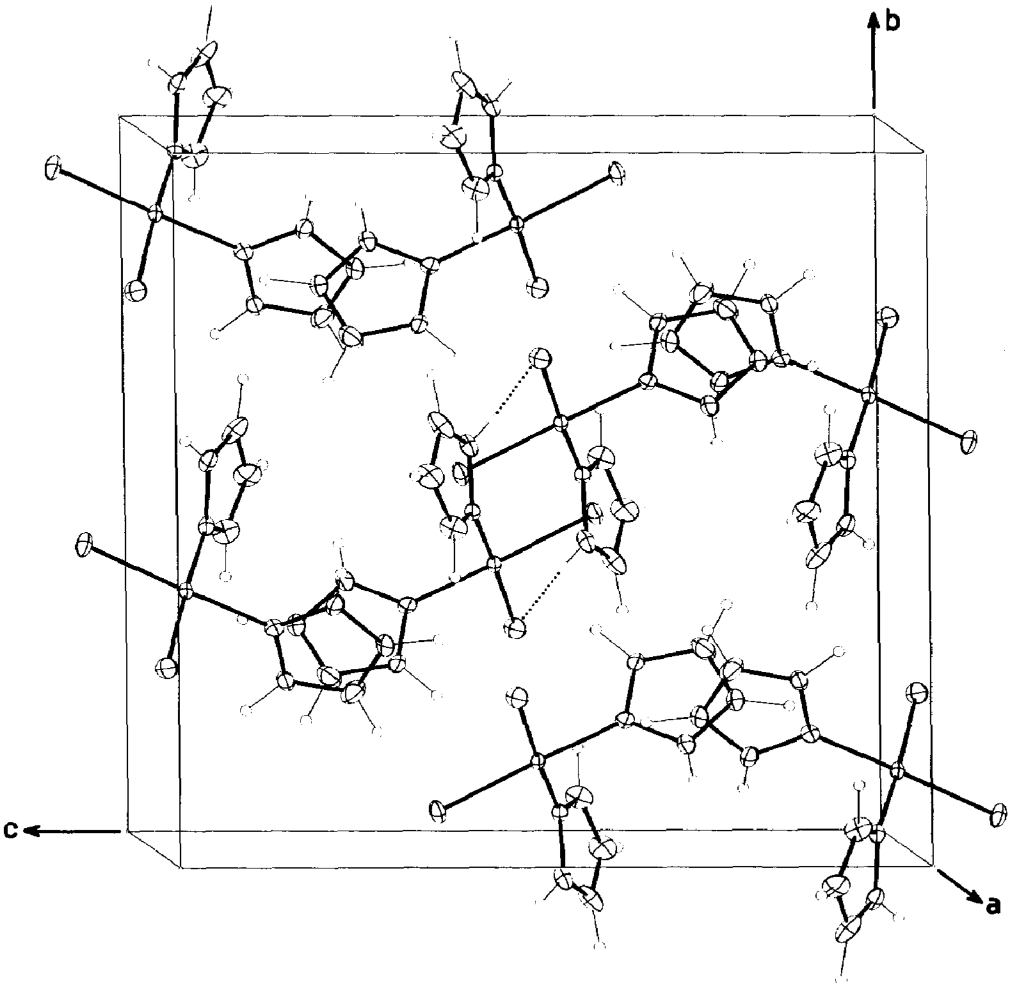


Fig. 2. Packing in the unit cell.

for Pt–N(2) and Pt–N(2a), respectively, are significantly unlike and shorter than the Pt–N(sp^2) average value (2.023(12) Å) recently derived by Palenik and Giordano [11], for *cis*-PtL_2Cl_2 compounds. Of the two Pt–Cl distances, the Pt–Cl(2) value, 2.291(3) Å, match the average value, 2.293(9) Å, whereas the Pt–Cl(1), 2.276(3) Å, is at the lower end of the observed range [11], e.g., 2.271 Å in *cis*-Pt(caffeine)$_2$Cl$_2$. It is noteworthy that the longer distances Pt–Cl(2) and Pt–N(2a) are mutually *trans*.

