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PREPARATION AND CHARACTERIZATION OF PALLADIUM(II) AND PLATINUM(II) COMPLEXES WITH BIS(PYRAZOLYL)ALKANES. CRYSTAL AND MOLECULAR STRUCTURES OF $[Pd\{CH_2(pz)_2\}_2][BF_4]_2$ AND OF $[PdCl_2\{(CH_3)_2C(pz)_2\}]$ (pzH = pyrazole), A NEW EXAMPLE OF A Pd · · · H–C AGOSTIC INTERACTION

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Summary

Neutral and cationic complexes of general formulae $(L–L)MCl_2$ (M = Pd, (L–L) = $CH_2(pz)_2$ (**1**); $CH_2(3,5\text{-}Me_2pz)_2$ (**2**); $(CH_3)_2C(pz)_2$ (**3**); M = Pt, (L–L) = $CH_2(pz)_2$ (**4**); $CH_2(3,5\text{-}Me_2pz)_2$ (**5**) and $[(L–L)_2M]^{2+}$ (M = Pd, (L–L) = $CH_2(pz)_2$ (**6**); $CH_2(3,5\text{-}Me_2pz)_2$ (**7**); $(CH_3)_2C(pz)_2$ (**8**); M = Pt, (L–L) = $CH_2(pz)_2$ (**9**); $CH_2(3,5\text{-}Me_2pz)_2$ (**10**) have been prepared and characterized by IR and ^1H NMR spectroscopy. The structures of **3** and **6** have been determined by X-ray diffraction; in both complexes the bis-(pyrazolyl)alkanes act as chelating ligands but the coordination around the palladium atom in the complex **6** is strictly square-planar whereas in **3** it is a slightly distorted towards pyramidal, with a significant Pd · · · H–C agostic interaction. The six-membered rings in both the complexes adopt a boat-type conformation.

Introduction

Although the coordination chemistry of the poly(pyrazolyl)borates has been extensively studied in recent years [1], the behaviour of the isoelectronic but neutral poly(pyrazolyl)alkanes has received little attention [2]; most of the published material concerns first-row transition metals such as vanadium [3], chromium [4], iron [5,6], cobalt [6] and nickel [6–8]. Examples of coordination to metals having the

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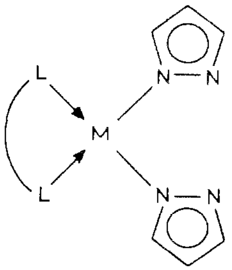
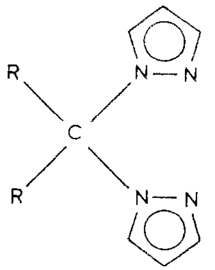
d^8 configuration are rare; they include complexes of rhodium(I) with bis(pyrazolyl)alkanes [9,10] and some derivatives of dimethylgold(III) [11] and methyl [12] or dimethylplatinum(II) [13] with tris(pyrazolyl)alkanes. The interaction of the bis(pyrazolyl)alkanes with palladium(II) and platinum(II) is still largely unexplored; a few cationic allylic complexes of palladium(II), e.g. $[\{R_2C(pz)_2\}Pd(\eta^3\text{-}C_3H_5)]^+$, were described by Trofimenko several years ago [2], and Clark and coworkers reported that no reaction occurs between $Me_2Pt(COD)$ and bis(1-pyrazolyl)methane [14]. (In the presence of iodine the last reaction gives platinum(IV) species.)

Following our previous work on the synthesis of complexes of type I [15] and



(I)

(M = Pd , Pt ;
L–L = neutral ligand)

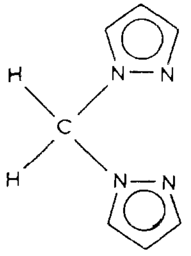


(II , R = H , CH_3)

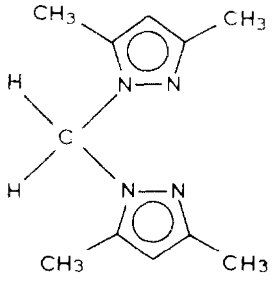
their reactivity as nitrogen ligands [16], we present here the results of an investigation of the coordination behaviour of some bis(pyrazolyl)alkanes (II) towards palladium(II) and platinum(II).

Results and discussion

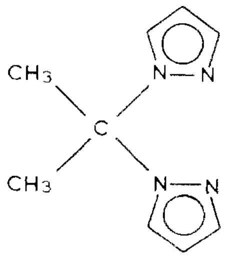
The interaction of the palladium(II) and platinum(II) species with the ligands **A**–**C** (L–L) was investigated in order to evaluate the influence of the CH_3 substituents on the pyrazole ring and on the methylene group. The reactions were carried out with a metal to ligand molar ratio of 1/1 and 1/2 in an attempt to



(A)



(B)



(C)

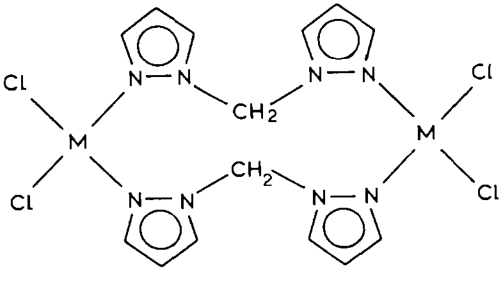
stituents on the pyrazole ring and on the methylene group. The reactions were carried out with a metal to ligand molar ratio of 1/1 and 1/2 in an attempt to obtain two series of complexes, namely the neutral adducts $(L-L)MX_2$ and the ionic species $[(L-L)_2M]^{2+}$.

