Synthetic and *X*-Ray Structural Studies of Complexes formed by Metallation of Tri(1-pyrazolyl)methane by Dimethylplatinum(II) *

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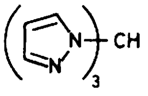
Dimethylplatinum(II) forms a complex [PtMe$_2$(tpzm)] (1) with tri(1-pyrazolyl)methane (tpzm), and on heating in pyridine metallation of one pyrazole ring occurs at C(5) to form [PtMe(tpzm − H)(py)] (2), which has a *cis*-PtC$_2$N$_2$ moiety and tpzm − H present as a bidentate (cyclometallated) ligand with one unco-ordinated pyrazole group to give square-planar co-ordination, Me(py)$\overline{\text{PtCNCNN}}$. Complexes (1) and (2) react with two equivalents of PPh$_3$ in hot pyridine to form [PtMe(tpzm − H)(PPh$_3$)$_2$] (3), which has PPh$_3$ both *cis* and *trans* to the methyl group. On heating slowly to 185 °C complex (3) forms [Pt(tpzm − H){PPh$_2$(C$_6$H$_4$)}] (4), which has PPh$_3$ *ortho*-metallated to give two cyclometallated ligands bound to Pt^{II}, $\overline{\text{NNCNCP}}\overline{\text{tCCP}}$, one forming a six-membered ring and one forming a four-membered ring. Crystal structures of complex (2) and an impurity crystal of [PtMe(tpzm − H)(py)(PPh$_3$)]·2py (5), obtained from a sample of (3), are reported. The latter complex has a *cis*-PtC$_2$NP moiety, with PPh$_3$ *trans* to the methyl group and pyridine *trans* to tpzm − H, which is bound *via* C(5) of a pyrazole ring only. Crystal data: (2), monoclinic, space group $P2_1/n$, a = 15.67(1), b = 9.193(5), c = 12.082(8) Å, β = 90.22(5)°, and Z = 4; (5), triclinic, space group $P\bar{1}$, a = 14.526(9), b = 12.133(7), c = 11.560(6) Å, α = 89.88(5), β = 87.35(5), γ = 87.66(5)°, and Z = 2.

The dimethylplatinum(II) group has the d^8 configuration and is thus expected to form square-planar complexes with little tendency toward higher co-ordination geometry, *e.g.* the complex [PtMe$_2${MeC(CH$_2$PPh$_2$)$_3$}] has the triphosphine present as a bidentate ligand although n.m.r. studies suggest formation of transient five-co-ordinate intermediates in fluxional processes.[1] However, recent synthetic and structural studies show that [Au^{III}Me$_2$]$^+$ forms a complex with tri(1-pyrazolyl]methane (tpzm), [AuMe$_2$(tpzm)]NO$_3$, which has square-planar co-ordination with an additional very weak axial Au ··· N interaction.[2] In view of these results we have studied the interaction of Pt^{II}Me$_2$ with tpzm, as this flexible tripod ligand may encourage five-co-ordination for platinum. A preliminary account of some of this work has been published.[3]



tpzm

Experimental

The ligands tri(1-pyrazolyl)methane (Columbia Organic Chemicals Company) and triphenylphosphine (BDH) were used as received; pyridine was dried and distilled from KOH. Analytical grade solvents were used. Diethyl ether was dried with a column of 4A molecular sieves and stored over sieves, light petroleum (b.p. 40—60 °C) was distilled from sieves and stored over sieves, and benzene was distilled from sodium and stored over sodium.

(Cyclo-octa-1,5-diene)dimethylplatinum(II), [PtMe$_2$(cod)], was prepared from K$_2$[PtCl$_4$] by a reported method,[4] using freshly prepared methyl-lithium and recrystallization from hexane. Microanalyses were by the Australian Microanalytical Service. Infrared spectra of complexes in Nujol mulls were recorded with a Perkin-Elmer 577 spectrophotometer, ^{1}H n.m.r. spectra for solutions in CDCl$_3$ with a JEOL JNM-4H-100 spectrometer, and Raman spectra of crystalline solids with a Cary 82 laser Raman spectrometer using 514.5-nm excitation. Some of the complexes decomposed using the latter and these were satisfactorily re-examined with a Coherent Radiation model 590 dye laser using Rhodamine 6G dye with excitation in the range 580—590 nm. Molecular weights were determined in chloroform at 37 °C and *ca.* 10^{-2} mol dm^{-3} with a Knauer vapour-pressure osmometer.

