Interaction of Palladium(II) with Polydentate Ligands, including the Synthesis and Structure† of Bis[tris(pyrazol-1-yl)borato-*N,N'*]palladium(II) and the Cations $[Pd(L)_2]^{2+}$ [L = tris(pyrazol-1-yl)methane-*N,N'* or tris(pyridin-2-yl)methane-*N,N'*]

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Palladium(II) forms the complexes $[Pd\{HB(pz)_3\}_2]$ (**1**), $[Pd\{(py)_3CH\}_2][NO_3]_2$ (**3**), and $[Pd\{(pz)_3CH\}_2]X_2$ [X = NO_3^-, BF_4^- (**2**), or ClO_4^-] on reaction of tetrachloropalladate(II) with tris(pyrazol-1-yl)borate $\{[HB(pz)_3]^-\}$, and removal of chloro-ligands from $[Pd(L)Cl_2]$ {L = tris(pyridin-2-yl)methane [$(py)_3CH$] or tris(pyrazol-1-yl)methane [$(pz)_3CH$]} by AgX followed by addition of a further mole of ligand L. The chloro-complexes $[Pd(L)Cl_2]$ are prepared from $[PdCl_4]^{2-}$ and $(py)_3CH$ in aqueous solution, and from $[Pd(NCPh)_2Cl_2]$ and $(pz)_3CH$ in benzene. *X*-Ray crystallographic studies show that for complexes (**1**)—(**3**) the potentially tridentate ligands are present as *N,N'*-bidentates to give square-planar PdN_4 geometry with a crystallographic centre of symmetry at palladium(II). ^1H N.m.r. spectra are consistent with similar structures in solution, with facile interconversion between co-ordinated and unco-ordinated ring environments. Complex (**3**) crystallises in the monoclinic space group $P2_1/c$, with a = 8.478(1), b = 10.356(3), c = 17.443(4) Å, β = 96.35(2)°, Z = 2; complex (**2**) is isomorphous with (**3**), with a = 8.096(5), b = 10.226(7), c = 16.508(11) Å, β = 99.45(5)°, Z = 2; complex (**1**) crystallises in the triclinic space group $P\bar{1}$, with a = 9.960(2), b = 8.250(2), c = 7.523(2) Å, α = 74.98(2), β = 68.93(2), γ = 89.32(2)°, and Z = 1.

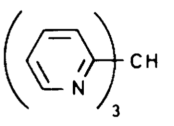
The polydentate ligands (L) tris(pyridin-2-yl)methane [$(py)_3CH$], tris(pyrazol-1-yl)methane [$(pz)_3CH$], and tris(pyrazol-1-yl)borate $\{[HB(pz)_3]^-\}$ are suitable for exploring the tendency of metal ions, which characteristically form square-planar complexes, to extend their co-ordination environment to square pyramidal or octahedral *via* axial interactions. Potential co-ordination modes include tridentate, and bidentate with the third donor group above the metal centre but unco-ordinated or directed away from the metal centre, as illustrated in (I)—(III) for $(pz)_3CH$. Thus, dimethylgold(III) forms complexes $[AuMe_2(L)]NO_3$ which have square-planar geometry, *cis*-AuC_2N_2, with conformations similar to (II) for $(py)_3CH$ (ref. 1) and $[HB(pz)_3]^-$ (ref. 2) but with conformation (I) for $(pz)_3CH$ (ref. 1) having Au $\cdots$ N 3.139(7) Å.

The differences in geometry and basicity offered by these ligands have been utilised to probe the tendency of the square-planar palladium(II) group 'PdN_4' to extend the co-ordination geometry of the metal centre.

Results and Discussion

Preparation and Characterization of Complexes.—The complex $[Pd\{HB(pz)_3\}_2]$ (**1**) was obtained directly by reaction of tetrachloropalladate(II) with tris(pyrazol-1-yl)borate [equation (1)].

$$[PdCl_4]^{2-} + 2[HB(pz)_3]^- \xrightarrow[(ii)\ OH^-]{(i)\ H^+/Cl^-/H_2O} \underset{(\mathbf{1})}{[Pd\{HB(pz)_3\}_2]} + 4Cl^- \quad (1)$$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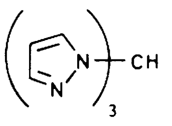
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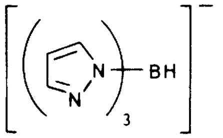
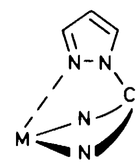
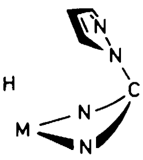
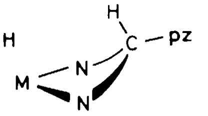

$[HB(pz)_3]^-$


(I)


(II)


(III)