The 1 : 1 adducts were obtained by reaction 1, which was successfull in all cases but one:

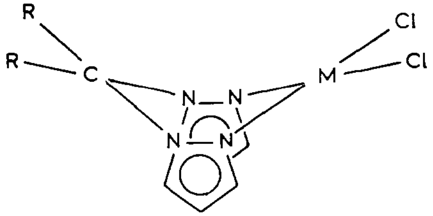
$$(PhCN)_2MCl_2 + (L-L) \rightarrow (L-L)MCl_2 + 2\ PhCN \qquad (1)$$

By this method the three palladium(II) derivatives $(L-L)PdCl_2$ ((L–L) = **A** (**1**); (L–L) = **B** (**2**); (L–L) = **C** (**3**)) were easily isolated. The platinum(II) complexes required somewhat more vigorous conditions, such as reflux in chloroform and a longer reaction time; ligands **A** and **B** gave the expected adducts $(L-L)PtCl_2$ ((L–L) = **A** (**4**); (L–L) = **B** (**5**)), whereas ligand **C** gave a mixture of products from which no pure compound was isolated. Analytical and other evidence shows that at least one of the products is likely to contain a pyrazolato anion, $C_3H_3N_2$, suggesting that cleavage of the ligand occurs.

Poor solubility in most of the usual solvents prevented full characterization of some of the new complexes; when measurements in solution were possible, the adducts were found to be non-electrolytes and monomeric, ruling out ionic isomers such as $[(L-L)_2M][MCl_4]$ and dimeric (or oligomeric) species such as III, which involve an exobidentate behaviour of the ligands. While other formulations cannot be excluded for the insoluble species, on the basis of the available data we suggest that in all the 1 : 1 adducts the bis(pyrazolyl)alkanes act as nitrogen-chelating ligands, IV.



(III)



(IV)

The presence of the chelating system was revealed unambiguously in the case of complex **3** by an X-ray structural determination (see later). The IR spectra of the 1 : 1 adducts show two M–Cl stretching vibrations in the range expected for a *cis*-N_2MCl_2 arrangement (see Table 1). The ^1H NMR data are listed in Table 2.

TABLE 1

ANALYTICAL AND OTHER DATA

Compound	M.p. (°C)	Analyses (Found (calcd.) (%)) C	H	N	IR [b] ν(M–Cl)	Λ_M [c] (Solvent)
(**A**)$PdCl_2$ (**1**)	[a]	25.83	2.54	17.03	335; 345	1.62 $(CH_3)_2CO$
		(25.82)	(2.46)	(17.21)		
(**B**)$PdCl_2$ (**2**)	[a]	34.45	4.09	14.29	330; 350	0.1 (CH_2Cl_2)
		(34.62)	(4.19)	(14.68)		
(**C**)$PdCl_2$ (**3**)	240–241	30.45	3.26	15.78	345	2.1 (CH_2Cl_2)
		(30.57)	(3.39)	(15.85)		
(**A**)$PtCl_2$ (**4**)	[a]	20.89	1.94	13.18	335; 345	9.7 $(CH_3)_2SO$
		(20.29)	(1.93)	(13.52)		
(**B**)$PtCl_2$ (**5**)	[a]	27.72	3.29	11.76	330; 340	0.43 $(CH_3)_2SO$
		(28.08)	(3.40)	(11.91)		
[(**A**)$_2$Pd][BF_4]$_2$ (**6**)	[a]	29.15	2.89	19.83		62 $(CH_3)_2SO$
		(29.16)	(2.77)	(19.44)		
[(**B**)$_2$Pd][BF_4]$_2$ (**7**)	[a]	39.56	4.78	16.44		185 $(CH_3)_2CO$
		(38.37)	(4.65)	(16.28)		
[(**C**)$_2$Pd][BF_4]$_2$ (**8**)	252–254	34.08	3.89	17.86		200 $(CH_3)_2CO$
		(34.17)	(3.79)	(17.72)		
[(**A**)$_2$Pt][BF_4]$_2$ (**9**)	[a]	25.26	2.57	16.65		74 $(CH_3)_2SO$
		(25.27)	(2.40)	(16.84)		
[(**B**)$_2$Pt][BF_4]$_2$ (**10**)	213–215	33.43	4.30	13.66		170 $(CH_3)_2CO$
		(33.99)	(4.12)	(14.42)		

[a] No decomposition is observed up to 280°C. [b] Nujol mull. [c] In ohm^{-1} cm^2 mol^{-1}; ca. 5.10^{-4} *M*.