Preparation of Complexes.—[PtMe$_2$(tpzm)] (1). Tri(1-pyrazolyl)methane (0.637 g, 2.98 mmol) and [PtMe$_2$(cod)] (0.860 g, 2.58 mmol) were refluxed under nitrogen for 30 h. A white solid began to form after about 3 h, and reflux was continued until bumping was difficult to control. The solid was collected by filtration, washed with cold benzene, and dried in a vacuum (0.656 g, 58%), m.p. 170 °C (decomp.) (Found: C, 32.3; H, 3.1; N, 19.0. C$_{12}$H$_{16}$N$_6$Pt requires C, 32.8; H, 3.7; N, 19.1%).

[PtMe(tpzm − H)(py)] (2). Complex (1) (0.103 g, 0.235 mmol) was dissolved in hot pyridine (py) (5 cm^3). The solution was cooled, filtered, and light petroleum (1—2 cm^3) was added. Colourless crystals of (2) were slowly deposited (0.073 g, 62%), m.p. 200 °C (decomp.) (Found: C, 38.5; H, 3.5; N, 19.8. C$_{16}$H$_{17}$N$_7$Pt requires C, 38.3; H, 3.4; N, 19.5%).

[PtMe(tpzm − H)(PPh$_3$)$_2$] (3). Triphenylphosphine (0.316 g, 1.21 mmol) in pyridine (10 cm^3) was added to a solution of complex (1) (0.255 g, 0.58 mmol) in hot pyridine (10 cm^3). The solution was reduced in volume to about 10 cm^3 (vacuum), light petroleum was added until cloudiness developed, and the solution cooled to −20 °C for 24 h. The pale yellow crystals formed were recrystallized from pyridine–light petroleum to

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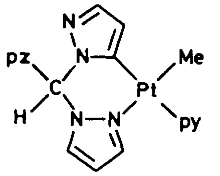
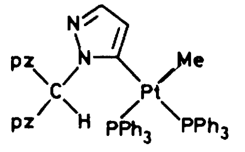
* *Supplementary data available* (No. SUP 23568, 31 pp.): thermal parameters, H-atom co-ordinates, ring geometries and least-squares planes, structure factors. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

give a white product (0.467 g, 85%), m.p. 113—116 °C (Found: C, 59.2; H, 4.6; N, 9.5. $C_{47}H_{42}N_6P_2Pt$ requires C, 59.6; H, 4.5; N, 8.9).

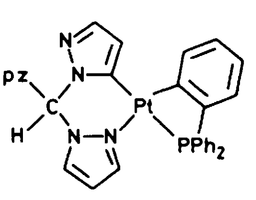
$[Pt(tpzm - H)\{PPh_2(C_6H_4)\}]$ (4). Complex (3) (0.245 g, 9.258 mmol) was placed in a vacuum tube fitted with a cold-finger. The solid was gradually heated over 1 h past its melting point to 185 °C at reduced pressure (0.03 mmHg ≈ 4 Pa) in an oil-bath. After the evolution of gas, on melting a white sublimate (PPh_3, i.r. identification) formed on the cold-finger and the liquid in the tube gradually solidified. The white solid remaining was dissolved in hot benzene, treated with activated charcoal, filtered, and cooled. On addition of a few drops of light petroleum and standing, colourless crystals of the product formed slowly (0.052 g, 30%), m.p. 212—215 °C (Found: C, 50.9; H, 4.0; N, 12.1. $C_{28}H_{23}N_6PPt$ requires C, 50.2; H, 3.5; N, 12.6%).