However, a similar approach for tris(pyridin-2-yl)methane gave orange crystals of $[Pd\{(py)_3CH\}Cl_2]$, and subsequent preparations with reactants in equimolar amounts also gave this complex together with red-brown crystals of analytical composition '$Pd_3\{(py)_3CH\}_2Cl_8 \cdot$*ca.*$3H_2O$' from the acidic solution prior to filtration and neutralization. The red-brown crystals have not been further characterized, but presumably involve protonated pyridin-2-yl groups and/or H_3O^+ for charge balance. The complex $[Pd\{(pz)_3CH\}Cl_2]$ was prepared by reaction of $[Pd(NCPh)_2Cl_2]$ with tris(pyrazol-1-yl)methane, and the cations $[Pd(L)_2]^{2+}$ obtained by metathesis reactions [equations (2) and (3)]. For $[Pd\{(pz)_3CH\}_2]^{2+}$ the tetrafluoro-

$$[Pd(L)Cl_2] + 2\,AgX \xrightarrow{H_2O} [Pd(L)]^{n+}(aq.) + 2X^- + 2AgCl \quad (2)$$

$$[Pd(L)]^{n+}(aq.) + 2X^- + L \longrightarrow [Pd(L)_2]X_2 \quad (3)$$

L = $(py)_3CH$, X = NO_3^- (**3**)
L = $(pz)_3CH$, X = NO_3^-, BF_4^- (**2**), or ClO_4^-

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† *Supplementary data available* (No. SUP 56416, 8 pp.): thermal parameters, H-atom parameters, ligand planes. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

Table 1. Analytical and spectroscopic data

Complex	M.p. (decomp.)/°C	Analysis (%)[a]			^{1}H N.m.r.[b]
		C	H	N	
$[Pd\{(py)_3CH\}Cl_2]$	>250	45.0 (45.3)	3.2 (3.1)	9.9[c] (9.9)	*d*
(**3**) $[Pd\{(py)_3CH\}_2][NO_3]_2$[e]	>250	53.0 (53.0)	3.5 (3.6)	15.1 (15.5)	6.94, **2**, CH; 7.6—8.6, **22**, *m*, H(6) for PdN_4 rings and all H(3,4,5); 8.84, **2**, *d*, H(6) for axial rings, J[H(5)H(6)] 5 Hz[f]
$[Pd\{(pz)_3CH\}Cl_2]$	>250	31.0 (30.7)	2.6 (2.6)	20.9[g] (21.5)	*d*
$[Pd\{(pz)_3CH\}_2][NO_3]_2$[h]	183—185	36.2 (36.5)	2.8 (3.1)	30.2 (29.8)	6.6, **6**; 7.66, **6**, *br*; 8.34, **6**; 9.6, **2**, CH[i]
(**2**) $[Pd\{(pz)_3CH\}_2][BF_4]_2$[j]	226—230	34.0 (33.9)	3.3 (2.9)	23.7 (23.7)	*d*
$[Pd\{(pz)_3CH\}_2][ClO_4]_2$[k]	240	32.6 (32.7)	2.9 (2.8)	22.4 (22.9)	*d*
(**1**) $[Pd\{HB(pz)_3\}_2]$	155—160	40.6 (40.6)	3.7 (3.8)	31.3 (31.6)	6.27, **6**, *br*; *ca.* 7.1, **4**, and *ca.* 7.6, **8** *vbr*[l]

[a] Calculated values are given in parentheses. [b] ^{1}H N.m.r. spectra tabulated as chemical shift, **relative intensity**, *multiplicity*, assignment. [c] Cl 17.2 (16.7%). [d] Insufficiently soluble. [e] $\nu(NO_3^-)$ 1 340s vbr cm^{-1}. [f] In D_2O at 15 °C, chemical shifts are in p.p.m. from sodium 4,4-dimethyl-4-silapentanesulphonate. [g] Cl 17.6 (18.1%). [h] $\nu(NO_3^-)$ 1 362s vbr cm^{-1}. [i] In CD_3OD at 40 °C, chemical shifts are in p.p.m. from $SiMe_4$. On lowering of temperature resonances at 6.6 and 8.34 p.p.m. broaden at 15—0 °C, to give, at −20 °C: 6.45, **2**, *br* and 6.68, **4**, *br*; 7.68, **6**; 8.0, **2**, *br* and 8.55, **4**, *br*; 9.61, **2**, CH. [j] $\nu(BF_4^-)$ 1 078, 1 032 cm^{-1} as maxima in broad feature at 1 080—1 020 cm^{-1}. [k] $\nu(ClO_4^-)$ 1 096, 1 074 as maxima in broad feature at 1 080—1 020 cm^{-1}. [l] In $CDCl_3$ at 40 °C, chemical shifts are in p.p.m. from $SiMe_4$. On lowering of temperature resonances at *ca.* 7.1 and 7.6 p.p.m. sharpen and split, to give, at −20 °C: 6.37, **6**; 7.05, **4**; 7.36, **2** and 7.64, **2**, and 7.84, **4**.