Although the overall pattern of the spectra is similar to that for the free ligands, upon coordination all the signals shift to lower field, as previously observed for some mercury(II) adducts [17]. The H(3) and H(5) resonances appear as doublets, owing to coupling with H(4). In two adducts, **1** and **3**, a further small coupling is observed (J(H(3)–H(5)) $\simeq$ 0.7–0.8 Hz).

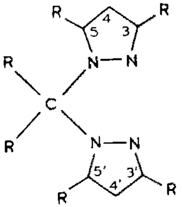
The H(4) resonance appears as a triplet, since J(H(3)–H(4)) $\simeq$ J(H(5)–H(4)) $\simeq$ 2.5 Hz. Assignment of the signals to the 3 and 5 protons, respectively, was possible by comparison with the spectrum of complex **4**, for which the signals flanked by satellites (1/4/1) arising from hydrogen–platinum coupling can be ascribed with certainty to the protons in 3. The value of J(Pt–H) $\simeq$ 5 Hz, is consistent with a spin–spin interaction through three bonds.

In the spectra of the adducts **1** and **4**, at room temperature, the CH_2 protons of the methylene chain appear as a singlet, suggesting that inversion of the metallocycle $M(N–N)_2C$ is fast on the NMR scale. In contrast, when CH_3 substituents are present on the pyrazole rings, i.e. in the adducts of the ligand **B**, **2**, and **5**, the molecules become less flexible and the CH_2 protons display a well resolved AB system at room temperature.

Complex **3**, $PdCl_2\{(CH_3)_2C(pz)_2\}$, in which in the solid state there is a significant interaction between the palladium atom and one hydrogen of a CH_3 group (see later), is fluxional in solution: the CH_3 resonance, observed as a singlet at room temperature (δ 2.76 ppm), splits at low temperature to give at ca. −50°C two sharp signals (δ 3.01 and 2.48 ppm).

TABLE 2

^{1}H NMR DATA ^{a,b}



Compound	Solvent	δ(R(3,3'))	δ(R(5,5'))	δ(R(4,4'))	δ(R)
$CH_2(pz)_2$ (**A**)	$CDCl_3$	7.50(d)[1.60]	7.60(d)[2.40]	6.24(t+s) ^{c}	
$CH_2(pz)_2$ (**A**)	DMSO	7.62(d)	8.05(d)	6.36(t)	6.50(s)
(**A**)$PdCl_2$ (**1**)	$(CD_3)_2CO$	8.09(dd)[2.4;0.7]	8.22(dd)[2.7;0.7]	6.56(t)[2.5]	6.97(s)
(**A**)$PtCl_2$ (**4**)	DMSO	8.04(d)[2.4]	8.26(d)[2.9]	6.59(t)[2.6]	6.78(s)
$[(\mathbf{A})_2Pd][BF_4]_2$ (**6**)	DMSO	7.82(d)[2.3]	8.46(d)[2.6]	6.74(t)[2.5]	7.28(s)
$[(\mathbf{A})_2Pt][BF_4]_2$ (**9**)	DMSO T −30 °C	7.97(d)[2.4]	8.54(d)[2.7]	6.82(t)[2.6]	7.31, 7.02 AB (J_{AB} 14.7)
	T +30 °C	7.92(d)[2.4]	8.49(d)[2.6]	6.78(t)[2.7]	7.23, 7.02
	T +70 °C	7.92(dd)[2.5;0.7]	8.49(dd)[2.8;0.7]	6.77(t)[2.7]	7.13(s)
$CH_2(3,5\text{-}Me_2pz)_2$ (**B**)	$CDCl_3$	2.18(s)	2.41(s)	5.78(s)	6.04(s)
(**B**)$PdCl_2$ (**2**)	CD_2Cl_2	2.31(s)	2.47(s)	5.88(s)	7.34, 5.95 AB (J_{AB} 14.7)
(**B**)$PtCl_2$ (**5**)	DMSO	2.41 ^{c}		6.15(s)	7.06, 6.45 AB (J_{AB} 15.4)
$[(\mathbf{B})_2Pd][BF_4]_2$ (**7**)	CD_2Cl_2	1.96(s)	2.48(s)	6.02(s)	7.43, 6.57 AB (J_{AB} 15.8)
$[(\mathbf{B})_2Pt][BF_4]_2$ (**10**)	$CDCl_3$	2.46 ^{c}		5.89(s)	6.21(s)
$(CH_3)_2C(pz)_2$ (**C**)	CD_2Cl_2	7.37(d)[2.3]	7.52(d)[1.9]	6.2(t)[2.0]	2.23(s)
(**C**)$PdCl_2$ (**3**)	CD_2Cl_2	7.75(dd)[2.9;0.8]	8.19(dd)[2.3;08]	6.43(t)[2.4]	2.76(s)

^{a} Chemical shifts δ (ppm); coupling constants (Hz) in brackets. ^{b} At room temperature unless otherwise stated. ^{c} Unresolved.