(2)



(3)



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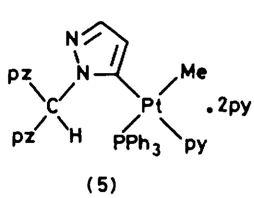
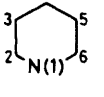
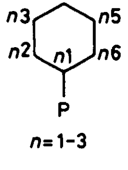
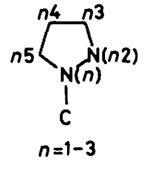


(5)

Crystallography.—Unique data sets were measured within the $2\theta_{max.}$ limits (listed below) using a Syntex $P2_1$ four-circle diffractometer in conventional 2θ—θ scan mode. 2 821 Independent reflections were obtained for complex (2) {5 349 for $[PtMe(tpzm - H)(py)(PPh_3)]\cdot 2py$ (5)}, 2 156 (2) and 4 462 (5) with $I > 2\sigma(I)$ being considered ' observed ' and, after analytical absorption correction, being used in the (basically) 9 × 9 block-diagonal least-squares refinements, after solution of the structures by the heavy-atom method. Non-hydrogen atom thermal parameters were refined in the anisotropic form; after identification of pyrazolyl C and N atoms by consideration of their geometric and thermal parameters and R after interchange of scattering factors, hydrogen atoms (x, y, z, U) were included as estimates. Refinement converged at R, R' = 0.034, 0.039 (2) and 0.036, 0.045 (5), with reflection weights of $[\sigma^2(F_o) + 0.0005(F_o)^2]^{-1}$. Neutral atom scattering factors were used, those for the non-hydrogen atoms being corrected for anomalous dispersion (f',f'').[5-7] Computation used the *X*-RAY 76 program system[8] implemented on a Perkin-Elmer 3240 computer by S. R. Hall. Ligand-atom numbering is as follows. Hydrogen-atom







numbering follows that of the parent atom, except for the methyl hydrogens which are suffixed A, B, C.

In the context of the high thermal motion of the solvent molecules, the possibility remains that identification of the nitrogen may not be unambiguous or that it may be disordered.

Crystal data. (2) $C_{16}H_{17}N_7Pt$, M = 503.5, Monoclinic, space group $P2_1/n$ [C^5_{2h}, no. 14 (variant)], a = 15.67(1), b = 9.193(5), c = 12.082(8) Å, β = 90.22(5)°, U = 1 741(2) Å^3, D_m = 1.89(1), Z = 4, D_c = 1.92 g cm^{-3}, $F(000)$ = 964, monochromatic Mo-K_α radiation, λ = 0.7106_9 Å, μ_{Mo} = 78 cm^{-1}, dimensions of specimen 0.25 × 0.15 × 0.04 mm, $2\theta_{max.}$ = 50°.

(5) $C_{44}H_{42}N_9PPt$, M = 923.0, Triclinic, space group $P\bar{1}$ (C^1_i, no. 2), a = 14.526(9), b = 12.133(7), c = 11.560(6) Å, α = 89.88(5), β = 87.35(5), γ = 87.66(5)°, U = 2 034(2) Å^3, D_m = 1.49(1), Z = 2, D_c = 1.51 g cm^{-3}, $F(000)$ = 924, radiation as above, μ_{Mo} = 34.0 cm^{-1}, dimensions of specimen 0.25 × 0.32 × 0.12 mm, 295(1) K, $2\theta_{max.}$ = 45°.

Results

Preparation and Characterization of Complexes.—The complex $[PtMe_2(tpzm)]$ (1) formed as a white powder on displacement of cyclo-octa-1,5-diene in refluxing benzene [equation (i)]. It is insufficiently soluble in organic solvents for

$$[PtMe_2(cod)] + tpzm \xrightarrow[reflux]{benzene} \underset{(1)}{[PtMe_2(tpzm)]} + cod \quad (i)$$

recrystallization, but has an i.r. spectrum indicating absence of reactants. In an attempt to grow crystals for a structural study the complex was dissolved in hot pyridine. The colourless crystals formed have i.r. and Raman spectra consistent with presence of ' $PtMe_n$,' pyridine, and ' tpzm,' with n = 1 giving best agreement with microanalysis (C, H, N). The complex has bands at 592m (i.r.) and 586s cm^{-1} (Raman) as expected[9] for ν(Pt–Me) mode(s), and the bands of pyridine are shifted in the usual manner[10] observed on co-ordination, *e.g.* absorption at 640 cm^{-1} compared with free pyridine, 601 cm^{-1}.[10] As there was no apparent decomposition during the crystallization from pyridine, *e.g.* to metallic platinum, and only one methyl group remains bonded to platinum, it is assumed that metallation of tpzm had occurred with loss of methane [equation (ii)].

$$\underset{(1)}{[PtMe_2(tpzm)]} \xrightarrow[pyridine]{hot} \underset{(2)}{[PtMe(tpzm - H)(py)]} + MeH \quad (ii)$$