As for the heterocyclic rings, they exhibit different orientations with respect to the coordination plane, the dihedral angles being 55.3(6)° for one pyrazole and 106.8(5)° for the other. The first angle is in the range of values reported for platinum(II) complexes with two heterocyclic nitrogen ligands [12], e.g., *cis*-Pt(N-methylimidazole)$_2$Cl$_2$, 41.7° or *trans*-Pt(pyridine)$_2$Cl$_2$, 56.2°. The other angle implies approach of a pyrazole ligand orthogonal to the coordination plane. The N–N, N–C, and C–C distances are compared with the average values, [13], in Table 6. They are alike in the two rings, at the upper end of the observed values, indicating a small expansion of the rings. A survey of the literature by F. Bonati [13], has revealed some trends to be established for internal and external angles of the ring of the coordinated pyrazoles and pyrazolates. For the adducts, i.e. for pyrazoles which have no free lone pair, there is the following order of size of bond angles: M–N(2)–C(3) > M–N(2)–N(1) (M = metal), N(2)–N(1)–C(5) > N(1)–N(2)–C(3) and N(2)–C(3)–C(4) > C(4)–C(5)–N(1). Such a trend is observed also in our compound for both rings; but the differences between the angles in the two rings are significant (see Table 6). The narrow angle N(1)–N(2)–C(3) in ring 1 may originate from the shorter distance Pt–N(2): Pt could repel N(1) and C(3) atoms, thus reducing the internal angle at N(2) and widening those at N(1) and C(3). The packing coefficient k [14] is 0.75, corresponding to a close molecular packing. The crystal cohesion is ensured by a hydrogen bridge between Cl(1)(x, y, z) and N(1)($1-x$, $1-y$, $1-z$), 3.31 Å, (Cl(1)...H(1) 2.47(8) Å, Cl(1)...H(1)–N(1) 146.3°) and by normal Van der Waals contacts. The unit-cell packing is given in Fig. 2. The shortest intermolecular approaches involve the molecule (x, y, z) and equivalent ones, $-x$, $-y$, $1-z$; $1-x$, $-y$, $1-z$; $1-x$, y, $1/2-z$; $1/2+x$, $1/2+y$, z and $1/2+x$, $1/2-y$, $1/2+z$.

In most of the structures of pyrazole metal adducts, the N–H groups have been found to be engaged in hydrogen bonds [15]. In our case a short intermolecular contact distance between nitrogen and chlorine is observed only for Cl(1) and N(1), suggesting that of the two pyrazole rings only one (ring 1) is involved in an intermolecular hydrogen bridge. This may explain the difference between the orientation of the two rings.

Experimental

The ligands $(CH_3)_2C(pz)_2$ (III) and pzH were purchased from Columbia Organic Chemicals and Janssen Chimica, respectively, and used without further purification. The ^1H and ^{13}C NMR data are reported in Table 1 and 2, respectively. The spectra were recorded with a Varian XL 200 or Bruker WP 80 and AC 200 instrument. The 2D experiments were performed with a Bruker AC 200 spectrometer. The mass spectra were recorded on a VG-7070EQ instrument under FAB conditions with 3-nitrobenzyl alcohol as matrix. Infrared spectra were recorded with Perkin–Elmer 1310 and 983 spectrophotometers.

Dichlorobis(benzonitrile)platinum(II), $(PhCN)_2PtCl_2$ [4]. Synthesis and separation of the cis and trans isomers.

A suspension of $PtCl_2$ (918.4 mg) in PhCN (5 ml) was stirred at 100 °C until a yellow solution was obtained. After filtration, a yellow precipitate was obtained on addition of petroleum ether. Yield 80%. The crude product (mixture of the two isomers) (900 mg) was separated by flash chromatography on a column (20 × 3 cm) of silica gel (Merck 230–400 mesh) with CH_2Cl_2 as the eluent. The *trans*- and *cis*-$(PhCN)_2PtCl_2$ isomers were obtained as the first (yield 70%) and second eluates (yield 25%), respectively.

Reaction of $(CH_3)_2C(pz)_2$ (III) with $K_2[PtCl_4]$

To a suspension of $(CH_3)_2C(pz)_2$ (III) (264 mg, 1.5 mmol) in water was added, an aqueous solution of $K_2[PtCl_4]$ (622 mg, 1.5 mmol) and 2*N* HCl (4.65 ml). The mixture was refluxed until a yellow solution was obtained. Pale yellow crystals were formed on cooling.