Attempts to obtain the 1 : 2 adducts, $[(L–L)_2M]^{2+}$ utilized reactions 2 and 3:

$$(PhCN)_2MCl_2 + 2\,(L–L) + 2\,NaBF_4 \rightarrow \left\{ \begin{array}{l} [(L–L)_2M][BF_4]_2 \\ (M = Pd;\ (L–L) = \mathbf{A}, \mathbf{B}) \\ (L–L)MCl_2 \\ (M = Pd;\ (L–L) = \mathbf{C}; \\ M = Pt;\ (L–L) = \mathbf{A}, \mathbf{B}) \end{array} \right. \tag{2}$$

$$(L–L)MCl_2 + (L–L) + 2\,AgBF_4 \rightarrow \begin{array}{l} [(L–L)_2M][BF_4]_2 \\ (M = Pd;\ (L–L) = \mathbf{C}; \\ M = Pt;\ (L–L) = \mathbf{A}, \mathbf{B}) \end{array} \tag{3}$$

Reaction 2 failed to give the $[(L–L)_2Pt]^{2+}$ species; prior removal of the chloride ligand from the platinum atom by means of silver ions was required to achieve coordination of the second molecule of the chelating ligand.

The preparation of the derivative $[(\mathbf{C})_2Pt]^{2+}$ by reaction 3 was prevented by the non-availability of the required starting material, $(\mathbf{C})PtCl_2$.

The ^1H NMR spectra suggest that the $[(L–L)_2M]^{2+}$ derivatives have high symmetry: thus only one set of signals is observed, consistent with equivalence of the two coordinated bis(pyrazolyl)alkanes. In the spectrum of complex **6**, $[(\mathbf{A})_2Pd]^{2+}$, a singlet resonance for the two methylene protons indicates that a fast exchange process occurs at room temperature. In the analogous platinum derivative, **9**, a broad singlet is observed at high temperature (70°C; DMSO); on cooling the exchange process is slowed down, and at −30°C a well resolved AB resonance is observed. The opposite behaviour is found for complexes **7** and **10** (see Table 2).

Structures in the solid state

The molecular structures of $[PdCl_2\{(CH_3)_2C(pz)_2\}]$ (**3**) and of the $[Pd\{CH_2(pz)_2\}_2]^{2+}$ cation (**6**) are presented in Figs. 1 and 2, respectively. Relevant bond

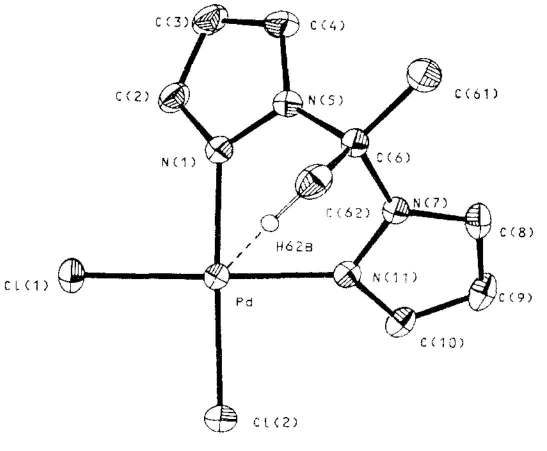


Fig. 1. ORTEP view of complex 3.

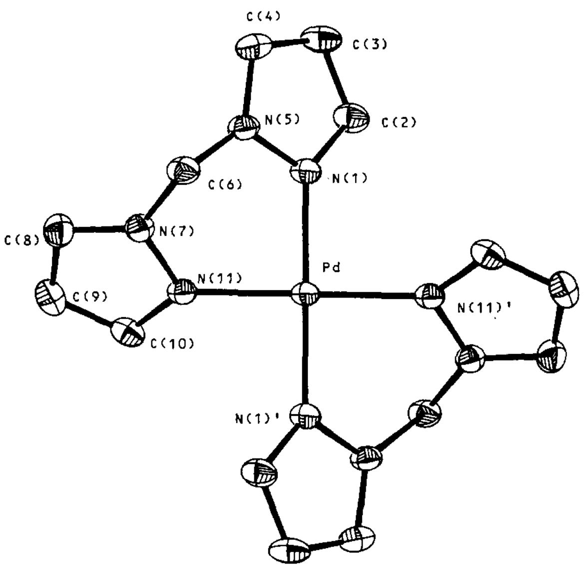


Fig. 2. ORTEP view of complex **6**.