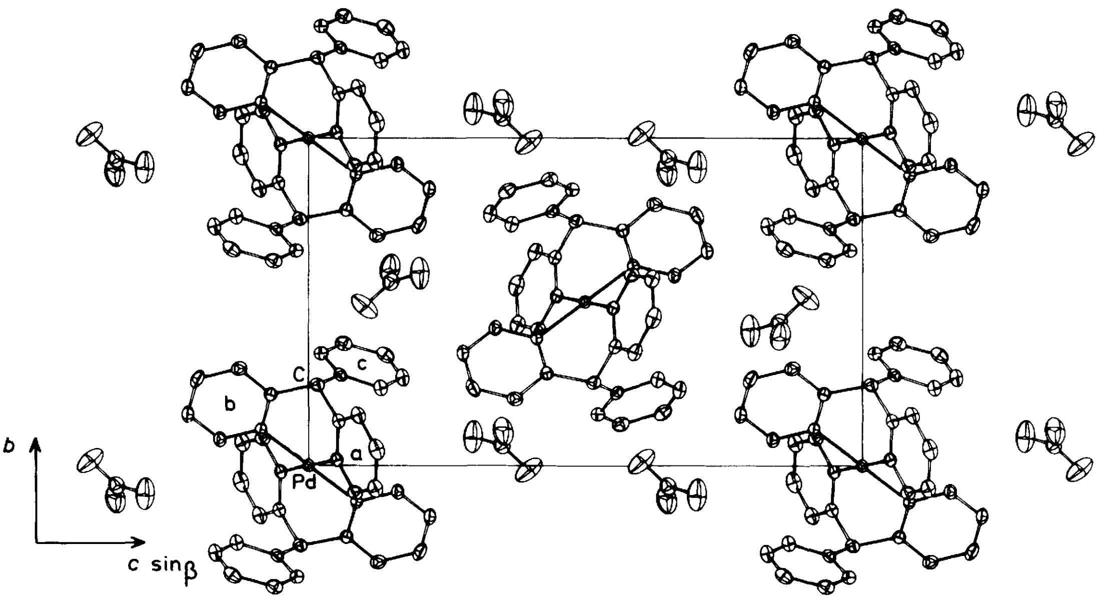

Figure 1. Unit-cell contents of $[Pd\{(py)_3CH\}_2][NO_3]_2$ (**3**), projected down *a*. Non-hydrogen atoms are shown with 20% thermal ellipsoids

borate and perchlorate complexes were prepared owing to the poor crystallinity of the nitrate salt, and the tetrafluoroborate salt (**2**) proved suitable for *X*-ray crystallographic study.

The complexes have appropriate microanalysis, i.r. spectra consistent with the presence of nitrogen donor ligand and ionic oxyanion and tetrafluoroborate groups, and ^{1}H n.m.r. spectra for soluble complexes exhibit resonances for ligand protons (Table 1).

Assignment of resonances to protons H(3), H(4), and H(5) for the $(pz)_3CH$ and $[HB(pz)_3]^-$ complexes has not been attempted, as often noted[3] for complexes of these ligands, and the borate proton is not observed. These complexes exhibit more complex H(3,4,5) resonances at lower temperatures (−20 °C) in CD_3OD and $CDCl_3$, with resonances in the ratio 4:2:6:4:2 [$(pz)_3CH$] and 4:2:2:4:6 {$[HB(pz)_3]^-$}, consistent with the presence of two pyrazole ring environments in the ratio 2:1, *e.g.* for the $(pz)_3CH$ complex 4 H:2 *H*:4 H + 2 *H*:4 H:2 *H*.

Similarly, the $(py)_3CH$ complex in D_2O at ambient temperature exhibits a very complex spectrum consistent with the presence of more than one pyridine ring environment, but ring proton resonances broaden above *ca.* 30 °C to give two very broad resonances at *ca.* 7.8 (6 H) and 8—8.7 (18 H) p.p.m.

Thus, variable-temperature ^{1}H n.m.r. spectra indicate the presence of rapid equilibria between donor ring environments in the expected square-planar PdN_4 group, and unco-ordinated and/or weakly co-ordinated environments.

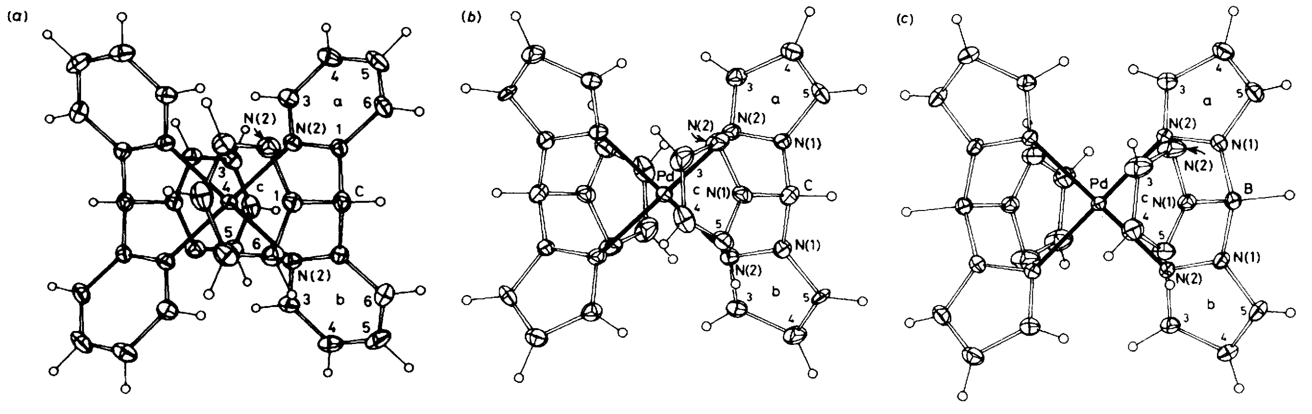

Figure 2. (*a*) The cation $[Pd\{(py)_3CH\}_2]^{2+}$ in its nitrate salt, (**3**), projected normal to the PdN_4 co-ordination plane. Hydrogen atoms are shown with an arbitrary radius of 0.1 Å. (*b*) The cation $[Pd\{(pz)_3CH\}_2]^{2+}$ in its tetrafluoroborate salt, (**2**). (*c*) A single molecule of $[Pd\{HB(pz)_3\}_2]$ (**1**)