Metallation could possibly occur at either the methine carbon atom or at one of the pyrazole ring-carbon atoms. For the latter case, metallation at C(5) appears most likely, as this allows intramolecular co-ordination of a pyrazole group to give square-planar geometry for Pt^{II} with a *cis*-PtC_2 unit. The complex is insufficiently soluble for ^1H n.m.r. spectroscopy, but Raman spectra indicate that metallation has not occurred at the methine group. Thus, comparison with spectra of pyrazole, substituted pyrazoles, and tpzm allows assignment of ν(C–H) (ring) 3 102—3 112s, ν(C–H) (methine) 2 918w, and ν(C–H) (MePt) 2 826w cm^{-1} for complex (2).

$$\underset{(2)}{[PtMe(tpzm - H)(py)]} + 2PPh_3 \xrightarrow{py} \underset{(3)}{[PtMe(tpzm - H)(PPh_3)_2]} + py \quad (iii)$$

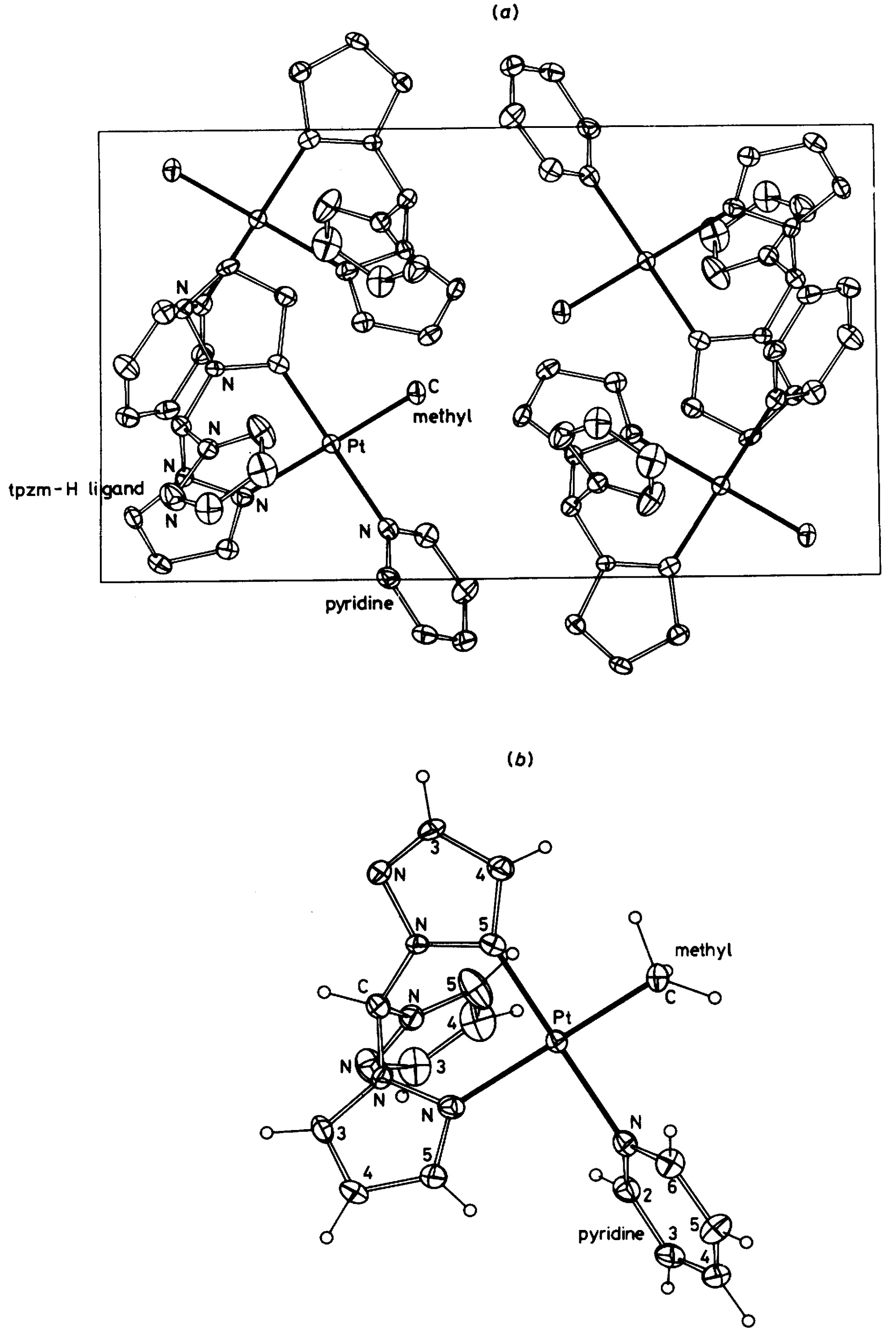