TABLE 3

CRYSTAL DATA AND INTENSITY COLLECTION PARAMETERS FOR COMPOUNDS **3** AND **6**

	3	**6**
Formula	$C_9H_{12}Cl_2N_4Pd$	$C_{14}H_{16}B_2F_8N_8Pd$
FW (amu)	353.5	576.3
Crystal system	orthorhombic	monoclinic
Space group	*Pbca*	$P2_1/n$
a (Å)	12.954(12)	7.031(4)
b (Å)	14.021(3)	9.588(2)
c (Å)	13.909(2)	15.742(5)
β (°)		99.60(2)
U (Å^3)	2526(3)	1046(1)
Z	8	2
$D_{\text{calcd.}}$ (g cm^{-3})	1.859	1.829
μ(Mo-K_α) (cm^{-1})	18.56	9.62
Min. transmission factor	0.77	–
Crystal dimensions (mm)	0.11 × 0.40 × 0.48	0.15 × 0.15 × 0.20
Scan mode	ω	ω
ω-scan width (°)	$1.1 + 0.35\tan\theta$	$1.1 + 0.35\tan\theta$
θ-range (°)	3–25	3–26
Octants of reciprocal space explored	$+h, +k, +l$	$\pm h, +k, +l$
Measured reflections	2207	2047
Unique observed reflections with $I > 3\sigma(I)$	1697	1626
final R and R_w indices [a]	0.021, 0.026	0.038, 0.054
No. of variables	145	178
ESD [b]	0.933	1.628

[a] $R = [\Sigma(F_0 - k|F_c|)/\Sigma F_0]$; $R_w = [\Sigma w(F_0 - k|F_c|)^2/\Sigma wF_0^2]^{1/2}$. [b] ESD $= [\Sigma w(F_0 - k|F_c|)^2/(NO - NV)]^{1/2}$.

TABLE 4

BOND DISTANCES (Å) AND SELECTED ANGLES (°) FOR COMPOUNDS **3** AND **6**

$[PdCl_2\{(CH_3)_2C(pz)_2\}]$ (3)

Pd–Cl(1)	2.297(1)	N(5)–C(6)	1.486(4)
Pd–Cl(2)	2.282(1)	C(6)–N(7)	1.484(4)
Pd–N(1)	2.018(3)	N(7)–C(8)	1.343(4)
Pd–N(11)	2.030(3)	C(8)–C(9)	1.366(5)
N(1)–N(5)	1.364(3)	C(9)–C(10)	1.386(5)
N(1)–C(2)	1.339(4)	C(10)–N(11)	1.330(4)
C(2)–C(3)	1.374(5)	N(11)–N(7)	1.356(3)
C(3)–C(4)	1.359(5)	C(6)–C(61)	1.518(4)
C(4)–N(5)	1.347(4)	C(6)–C(62)	1.523(5)

Cl(1)–Pd–Cl(2)	91.78(3)	N(7)–N(11)–Pd	123.8(1)
Cl(1)–Pd–N(1)	90.76(7)	N(1)–C(2)–C(3)	110.4(3)
Cl(2)–Pd–N(11)	89.61(7)	C(2)–C(3)–C(4)	105.9(3)
N(1)–Pd–N(11)	87.8(1)	C(3)–C(4)–N(5)	108.3(3)
Cl(1)–Pd–N(11)	177.00(7)	C(4)–N(5)–N(1)	109.5(3)
Cl(2)–Pd–N(1)	177.29(7)	N(5)–N(1)–C(2)	105.9(3)
Pd–N(1)–N(5)	122.6(1)	N(7)–C(8)–C(9)	107.8(3)
N(1)–N(5)–C(6)	120.6(2)	C(8)–C(9)–C(10)	105.5(3)
C(4)–N(5)–C(6)	129.9(3)	C(9)–C(10)–N(11)	110.4(3)
N(5)–C(6)–N(7)	106.4(2)	C(10)–N(11)–N(7)	106.1(3)
C(6)–N(7)–N(11)	119.9(2)	N(11)–N(7)–C(8)	110.3(3)
C(8)–N(7)–C(6)	129.8(3)	C(61)–C(6)–C(62)	110.8(3)

$[Pd\{CH_2(pz)_2\}_2][BF_4]_2$ (6)

Pd–N(1)	2.003(2)	N(7)–C(8)	1.351(4)
Pd–N(11)	2.004(3)	C(8)–C(9)	1.364(5)
N(1)–N(5)	1.367(4)	C(9)–C(10)	1.368(5)
N(1)–C(2)	1.321(4)	C(10)–N(11)	1.333(4)
C(2)–C(3)	1.387(5)	N(11)–N(7)	1.359(7)
C(3)–C(4)	1.347(5)	B–F(1)	1.395(5)
C(4)–N(5)	1.340(5)	B–F(2)	1.388(5)
N(5)–C(6)	1.439(4)	B–F(3)	1.356(5)
C(6)–N(7)	1.437(4)	B–F(4)	1.288(5)