Table 2. Geometry for ligands and anions in the complexes; distances (Å) and angles (°)

(*a*) $[Pd\{(py)_3CH\}_2][NO_3]_2$ (**3**)

	Distance for ring			NO_3^-			Angle for ring			Apical carbon and NO_3^-	
	py(a)	py(b)	py(c)								
C–C(1)	1.522(7)	1.506(7)	1.533(6)	N–O(a)	1.219(9)	C–C(1)–N(2)	117.0(4)	116.8(4)	115.9(4)	C(a1)–C–C(b1)	110.0(4)
C(1)–N(2)	1.345(6)	1.355(6)	1.334(6)	N–O(b)	1.192(8)	C–C(1)–C(6)	122.3(5)	122.8(4)	121.4(4)	C(al)–C–C(c1)	111.9(4)
C(1)–C(6)	1.380(7)	1.377(7)	1.370(7)	N–O(c)	1.186(9)	N(2)–C(1)–C(6)	120.7(5)	120.4(4)	122.6(4)	C(b1)–C–C(c1)	113.0(4)
N(2)–C(3)	1.347(6)	1.349(6)	1.346(6)			C(1)–N(2)–C(3)	119.5(4)	119.7(4)	117.1(4)		
C(3)–C(4)	1.373(8)	1.370(7)	1.364(8)			N(2)–C(3)–C(4)	121.8(5)	121.6(5)	123.4(5)	O(a)–N–O(b)	120.5(6)
C(4)–C(5)	1.370(10)	1.369(9)	1.366(8)			C(3)–C(4)–C(5)	118.5(6)	118.7(5)	118.9(5)	O(a)–N–O(c)	118.1(7)
C(5)–C(6)	1.369(9)	1.374(8)	1.382(7)			C(4)–C(5)–C(6)	120.1(5)	120.4(5)	118.5(5)	O(b)–N–O(c)	121.3(7)
						C(1)–C(6)–C(5)	119.4(5)	119.2(5)	119.3(5)		
						Pd–N(2)–C(1)	118.6(3)	118.8(3)			
						Pd–N(2)–C(3)	121.8(3)	121.6(3)			

(*b*) $[Pd\{(pz)_3CH\}_2][BF_4]_2$ (**2**)

	Distance for ring			BF_4^-			Angles for ring			Apical carbon and BF_4^-	
	pz(a)	pz(b)	pz(c)								
C–N(1)	1.46(1)	1.45(1)	1.45(1)	B–F(a)	1.30(2)	C–N(1)–N(2)	120.7(9)	119.5(8)	120.3(10)	N(a1)–C–N(b1)	110.0(9)
N(1)–N(2)	1.34(1)	1.35(1)	1.35(1)	B–F(b)	1.35(2)	C–N(1)–C(5)	129.5(10)	130.6(10)	127.4(10)	N(al)–C–N(c1)	108.0(8)
N(2)–C(3)	1.34(1)	1.32(1)	1.32(2)	B–F(c)	1.37(2)	C(5)–N(1)–N(2)	109.7(9)	109.9(8)	112.0(10)	N(b1)–C–N(c1)	109.7(10)
C(3)–C(4)	1.38(2)	1.42(2)	1.37(2)	B–F(d)	1.35(2)	N(1)–N(2)–C(3)	107.2(9)	105.9(8)	102.5(10)		
C(4)–C(5)	1.35(2)	1.32(2)	1.35(2)			N(2)–C(3)–C(4)	108.5(10)	110.2(10)	113.7(12)	F(a)–B–F(b)	111.7(14)
C(5)–N(1)	1.35(1)	1.35(1)	1.33(2)			C(3)–C(4)–C(5)	106.7(11)	104.9(10)	103.5(13)	F(a)–B–F(c)	106.8(13)
						C(4)–C(5)–N(1)	107.8(10)	109.1(11)	108.1(12)	F(a)–B–F(d)	111.4(12)
						Pd–N(2)–N(1)	120.0(7)	121.1(6)		F(b)–B–F(c)	108.5(11)
						Pd–N(2)–C(3)	132.7(7)	132.8(8)		F(b)–B–F(d)	111.1(12)
										F(c)–B–F(d)	107.1(14)

(*c*) $[Pd\{HB(pz)_3\}_2]$ (**1**)