Figure 1. Structure of [PtMe(tpzm − H)(py)] (2): (*a*) unit-cell contents projected down *c*, non-hydrogen atoms being shown with 20% thermal ellipsoids; (*b*) molecular projection normal to the platinum co-ordination plane showing atom labelling. Hydrogen atoms have arbitrary radii of 0.1 Å

A derivative of (2) was prepared by reaction with triphenylphosphine in hot pyridine. Reaction in 1 : 2 mol ratio gave [PtMe(tpzm − H)(PPh_3)$_2$] (3) and this complex can also be conveniently synthesized directly from [PtMe$_2$(tpzm)] (1), equations (iii) and (iv). Complex (3) has molecular weight 905 (calc. 948) in chloroform at 37 °C, and has a ^{1}H n.m.r. spectrum consistent with PPh_3 both *cis* and *trans* to the methyl group as the complex methyl-group resonance centred at 0.11 p.p.m. is very similar to that reported [11] for *cis*-[PtMe$_2$(PPh_3)$_2$]. Phenyl resonances of PPh_3 occur at 6.9—

$$\underset{(1)}{[\mathrm{PtMe_2(tpzm)}]} + 2\mathrm{PPh_3} \xrightarrow{\mathrm{py}} \underset{(3)}{[\mathrm{PtMe(tpzm - H)(PPh_3)_2}]} + \mathrm{MeH} \quad \text{(iv)}$$