N(1)–Pd–N(11)	89.0(1)	C(2)–C(3)–C(4)	106.3(3)
N(1)–Pd–N(11)′	91.0(1)	C(3)–C(4)–N(5)	108.0(3)
Pd–N(1)–N(5)	120.8(2)	C(4)–N(5)–N(1)	109.7(3)
N(1)–N(5)–C(6)	118.8(3)	N(5)–N(1)–C(2)	106.2(3)
C(4)–N(5)–C(6)	131.4(3)	N(7)–C(8)–C(9)	106.6(3)
N(5)–C(6)–N(7)	109.4(3)	C(8)–C(9)–C(10)	106.8(3)
C(6)–N(7)–N(11)	119.0(3)	C(9)–C(10)–N(11)	110.4(3)
C(8)–N(7)–C(6)	130.5(3)	C(10)–N(11)–N(7)	105.7(3)
N(7)–N(11)–Pd	120.6(2)	N(11)–N(7)–C(8)	110.6(3)
N(1)–C(2)–C(3)	109.8(3)		

distances and angles are listed in Table 4. The coordination around the Pd^{II} atom in compound **3** is only slightly distorted towards pyramidal from the ideal square-planar geometry; the distortion is indicated, for instance by the dihedral angle between the Pd, Cl(1), Cl(2) and Pd, N(1), N(11) planes (2.8°), and by the N(1)–Pd–Cl(2) and N(11)–Pd–Cl(1) angles which depart significantly from 180°. In **6** a square-planar

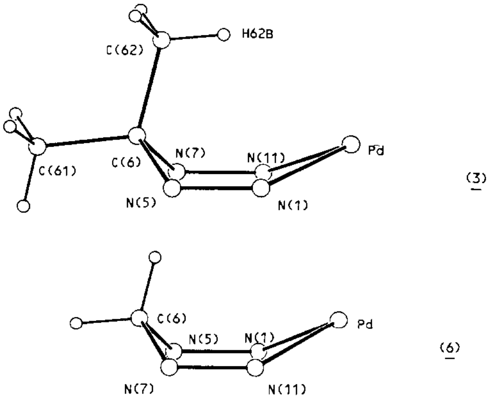


Fig. 3. Comparison of the two boat-type conformations in the complexes **3** and **6**.

geometry is rigorously imposed by the presence of the palladium atom on a crystallographic inversion center. The six-membered chelate rings in both compounds are in a "boat-type" conformation, with only a slight twisting of the N(1)–N(5) with respect to the N(7)–N(11) bond (see Table 5). The conformations of the boats in the two complexes **3** and **6** are significantly different owing to the presence in **3** of an "agostic" [18] intramolecular interaction between the methylic hydrogen H62B and the palladium atom. The value of the Pd ··· H62B distance (2.57 Å) is smaller than the sum of the Van der Waals radii (r_H 1.2, r_{Pd} 1.9 [19] or 1.63 Å [20]) although longer than that in $[Pd(PPh_3)_2Br\{C_4(CO_2Me)_4H\}]$ (2.3 Å [21]). The main structural consequences of this interaction on the conformation of the six-membered rings are the larger dihedral angles in **3** compared with **6** between the "best" plane of atoms N(1), N(11), N(7), N(5) and planes Pd, N(1), N(11) and N(5), C(6), N(7) (Fig. 3). Accordingly the Pd ··· C(6) distance is 3.261(3) in **3** and 3.126(3) Å in **6**. In complex **3** the Pd ··· C(62) distance is 3.296(3) Å and the Pd ··· H62B–C(62) angle is 134°, a value in the range expected for a M ··· H–C interaction [22]. The two Pd–N distances in **3** (2.018(3) and 2.030(3) Å) can be

TABLE 5

CONFORMATIONAL PARAMETERS OF THE SIX-MEMBERED RINGS

Angles between least-squares planes (°)			
Plane 1	Plane 2	**3**	**6**
Pd, N(1), N(11)	N(1), N(11), N(7), N(5)	157.6	153.4
N(5), C(6), N(7)	N(1), N(11), N(7), N(5)	129.7	127.4
Torsional angles (°)		**3**	**6**
Pd–N(11)–N(7)–C(6)		10.3	−11.8
N(11)–N(7)–C(6)–N(5)		−59.8	64.7
N(7)–C(6)–N(5)–N(1)		63.5	−62.3
C(6)–N(5)–N(1)–Pd		−15.9	7.9
N(5)–N(1)–Pd–N(11)		−25.3	31.8
N(1)–Pd–N(11)–N(7)		28.3	−30.0