	Distances for ring				Angles for ring			Apical boron	
	pz(a)	pz(b)	pz(c)						
B–N(1)	1.536(4)	1.554(4)	1.541(4)	B–N(1)–N(2)	122.3(3)	121.9(2)	119.6(3)	N(al)–B–N(b1)	108.8(2)
N(1)–N(2)	1.354(3)	1.362(3)	1.347(3)	B–N(1)–C(5)	129.6(2)	130.7(2)	129.7(2)	N(a1)–B–N(c1)	109.1(2)
N(2)–C(3)	1.340(5)	1.340(4)	1.355(7)	C(5)–N(1)–N(2)	108.1(2)	107.4(2)	110.0(3)	N(b1)–B–N(c1)	108.2(3)
C(3)–C(4)	1.379(5)	1.383(4)	1.355(6)	N(1)–N(2)–C(3)	107.7(3)	108.7(2)	104.7(3)		
C(4)–C(5)	1.371(5)	1.371(5)	1.366(5)	N(2)–C(3)–C(4)	109.8(3)	108.7(3)	111.9(3)		
C(5)–N(1)	1.342(5)	1.345(3)	1.337(6)	C(3)–C(4)–C(5)	104.7(4)	105.6(2)	104.3(4)		
				C(4)–C(5)–N(1)	109.7(3)	109.6(2)	109.1(3)		
				Pd–N(2)–N(1)	121.1(2)	120.6(2)			
				Pd–N(2)–C(3)	131.1(2)	130.7(2)			

Solid-state Structures of $[Pd\{HB(pz)_3\}_2]$ (**1**), $[Pd\{(py)_3CH\}_2][NO_3]_2$ (**3**), and $[Pd\{(pz)_3CH\}_2][BF_4]_2$ (**2**).—Aspects of the molecular geometry of the complexes are given in Tables 2 and 3, and views of the complexes are shown in Figures 1 and 2. The ionic complexes (**2**) and (**3**) are isomorphous (Table 4), and a unit-cell diagram is shown for one of these to illustrate the absence of Pd ··· anion interactions; anion thermal motion is high in consequence.

Table 3. Co-ordination geometry for the palladium atom in complexes $[Pd\{HB(pz)_3\}_2]$ (**1**), $[Pd\{(pz)_3CH\}_2][BF_4]_2$ (**2**), and $[Pd\{(py)_3CH\}_2][NO_3]_2$ (**3**); distances (Å) and angles (°)*

	Complex				Complex		
	(**3**)	(**2**)	(**1**)		(**3**)	(**2**)	(**1**)
Pd–N(a2)	2.029(4)	2.006(9)	2.010(3)	N(a2)–Pd–N(b2)	87.0(1)	87.4(3)	90.1(1)
Pd–N(b2)	2.024(3)	1.987(8)	2.025(2)	N(a2)–Pd–N(b2)^i	93.0(1)	92.6(3)	89.9(1)

* i is the inversion related atom.

The pyridine and pyrazole rings are planar [maximum deviation from mean plane is 0.022 Å for C(4) in ring c of complex (**3**)] with the apical carbon and boron atoms also close to the projected ring planes [maximum deviation 0.199 Å for B from ring c of (**1**)], and the nitrate and tetrafluoroborate ions are regular (within 3σ in bond lengths and angles).

All three complexes have square-planar geometry for the palladium atom, PdN_4, with Pd atoms at crystallographic centres of symmetry. The ligands are present as bidentate *N,N'*-donors with Pd–N 1.987(8)—2.029(4) Å, intraligand N–Pd–N angles 87.0(1)—90.1(1)°, and interligand N–Pd–N angles 89.9(1)—93.0(1)°. The co-ordinated rings are inclined to the PdN_4 plane, with dihedral angles between ring and PdN_4 planes of 44.6° (ring a) and 45.0° (ring b) for complex (**3**), 36.8 and 39.9° for complex (**2**), and 37.2 and 37.6° for complex (**1**). The unco-ordinated rings are above the PdN_4 planes, forming dihedral angles of 45.0 [(**3**)], 51.0 [(**2**)], and 58.1° [(**1**)] with the PdN_4 planes.

The Lewis acidity of the palladium(II) centre in the square-planar PdN_4 kernel is clearly very low toward the nitrogen-donor ligands studied. However, variable-temperature ^1H n.m.r. spectra for complexes of all three ligands indicate facile interconversion of co-ordinated and unco-ordinated environments for the donor rings, consistent with intramolecular processes involving five-co-ordinate intermediates. These intermediates presumably involve more than one co-ordination geometry, although a geometry similar to that of $[AuMe_2\{(pz)_3CH\}]^+$ (ref. 1) may be involved.

Experimental

Preparation and Characterization of Complexes.—Palladium(II) chloride (Matthey-Garrett) and potassium tris(pyrazol-1-yl)borate (Columbia Organic Chemicals Company, Inc.) were used as received, ethanol was distilled, and the ligands tris(pyridin-2-yl)methane and tris(pyrazol-1-yl)methane were prepared as reported.[4,5] ^1H N.m.r. spectra were recorded with a JEOL JNM-4H-100 spectrometer, and i.r. spectra (400—4 000 cm^{-1}) of complexes in Nujol and hexachlorobutadiene mulls between KBr plates were recorded with an Hitachi 270—30 spectrophotometer. Melting points are uncorrected, and microanalyses were by the Australian Microanalytical Service, Melbourne.