A second crop was obtained by concentration of the solution. The combined precipitates were recrystallized from $(CH_3)_2CO/Et_2O$ to give the analytical sample: *cis*-$Pt(pzH)_2Cl_2$, yield ca. 65%. M.p. 194–195 °C. Analysis: found: C, 18.64; H, 2.15; Cl, 17.0; N, 14.51; Pt, 48.8. $C_6H_8Cl_2N_4Pt$ calc.: C, 17.91; H, 1.99; Cl, 17.63; N, 13.93; Pt, 48.53%. Mass spectrum: $[M]^+$, m/z 402. IR (Nujol) (cm^{-1}): 3280s, v(NH); 1520w, pyrazole ring; 345, 336, ν(Pt–Cl) (lit. [8] 348, 336).

Reaction of $(CH_3)_2C(pz)_2$ (III) with $PtCl_2$

A chloroform suspension of $PtCl_2$ (400 mg, 1.5 mmol) and $(CH_3)_2C(pz)_2$ (264 mg, 1.5 mmol) was refluxed until a yellow solution was obtained (ca. 30 h). A small amount of $PtCl_2$ was filtered off, the solution was concentrated, and diethyl ether was added. The pale yellow precipitate was recrystallized from $(CH_3)_2CO/Et_2O$, and identified as *cis*-$Pt(pzH)_2Cl_2$; yield 65%.

Reaction of $(CH_3)_2C(pz)_2$ (III) with cis-$(PhCN)_2PtCl_2$

A solution of $(CH_3)_2C(pz)_2$ (176 mg, 1 mmol) and *cis*-$(PhCN)_2PtCl_2$ (472 mg, 1 mmol) in chloroform (ca. 50 ml) was refluxed for 30 h. A pale yellow precipitate was formed. It was filtered off, recrystallized from $(CH_3)_2CO/Et_2O$ and identified as *cis*-$Pt(pzH)_2Cl_2$, yield 20–25%.

The chloroform solution was concentrated to ca. 10 ml and diethyl ether was added to give a yellow precipitate which was recrystallized from $CHCl_3/Et_2O$; m.p. 127–130 °C. Analysis: found: C, 23.51; H, 2.77; N, 12.40. Further concentration of the solution to small volume and addition of n-hexane gave a precipitate of a third product. This was recrystallized from $CHCl_3$ and n-hexane to give an analytical sample, yield 25%; m.p. 201–202 °C. Analysis: found: C, 20.49; H, 2.17; N, 13.02. $C_6H_8Cl_2N_4Pt \cdot \frac{1}{3}Et_2O$ calc.: C, 20.62; H, 2.65; N, 13.12%. The IR and ^1H NMR spectra were identical to those of *trans*-$Pt(pzH)_2Cl_2$, obtained from the reaction of III with *trans*-$(PhCN)_2PtCl_2$ (see infra).

Reaction of $(CH_3)_2C(pz)_2$ (III) with trans-$(PhCN)_2PtCl_2$

A chloroform solution of $(CH_3)_2C(pz)_2$ (176 mg, 1 mmol) and *trans*-$(PhCN)_2PtCl_2$ (472 mg, 1 mmol) was refluxed for 5–6 days. The red solid was filtered off and crystallized from $(CH_3)_2CO/Et_2O$. Pt[HN=C(Ph)pz]Cl_2, yield 30%

m.p. 224–226 °C. Analysis: found: C, 27.95; H, 2.35; Cl, 16.1; N, 9.85; Pt, 44.4. $C_{10}H_9Cl_2N_3Pt$ calc.: C, 27.46; H, 2.06; Cl, 16.2; N, 9.61; Pt, 44.6%. Mass spectrum: $[M]^+$, m/z 437. IR (Nujol) (cm^{-1}): 3330s, v(NH); 1630s, ν(C=N) amidine; 1520w, pyrazole ring; 343vs (with a shoulder), ν(Pt–Cl). The chloroform mother liquor was concentrated and n-hexane was added: the yellow precipitate was filtered off and recrystallized from $CHCl_3$/n-hexane. *trans*-$Pt(pzH)_2Cl_2$, yield 60%. m.p. 231–232 °C. Analyses: found: C, 18.18; H, 2.02; N, 13.95. $C_6H_8Cl_2N_4Pt$ calc.: C, 17.91; H, 1.99; N, 13.93%. Mass spectrum: $[M]^+$, m/z 402. IR (nujol) (cm^{-1}): 3320s; 3180vs; 1540w; 1510w; 345vs; 284 vs.