compared with the values of 2.014(6) and 2.032(6) Å found in $PdCl_2(dpk \cdot H_2O)$ [23], and are significantly longer than the corresponding interactions in **6**, 2.003(2) and 2.004(3) Å. The lengthening in **3** seems not to be due to a different *trans*-influence of the chlorine with respect to the nitrogen-donor ligand but only to packing effects. For $Pd(C_{18}H_{15}N_2)Cl$ [24] we found a distance of 2.008(4) Å for a Pd–N *trans* to a chlorine, and distances as long as 2.023(2) Å in $[Pd(C_{17}H_{24}N_4)]Cl_2 \cdot 3H_2O$ [25] and 2.025(12) Å (average value) in *trans*-(Prazepam)$_2$PdCl$_2$ [26] have been observed even for Pd–N bonds *trans* to nitrogen atoms. Packing effects are also responsible of the different Pd–Cl distances found in **3** (shortest intermolecular contacts H(4) ··· Cl(1), H61A ··· Cl(2), H62A ··· Cl(2) equal to 2.82 Å). No unexpected feature is observed in the structure of the bis(pyrazolyl)alkane ligands, which are comparable in **3** and **6**; a significant difference is found only for the N(5)–C(6) and N(7)–C(6) distances, whose mean values are 1.485(4) in **3** and 1.438(4) Å in **6**. The bond distances and angles within the pyrazolyl rings are consistent with previously reported values [27].

Conclusions

It has been shown that the bis(pyrazolyl)alkanes **A**–**C** can act as endobidentate ligands towards palladium(II) and platinum(II) whether or not CH_3 substituents are present on the heterocyclic rings or on the sp^3-carbon atom of the aliphatic chain. The 1 : 1 and 1 : 2 adducts of the ligands **A** and **B** are thermally very stable, no decomposition being observed up to ca. 280 °C, and are insoluble or only very slightly soluble in most of the usual solvents.

The adducts of the ligands **C** are less easily obtained, and show some peculiar properties, as exemplified, inter alia, by the structure of complex **3**. The presence in **3** of a weak Pd ··· H–C interaction may possibly account for the cleavage of the ligand observed in the reaction with platinum(II) chloride. As far as we know such an interaction is the first to be observed in a complex with pyrazolyl alkanes; M ··· H–C interactions however, have been reported for some bis(pyrazolyl)borate complexes [28]. It is noteworthy that with **3** there is no buckling of the chelate ring as a consequence of the metal–hydrogen interaction [29].

Experimental

The ligands $CH_2(pz)_2$ (**A**), $CH_2(3,5\text{-}Me_2pz)_2$ (**B**) and $(CH_3)_2C(pz)_2$ (**C**) were purchased from Columbia Organic Chemicals and used without further purification.

Analytical and other data are reported in Table 1 and ^1H NMR data in Table 2.

Infrared spectra were recorded with Perkin–Elmer 1310 and 983 photometers using Nujol mulls. ^1H NMR spectra were recorded with a Varian XL 200 and a Bruker instrument operating at 80 MHz.

Synthesis of the adducts (L–L)MCl$_2$

Palladium derivatives: (A)PdCl$_2$ (1), (B)PdCl$_2$ (2), (C)PdCl$_2$ (3). Typically, a solution of the ligand in dichloromethane was added to a solution of $(PhCN)_2PdCl_2$ (ca. 300 mg) (molar ratio 1/1) in the same solvent. The mixture was refluxed for 5–10 h then concentrated to small volume. The first precipitate was filtered off and a second crop obtained from the mother solution by addition of diethyl ether. The combined precipitates were crystallized from CH_2Cl_2/Et_2O to give orange-yellow analytical samples yield ca. 70–80%.

*Platinum derivatives: (A)$PtCl_2$ (4), (**B**)$PtCl_2$ (5).* A solution of the ligand in chloroform was added to a solution of $(PhCN)_2PtCl_2$ (ca. 400 mg) (molar ratio 1/1) in the same solvent, and the mixture was refluxed for 40 h then cooled. The precipitate was filtered off and washed with chloroform and diethyl ether to give the pale-yellow analytical samples, yield 60–70%.

Compounds **4** and **5** are insoluble in most of the usual solvents and slightly soluble in dimethylsulfoxide.

Synthesis of the adducts $[(L-L)_2M][BF_4]_2$

The palladium compounds $[(\mathbf{A})_2Pd][BF_4]_2$ (**6**) and $[(\mathbf{B})_2Pd][BF_4]_2$ (**7**) were prepared by reaction 2.

An acetone solution of $(PhCN)_2PdCl_2$ (ca. 380 mg), the ligand (molar ratio 1/2), and an excess of $NaBF_4$ was refluxed for ca. 20 h. After evaporation of the solvent the residue was taken up in dichloromethane and the solution was filtered then concentrated to small volume. Addition of diethyl ether gave a crude product, which was crystallized from acetone/diethyl ether to give the pale-yellow analytical samples, yield ca. 80%.

The platinum compounds $[(\mathbf{A})_2Pt][BF_4]_2$ (**9**), $[(\mathbf{B})_2Pt][BF_4]_2$ (**10**) and the palladium complex $[(\mathbf{C})_2Pd][BF_4]_2$ (**8**) were prepared by reaction 3. To a methanol suspension of $(L-L)PtCl_2$ (ca. 180 mg) was added a methanol solution of $AgBF_4$ (molar ratio 1/2). The mixture was refluxed for 1 h then cooled. After removal of AgCl, a solution of a second mole of the ligand in methanol was added, and the mixture was refluxed for 1 h.