Preparation of Complexes.—$[Pd\{HB(pz)_3\}_2]$ (**1**). Potassium tris(pyrazol-1-yl)borate (1.895 g, 7.52 mmol) in water (20 cm^3) was added to a filtered solution obtained by addition of HCl (5 mol dm^{-3}) to palladium(II) chloride (0.635 g, 3.58 mmol) in water (10 cm^3) until the $PdCl_2$ had just dissolved, resulting in a discharge of colour from red-brown to pale yellow and formation of a tan precipitate. The solution was made slightly alkaline (litmus paper) by addition of NaOH solution, and an off-white precipitate was collected and washed with a large quantity of water. The crude product was dried, and recrystallized quickly from boiling ethanol to give pale yellow crystals of $[Pd\{HB(pz)_3\}_2]$ (**1**) on cooling (1.271 g, 67%). I.r.: 3 124m br, 2 440w, 1 504m, 1 402s, 1 322m, 1 284m, 1 234m and 1 222m, 1 202m, 1 126m and 1 114m, 1 078m, 1 062m, 1 034m, 960w, 918w, 770m and 756m and 724s, 654w, 618w cm^{-1}.

$[Pd\{(py)_3CH\}Cl_2]$. Tris(pyridin-2-yl)methane (1.03 g, 4.16 mmol) was dissolved in water (10 cm^3) by the dropwise addition of HCl (5 mol dm^{-3}), filtered, and added to a solution obtained similarly from palladium(II) chloride (0.736 g, 4.15 mmol) in water (10 cm^3) as above. Red-brown crystals formed immediately, and were collected and washed with water 30 min later (0.731 g) [Found: C, 32.9; H, 2.6; Cl, 24.6; N, 7.4. Calc. for '$Pd_3\{(py)_3CH\}_2Cl_8{\cdot}3H_2O$': C, 33.3; H, 3.0; Cl, 24.6; N, 7.3]. I.r.: 3 460w vbr and 3 108m vbr, 1 618w and 1 604w, 1 478w and 1 458w and 1 422w and 1 404s, 1 298w, 1 190w and 1 172w, 788w and 773w and 756m and 720m, 675w, 658w, 642w, 624w, 612w cm^{-1}. The clear orange filtrate was transferred to a sealed chamber, and neutralized by slow transfer of NH_3 (g) from a solution of NH_3 (aq.) resulting in slow discharge of the orange colour and deposition of orange crystals. On clarification of the solution (2—3 h), the crystals of $[Pd\{(py)_3CH\}Cl_2]$ were collected and washed with water (0.591 g, 33%). I.r.: 1 612w, 1 582w and 1 562w, 1 404m br, 1 310vw, 1 152w, 762s and 722s, 630m, 614m cm^{-1}. Continued neutralization of the resultant filtrate, in the same manner, gave crystals of $(py)_3CH$ (0.31 g, 30%).

$[Pd\{(py)_3CH\}_2][NO_3]_2$ (**3**). Silver nitrate (0.471 g, 2.77 mmol) was added to a suspension of $[Pd\{(py)_3CH\}Cl_2]$ (0.591 g, 1.39 mmol) in water (20 cm^3) and stirred in darkness for 2 h, followed by removal of silver chloride to give a bright yellow filtrate. Tris(pyridin-2-yl)methane (0.335 g, 1.36 mmol) was added to the filtrate with stirring, and rapidly dissolved to give a pale yellow solution. The solution was filtered, and allowed to evaporate in a draught to give the crude product as a pale yellow crystalline solid. Recrystallization from water with slow evaporation gave $[Pd\{(py)_3CH\}_2][NO_3]_2$ (**3**) as pale yellow crystals (0.4 g, 41%). I.r.: 3 108w, 3 084w, 2 924w, 1 608m, 1 586m, 1 568m, 1 474m, 1 444m, 1 428m, 1 340s vbr, 1 150m, 1 116w, 1 094w, 1 066w, 1 042w, 992m, 918w, 884w, 830w, 780s, 722s, 690w, 644m, 632m, 498w, 460w cm^{-1}.

$[Pd\{(pz)_3CH\}Cl_2]$. Tris(pyrazol-1-yl)methane (0.542 g, 2.53 mmol) in benzene (30 cm^3) was added to a solution of $[Pd(NCPh)_2Cl_2]$ (0.945 g, 2.47 mmol) in benzene (50 cm^3), and the mixture stirred for 2 h. Orange crystals of $[Pd\{(pz)_3CH\}Cl_2]$ were collected and washed with benzene (0.763 g, 79%). I.r.: 3 112w, 1 514w, 1 458w, 1 402s, 1 300m and 1 282m, 1 218m, and 1 202w, 1 100w and 1 084w and 1 072m, 1 042m, 1 002w, 962w, 916w and 904w, 842m, 812m, 796m, 770m and 756s and 746s, 642w, 608w, 592w cm^{-1}.