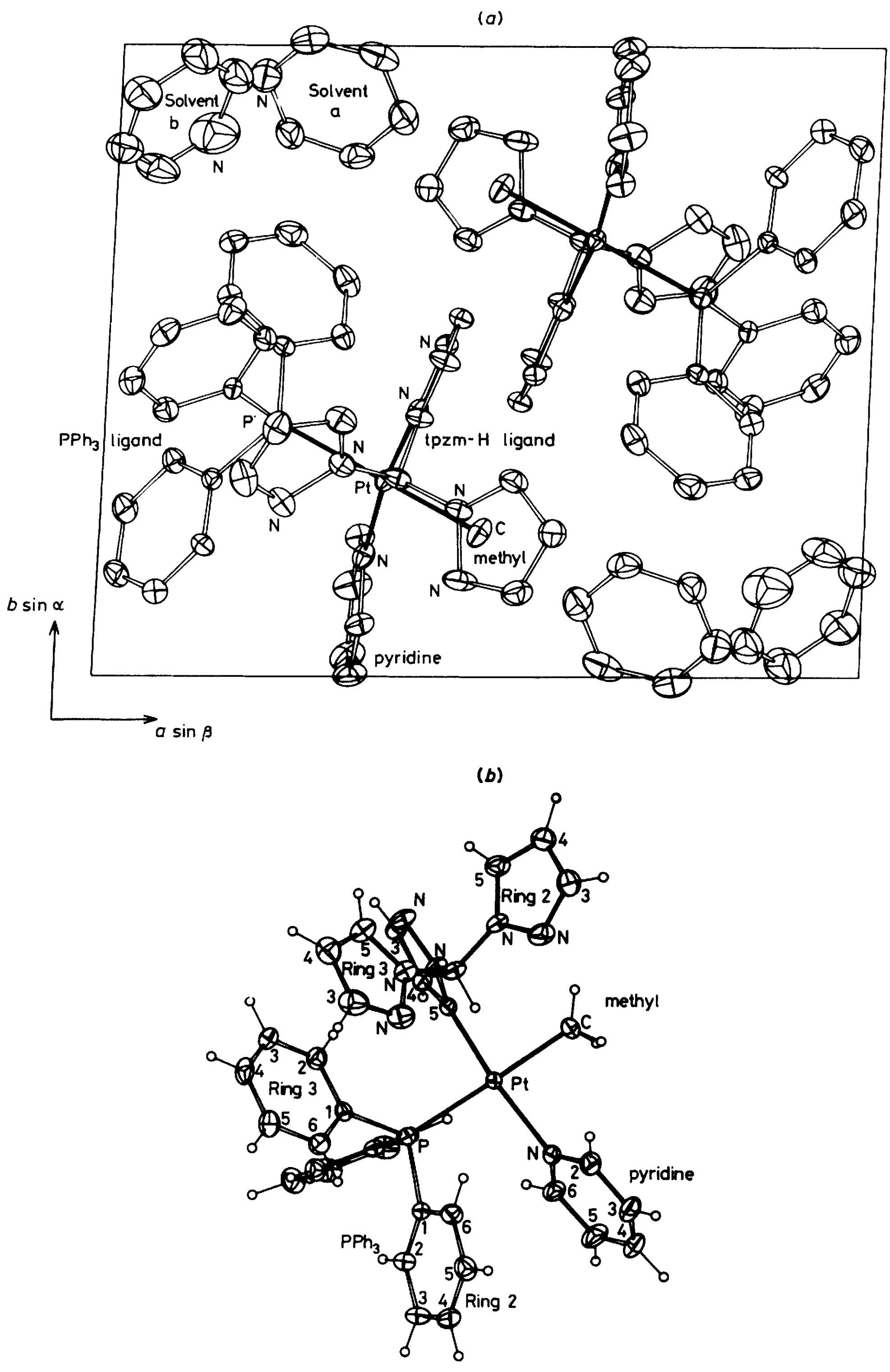


Figure 2. Projections of the structure of [PtMe(tpzm – H)(py)(PPh$_3$)]·2py (5) as in Figure 1

7.5 p.p.m. and evidence for metallation of a pyrazole ring is obtained by observation of a resonance for the methine proton at 8.60 p.p.m., and protons of a metallated ring at 5.40 and 6.17 p.p.m., upfield from resonances of co-ordinated and/or free pyrazole protons, 7.60 and 7.72 p.p.m. With metallation assumed to occur at C(5) (see below) the complex is expected to have a structure involving two unco-ordinated pyrazole rings to give square-planar geometry for platinum.

It was noticed that complex (3) melts at 114—116 °C with evolution of PPh$_3$ (as a sublimate) and a gas, presumably methane, and subsequent experiments led to synthesis of (4) by slow heating of solid (3) to 185 °C in a vacuum. Complex (4) does not contain a methyl group (microanalysis, n.m.r. spectrum), suggesting that a second metallation reaction has occurred. Both i.r. and n.m.r. spectra indicate *ortho*-metallation of PPh$_3$ rather than metallation of a second pyrazole