Compound **9**, which is insoluble in methanol, was filtered off and washed successively with methanol, dichloromethane, and diethyl ether, yield 60%.

Compounds **10** and **8**: The methanol solution was evaporated to dryness and the residue dissolved in dichloromethane. The filtered solution was concentrated to small volume and diethyl ether was added to give **10** or **8**, white, yield 60–70%.

X-ray structure of compounds 3 and 6

Crystal data for compounds **3** and **6** and other experimental details are summarized in Table 3. The reflections were collected on an Enraf–Nonius CAD-4 diffractometer at room temperature with graphite-monochromated Mo-K_α radiation (λ 0.71073 Å) and corrected for Lorentz and polarization. An empirical absorption correction [30] was applied for compound **3**, but no correction was necessary for compound **6** because of the low absorption coefficient and the almost isotropic shape of the crystal. Both structures were solved by Patterson and Fourier techniques and refined by a full matrix least-squares calculation, the minimized function being $\Sigma w[|F_0|-k|F_c|]^2$. Weights assigned to individual observations were $w = 1/(\sigma(F_0))^2$, where $\sigma(F_0)=[\sigma^2(I)+(iI)^2]^{1/2}/2F_0Lp$, and i, the "ignorance factor" equal to 0.04 and 0.06 for **3** and **6**, respectively. A difference Fourier computed before the last cycles of the refinement revealed the positions of all the hydrogen atoms with distances from the corresponding C atoms in the range 0.8–1.1 Å. Nevertheless they were placed in calculated positions (C–H 0.95 Å), and their contribution to the structure factor was included, but they were not refined. All the computations were carried out on a PDP 11/34 computer using the Enraf–Nonius

TABLE 6

FRACTIONAL ATOMIC COORDINATES FOR NON-HYDROGEN ATOMS IN $[PdCl_2\{(CH_3)_2C(pz)_2\}]$ (**3**)

Atom	*x*	*y*	*z*
Pd	0.16208(2)	0.12169(1)	0.02296(2)
Cl(1)	0.33589(6)	0.09400(7)	0.03982(6)
Cl(2)	0.17472(6)	0.12138(6)	−0.14066(6)
N(1)	0.1437(2)	0.1207(2)	0.1671(2)
N(5)	0.0626(2)	0.1642(2)	0.2116(2)
N(7)	−0.0517(2)	0.1832(2)	0.0792(2)
N(11)	0.0070(2)	0.1395(2)	0.0115(2)
C(2)	0.1857(3)	0.0628(2)	0.2328(2)
C(3)	0.1327(3)	0.0690(3)	0.3182(2)
C(4)	0.0559(3)	0.1333(3)	0.3030(2)
C(6)	−0.0016(2)	0.2353(2)	0.1594(2)
C(8)	−0.1523(2)	0.1735(2)	0.0580(2)
C(9)	−0.1596(2)	0.1215(2)	−0.0248(3)
C(10)	−0.0587(2)	0.1010(2)	−0.0508(2)
C(61)	−0.0840(3)	0.2734(3)	0.2269(2)
C(62)	0.0648(3)	0.3162(2)	0.1205(2)

TABLE 7

FRACTIONAL ATOMIC COORDINATES FOR NON-HYDROGEN ATOMS IN $[Pd\{CH_2(pz)_2\}_2][BF_4]_2$ (**6**)

Atom	*x*	*y*	*z*
Pd	0.000	0.000	0.000
F(1)	0.4714(6)	0.4697(4)	0.1936(3)
F(2)	0.5107(5)	0.2616(4)	0.2575(2)
F(3)	0.3186(6)	0.2852(4)	0.1308(2)
F(4)	0.2364(6)	0.3757(7)	0.2494(3)
N(1)	0.2022(4)	0.0577(4)	−0.0687(2)
N(5)	0.2517(5)	−0.0275(3)	−0.1311(2)
N(7)	0.1537(5)	−0.2420(3)	−0.0809(2)
N(11)	0.0802(4)	−0.1989(3)	−0.0108(2)
C(2)	0.3253(6)	0.1629(4)	−0.0612(3)
C(3)	0.4491(6)	0.1485(5)	−0.1207(3)
C(4)	0.3999(6)	0.0282(5)	−0.1629(3)
C(6)	0.1394(6)	−0.1513(4)	−0.1544(2)
C(8)	0.2309(6)	−0.3707(4)	−0.0678(3)
C(9)	0.2047(6)	−0.4107(4)	0.0126(3)
C(10)	0.1140(6)	−0.3025(4)	0.0461(3)
B	0.3755(7)	0.3470(6)	0.2083(3)

Structure Determination Package (SDP) [31]. Scattering factors and anomalous dispersion corrections were taken from Ref. 32. The atomic positional parameters of non-hydrogen atoms for **3** and **6** are listed in Tables 6 and 7, respectively.

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