$[Pd\{(pz)_3CH\}_2]X_2$ [$X = NO_3$ or BF_4 (**2**)]. These complexes were prepared in a similar manner to $[Pd\{(py)_3CH\}_2][NO_3]_2$ (**3**) using $AgNO_3$ and $AgBF_4$ salts, respectively, giving pale yellow crystals for $X = NO_3$ (62%) (i.r.: 3 132m and 3 100m, 2 964w and 2 920w, 1 516m, 1 470m, *ca.* 1 362s vbr, 1 102m and 1 090m, 1 074m, 1 048m, 1 010w, 960m, 844m, 826w, 804m and 788m and 766s and 722s, 644w, 598m cm^{-1}), and yellow crystals for $X = BF_4$ (58%) [i.r.: 3 152m, 3 016w, 2 724m and 2 672w, 1 516w, 1 462w, 1 414s br, 1 328m, 1 300s and 1 272m and

Table 4. Specific crystallographic details

Complex	$[Pd\{(py)_3CH\}_2][NO_3]_2$ **(3)**	$[Pd\{(pz)_3CH\}_2][BF_4]_2$ **(2)**	$[Pd\{HB(pz)_3\}_2]$ **(1)**
Formula	$C_{32}H_{24}N_8O_6Pd$	$C_{20}H_{20}B_2F_8N_{12}Pd$	$C_{18}H_{20}B_2N_{12}Pd$
M	723.1	708.8	532.8
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$ (C^5_{2h}; no. 14)	$P2_1/c$ (C^5_{2h}; no. 14)	$P\bar{1}$ (C^1_i; no. 2)
a/Å	8.478(1)	8.096(5)	9.960(2)
b/Å	10.356(3)	10.226(7)	8.250(2)
c/Å	17.443(4)	16.508(11)	7.523(2)
$\alpha/^\circ$			74.98(2)
$\beta/^\circ$	96.35(2)	99.45(5)	68.93(2)
$\gamma/^\circ$			89.32(2)
U/Å^3	1 530.2(6)	1 348(1)	554.9(2)
D_m/g cm^{-3}		1.74(1)	1.58(1)
D_c/g cm^{-3}	1.57	1.75	1.59
Z	2	2	1
F(000)	732	704	268
μ/cm^{-1}	7.2	7.8	8.6
Specimen/mm	0.4 × 0.20 × 0.26	0.20 × 0.04 × 0.06	0.22 × 0.08 × 0.25
Transmission factors, min; max	0.86; 0.91	0.95; 0.97	0.84; 0.94
$2\theta_{max.}/^\circ$	50	45	60
N	2 685	1 738	3 017
N_o	2 142	945	2 988
$n\sigma(I)$	$n = 2$	$n = 3$	$n = 3$
R	0.042	0.048	0.029
R'	0.048	0.042	0.020
(x,y,z,U_{iso})	estimated	estimated	(x,y,z) refined; U_{iso} estimated

Table 5. Non-hydrogen atomic co-ordinates for $[Pd\{(py)_3CH\}_2][NO_3]_2$ (**3**)

	Atom	x	y	z
Feature	Pd	0	0	0
$(py)_3CH$	C	−0.188 3(5)	0.246 3(5)	0.016 2(3)
Ring a	C(1)	−0.268 8(5)	0.135 8(5)	0.054 2(3)
	N(2)	−0.202 9(4)	0.018 1(4)	0.050 8(2)
	C(3)	−0.268 8(6)	−0.083 1(5)	0.083 9(3)
	C(4)	−0.402 8(6)	−0.069 9(7)	0.120 8(3)
	C(5)	−0.470 8(6)	0.049 8(7)	0.123 3(3)
	C(6)	−0.404 4(6)	0.153 3(6)	0.090 1(3)
Ring b	C(1)	−0.184 4(5)	0.218 5(5)	−0.068 3(3)
	N(2)	−0.105 3(4)	0.111 0(4)	−0.086 5(2)
	C(3)	−0.098 6(6)	0.080 2(5)	−0.161 2(3)
	C(4)	−0.168 9(6)	0.155 7(6)	−0.219 8(3)
	C(5)	−0.249 0(7)	0.264 1(6)	−0.201 4(3)
	C(6)	−0.257 8(6)	0.296 3(5)	−0.125 6(3)
Ring c	C(1)	−0.024 1(5)	0.276 6(5)	0.058 3(3)
	N(2)	0.001 2(5)	0.237 5(4)	0.131 5(2)
	C(3)	0.141 4(6)	0.268 9(6)	0.171 0(3)
	C(4)	0.255 8(6)	0.337 9(6)	0.140 0(4)
	C(5)	0.231 3(6)	0.372 7(5)	0.064 1(3)
	C(6)	0.087 4(6)	0.342 8(5)	0.022 8(3)
Nitrate	N	0.338 1(6)	0.061 6(6)	0.350 3(3)
	O(a)	0.204 5(8)	0.104 1(7)	0.352 4(3)
	O(b)	0.411 9(7)	0.088 4(8)	0.298 1(3)
	O(c)	0.387 5(8)	−0.013 5(6)	0.398 4(5)

Table 6. Non-hydrogen atomic co-ordinates for $[Pd\{(pz)_3CH\}_2][BF_4]_2$ (**2**)