Reaction of $(CH_3)_2C(pz)_2$ (III) with $(CH_3CN)_2PtCl_2$

To a suspension of $(CH_3CN)_2PtCl_2$ [16] (348 mg, 1 mmol) in CH_3CN was added a solution of $(CH_3)_2C(pz)_2$ (176 mg, 1 mmol) in the same solvent. The mixture was refluxed for ca. 1 h to give, first, a yellow solution and later an orange-yellow precipitate. The crude product was filtered off and recrystallized from $(CH_3)_2CO/Et_2O$. $Pt[HN{=}C(CH_3)pz]Cl_2$, yield 50%. m.p. > 280 °C. Analyses: found: C, 16.02; H, 1.89; N, 11.09. $C_5H_6Cl_2N_3Pt$ calc.: C, 16.00; H, 1.86; N, 11.20%. Mass spectrum: $[M]^+$, m/z 375. IR (nujol) (cm^{-1}): 3200vs, ν(NH); 3080vs; 1615vs, ν(C=N) amidine; 1515s, pyrazole ring; 352vs; 339vs; 314s.

Reaction of pzH with $K_2[PtCl_4]$

To a solution of pzH (102 mg, 1.5 mmol) in water was added an aqueous solution of $K_2[PtCl_4]$ (311 mg, 0.75 mmol), and 2*N* HCl (2.4 ml). The mixture was refluxed until a yellow solution was obtained. Pale yellow crystals of *cis*-$Pt(pzH)_2Cl_2$ separated on cooling. A second crop was obtained by concentration of the solution. The combined precipitates were recrystallized from $(CH_3)_2CO/Et_2O$. Yield 80%.

Reaction of pzH with $PtCl_2$

A chloroform suspension of $PtCl_2$ (266 mg, 1 mmole) and pzH (136 mg, 2 mmole) was refluxed until a yellow solution was obtained (ca. 20 hours). A small amount of $PtCl_2$ was filtered off, the solution was concentrated, and diethyl ether was added. The yellow product, *cis*-$Pt(pzH)_2Cl_2$, was recrystallized from $(CH_3)_2CO/Et_2O$. Yield 70%.

Reaction of pzH with cis-$(PhCN)_2PtCl_2$

A solution of pzH (34 mg, 0.5 mmol) and *cis*-$(PhCN)_2PtCl_2$ (118 mg, 0.25 mmol) was refluxed for 15 h. A small precipitate of the yellow *cis*-$Pt(pzH)_2Cl_2$ was formed. The filtered solution was concentrated to small volume and n-hexane was added, to give a yellow precipitate of *trans*-$Pt(pzH)_2Cl_2$, which was recrystallized from $CHCl_3$/n-hexane. Yield 75%.

Reaction of pzH with trans-$(PhCN)_2PtCl_2$

A chloroform solution of pzH (68 mg, 1 mmol) was added to a solution of *trans*-$(PhCN)_2PtCl_2$ (472 mg, 1 mmol), (molar ratio 1/1), in the same solvent. The mixture was refluxed until a red precipitate of $Pt[HN{=}C(Ph)pz]Cl_2$ was formed. The crude product was crystallized from $(CH_3)_2CO/Et_2O$. Yield 25%.

When a molar ratio pzH/*trans*-$(PhCN)_2PtCl_2 = 2$ was used, the red compound initially formed disappeared, to give eventually *trans*-$Pt(pzH)_2Cl_2$. Yield 95% (Scheme 1).

X-ray structure of cis-$Pt(pzH)_2Cl_2$

Suitable crystals of compound *cis*-$Pt(pzH)_2Cl_2$ were obtained by slow evaporation of an acetone solution in the presence of diethyl ether. A prismatic crystal was used for data collection. Accurate unit-cell dimensions were obtained by least-squares fit of 2θ values for 28 reflections.