	Atom	x	y	z
Feature	Pd	0	0	0
$(pz)_3CH$	C	−0.199(1)	0.262 5(11)	−0.004 9(7)
Ring a	N(1)	−0.276(1)	0.160 0(9)	0.037 8(5)
	N(2)	−0.207(1)	0.040 7(8)	0.047 4(5)
	C(3)	−0.298(1)	−0.029 5(11)	0.092 7(6)
	C(4)	−0.426(1)	0.049 0(12)	0.111 8(7)
	C(5)	−0.411(1)	0.165 4(12)	0.075 3(7)
Ring b	N(1)	−0.183(1)	0.219 2(9)	−0.086 6(5)
	N(2)	−0.095(1)	0.108 8(9)	−0.096 1(5)
	C(3)	−0.104(1)	0.092 9(12)	−0.175 8(7)
	C(4)	−0.196(2)	0.196 6(13)	−0.218 7(7)
	C(5)	−0.241(1)	0.271 7(12)	−0.160 7(7)
Ring c	N(1)	−0.035(1)	0.290 2(9)	0.041 7(6)
	N(2)	−0.002(1)	0.264 6(11)	0.122 9(6)
	C(3)	0.150(2)	0.312 5(16)	0.144 2(8)
	C(4)	0.213(2)	0.370 8(13)	0.080 8(10)
	C(5)	0.091(2)	0.352 6(13)	0.015 9(8)
BF_4	B	0.356(2)	0.077(2)	0.363 7(9)
	F(a)	0.316 5(13)	−0.026 7(9)	0.402 2(6)
	F(b)	0.438 8(9)	0.046 0(8)	0.301 5(4)
	F(c)	0.209 0(11)	0.137 3(10)	0.331 2(5)
	F(d)	0.444 6(9)	0.163 1(9)	0.415 9(5)

1 248w, 1 224w, 1 208w, 1 078 and 1 032 as part of strong (broad) absorption at 1 080—950, 846m, 798m, 766s and 722s, 644w, 602m, 520m cm^{-1}].

$[Pd\{(pz)_3CH\}_2][ClO_4]_2$. This complex was prepared in a similar manner to the above complexes, except that an aqueous solution of two equivalents of $AgClO_4$ was generated by addition of standardized perchloric acid to an excess quantity of freshly collected silver(I) oxide followed by filtration. Pale yellow crystals of the complex were collected (75%). I.r.: 3 128m, 2 728w, 1 518w, 1 462w, 1 410s br, 1 326w, 1 300m and 1 268w, 1 224w, 1 206w, 1 096 and 1 074 as part of strong (broad) absorption at 1 080—1 020, 956w, 916w, 846w, 798w, 768s, 722m, 624m, 604w cm^{-1}.

Table 7. Non-hydrogen atomic co-ordinates for $[Pd\{HB(pz)_3\}_2]$ (**1**)

Feature	Atom	x	y	z
	Pd	0	0	0
$[HB(pz)_3]^-$	B	0.278 9(3)	−0.063 6(4)	−0.356 3(5)
Ring a	N(1)	0.133 0(2)	−0.132 3(3)	−0.3463(3)
	N(2)	0.006 3(2)	−0.119 3(3)	−0.204 1(3)
	C(3)	−0.099 7(3)	−0.191 1(4)	−0.235 9(5)
	C(4)	−0.042 1(4)	−0.252 2(4)	−0.399 3(5)
	C(5)	0.104 0(4)	−0.212 0(4)	−0.464 5(5)
Ring b	N(1)	0.269 9(2)	0.122 9(3)	−0.349 2(3)
	N(2)	0.161 2(2)	0.170 6(3)	−0.206 3(3)
	C(3)	0.181 8(3)	0.337 4(3)	−0.236 9(4)
	C(4)	0.305 9(3)	0.399 0(4)	−0.401 8(5)
	C(5)	0.357 6(3)	0.262 1(4)	−0.467 6(5)
Ring c	N(1)	0.309 3(2)	−0.165 6(3)	−0.174 0(3)
	N(2)	0.275 1(3)	−0.333 4(3)	−0.108 2(5)
	C(3)	0.333 5(5)	−0.386 4(4)	0.031 8(6)
	C(4)	0.402 6(4)	−0.257 2(5)	0.054 5(5)
	C(5)	0.384 9(4)	−0.118 3(4)	−0.077 9(5)

Crystallography.—Crystals of complex (**1**) were obtained from ethanol, and (**2**) and (**3**) from water.

Unique data sets were measured to the specified $2\theta_{max.}$ limit at 295 K using a Syntex $P2_1$ four-circle diffractometer fitted with a Mo-K_α radiation source (λ = 0.710 69 Å), and operating in conventional $2\theta/\theta$ scan mode. N independent reflections were obtained, N_o with $n\sigma(I)$ being considered 'observed' and used in the full-matrix least-squares refinement after Gaussian absorption correction. For the non-hydrogen atoms, anisotropic thermal parameters were refined; for the hydrogen atoms the refinement status of (x, y, z, U_{iso}) is shown in Table 4, which gives specific details. Residuals R, R' (statistical weights) at convergence are quoted on $|F|$. Neutral complex scattering factors were used;[6] computation used the XTAL 83 program system [7] implemented on a Perkin-Elmer 3240 computer by S.R. Hall. Atomic co-ordinates are given in Tables 5—7. Complexes (**2**) and (**3**) are isomorphous.

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