Details of the data collection are summarized in the Table 3. A total of 5982 reflections, $\pm h$, $+k$, $+l$, were measured. Data were corrected for Lorentz and polarization effects and an empirical absorption correction [17] based on azimuthal scan of six reflections with Eulerian angle χ near 90° was made. Averaging of equivalent reflections yielded the unique data set, with a factor $R(1) = 0.070$ for the whole set of observed intensities. Systematic absences, $(h\ 0\ l)$, l odd and $h\ k\ l$, $(h+k)$ odd, indicated the possible space groups $C2/c$ and Cc. The statistical distribution of the normalized structure factors $E(\langle E \rangle = 0.824$, $\langle E^2 - 1 \rangle = 0.908$, $\langle E^3 \rangle = 1.449$, $\langle E^4 \rangle = 2.330)$ indicated a centric distribution. The correct space group is therefore $C2/c$, as confirmed by the subsequent structure solution and refinement; the space group Cc did not lead to successful refinement.

The position of the platinum was obtained from a three-dimensional Patterson map. A difference electron density synthesis based upon the Pt signs revealed the positions of all the non-hydrogen atoms. The full-matrix least-squares refinement of the positional and first isotropic and later anisotropic thermal parameters of the non-hydrogen atoms reduced R to 0.057. At this point a three-dimensional difference Fourier synthesis revealed the approximate positions of the 8 hydrogen atoms.

The subsequent least-squares refinement, with inclusion of the hydrogen atoms with the same isotropic thermal parameters as the atoms to which they are attached, reduced the conventional R index to 0.039 ($R_W = 0.040$) after three cycles, with a final maximum shift/error of 0.77 for the non-hydrogen atoms. At all stages of the structure analysis, the observed reflections were given unit weights. Attempts to use weights $= \sigma^{-2}(|F_0|)$, made at the end of the refinement, did not lead to better results. The maximum and minimum $\Delta\rho$ values in the final difference Fourier map

Table 7

Final coordinates and equivalent isotropic thermal parameters (with e.s.d.'s in parentheses)

Atom	x	y	z	B (Å^2)
Non-hydrogen atoms				
Pt	0.35767(4)	0.11699(2)	0.47963(2)	2.19(1)
Cl(1)	0.5463(3)	0.2161(2)	0.5193(2)	3.95(6)
Cl(2)	0.4191(3)	0.0495(2)	0.6167(2)	3.68(6)
N(1)	0.2043(13)	−0.0550(7)	0.4366(6)	3.4(2)
N(2)	0.1942(9)	0.0360(5)	0.4401(5)	2.9(2)
C(3)	0.0481(14)	0.0509(10)	0.4046(8)	4.2(3)
C(4)	−0.0286(15)	−0.0252(9)	0.3690(8)	4.5(3)
C(5)	0.0718(15)	−0.0913(9)	0.3916(7)	5.8(3)
N(1a)	0.2379(12)	0.2522(7)	0.3406(6)	3.5(2)
N(2a)	0.3069(10)	0.1719(5)	0.3597(5)	2.5(1)
C(3a)	0.3292(16)	0.1389(8)	0.2801(7)	3.3(2)
C(4a)	0.2731(14)	0.1979(8)	0.2104(6)	3.1(2)
C(5a)	0.2178(16)	0.2672(8)	0.2490(7)	5.0(3)

were 0.163 and -0.290 eÅ^{-3}, both close to the Pt atom. Anomalous dispersion effects were included in the scattering factors for Pt [18]. No extinction correction was applied. The atomic scattering factors for the non-hydrogen atoms were taken from ref. 18, while for hydrogen atoms those from ref. 19 were used. Final atomic positional parameters and isotropic equivalent thermal parameters are given in Table 7. A locally modified version of the ORFLS program was used [20].

Thermal parameters, the average interatomic distances and angles (with standard deviations [21] in the two pyrazoles, hydrogen coordinates, bond lengths and angles for hydrogen atoms, intermolecular contacts and lists of structure factors can be obtained from B. Bovio.

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