Table 1. Non-hydrogen atom co-ordinates

Atom	*x*	*y*	*z*
(*a*) Complex (2)			
Pt	0.296 17(2)	0.300 71(3)	0.416 89(3)
(*i*) Methyl ligand			
C	0.406 1(6)	0.412 5(10)	0.439 7(8)
(*ii*) Pyridine ligand			
N(1)	0.368 5(5)	0.111 2(8)	0.391 8(6)
C(2)	0.368 4(6)	0.003 5(10)	0.465 7(8)
C(3)	0.414 6(7)	−0.120 9(10)	0.451 6(10)
C(4)	0.465 6(7)	−0.135 9(11)	0.361 5(12)
C(5)	0.466 6(7)	−0.025 5(12)	0.283 4(9)
C(6)	0.417 8(6)	0.096 0(11)	0.301 9(8)
(*iii*) Tri(1-pyrazolyl)methane ligand			
C	0.103 5(6)	0.343 3(9)	0.524 6(8)
N(11)	0.147 1(4)	0.469 5(6)	0.487 0(6)
N(12)	0.107 5(5)	0.602 6(8)	0.502 4(6)
C(13)	0.165 0(6)	0.694 1(9)	0.463 9(8)
C(14)	0.239 0(6)	0.628 1(10)	0.427 5(8)
C(15)	0.228 9(6)	0.478 2(9)	0.443 2(7)
N(21)	0.107 4(5)	0.229 7(7)	0.442 0(6)
N(22)	0.181 8(5)	0.184 7(7)	0.395 8(6)
C(23)	0.162 1(6)	0.069 7(9)	0.334 6(8)
C(24)	0.075 7(6)	0.039 3(9)	0.342 8(8)
C(25)	0.042 1(6)	0.141 2(10)	0.411 6(8)
N(31)	0.137 9(5)	0.291 8(8)	0.630 3(6)
N(32)	0.092 7(6)	0.186 5(10)	0.681 7(8)
C(33)	0.138 9(9)	0.159 9(14)	0.772 4(10)
C(34)	0.207 5(9)	0.244 3(16)	0.778 3(10)
C(35)	0.206 4(8)	0.329 0(14)	0.685 2(9)
(*b*) Complex (5)			
Pt	0.369 31(2)	0.308 21(3)	0.060 40(3)
(*i*) Methyl ligand			
C	0.496 2(6)	0.226 6(8)	0.082 7(8)
(*ii*) Pyridine ligand			
N(1)	0.346 7(4)	0.189 5(6)	−0.069 1(6)
C(2)	0.346 1(7)	0.081 2(8)	−0.043 0(8)
C(3)	0.336 8(8)	0.002 9(8)	−0.125 2(10)
C(4)	0.332 4(8)	0.031 9(10)	−0.238 8(11)
C(5)	0.334 1(9)	0.143 5(10)	−0.266 0(9)
C(6)	0.340 4(7)	0.219 4(8)	−0.179 8(7)
(*iii*) Triphenylphosphine ligand			
P	0.227 2(1)	0.399 9(2)	0.042 7(2)
C(11)	0.164 3(5)	0.452 8(7)	0.173 7(7)
C(12)	0.203 3(6)	0.532 7(7)	0.239 2(8)
C(13)	0.158 1(7)	0.576 3(8)	0.336 9(9)
C(14)	0.072 6(8)	0.541 8(9)	0.371 5(8)
C(15)	0.032 2(7)	0.464 7(9)	0.308 1(9)
C(16)	0.078 5(6)	0.418 8(7)	0.209 5(8)
C(21)	0.143 8(5)	0.309 8(7)	−0.020 6(7)
C(22)	0.092 6(6)	0.338 5(7)	−0.113 1(7)
C(23)	0.032 2(7)	0.263 5(9)	−0.156 6(9)
C(24)	0.025 7(7)	0.160 4(9)	−0.107 2(10)
C(25)	0.077 3(7)	0.132 3(8)	−0.015 3(10)
C(26)	0.136 2(6)	0.205 9(7)	0.029 0(8)
C(31)	0.228 0(6)	0.520 8(6)	−0.050 5(7)
C(32)	0.305 0(6)	0.535 9(7)	−0.123 7(7)
C(33)	0.306 5(7)	0.624 8(9)	−0.200 8(9)
C(34)	0.230 7(9)	0.699 2(9)	−0.201 1(11)
C(35)	0.155 8(8)	0.686 1(8)	−0.125 5(11)
C(36)	0.154 2(6)	0.599 8(8)	−0.051 7(8)
(*iv*) Tri(1-pyrazolyl)methane ligand			
C	0.385 5(6)	0.311 9(7)	0.357 0(7)
N(11)	0.410 6(5)	0.407 5(5)	0.289 2(6)
N(12)	0.440 0(6)	0.498 6(6)	0.346 4(6)
C(13)	0.458 9(6)	0.566 4(7)	0.259 2(8)
C(14)	0.441 4(6)	0.523 5(7)	0.151 8(7)
C(15)	0.408 3(5)	0.419 6(6)	0.171 2(6)
N(21)	0.468 0(5)	0.262 0(6)	0.408 8(6)
N(22)	0.473 9(7)	0.151 3(6)	0.420 8(8)
C(23)	0.549 1(8)	0.131 8(9)	0.478 5(10)
C(24)	0.591 4(7)	0.226 4(9)	0.504 5(9)
C(25)	0.537 7(7)	0.308 1(8)	0.460 1(9)
N(31)	0.312 2(5)	0.333 3(6)	0.442 2(6)
N(32)	0.236 0(6)	0.273 8(7)	0.439 9(8)
C(26)	0.185 2(8)	0.311 3(12)	0.530 5(11)
C(24)	0.225 1(8)	0.390 6(10)	0.591 4(9)
C(25)	0.308 2(8)	0.403 3(9)	0.533 9(9)
(*v*) Solvent pyridine *a*			
N(1)	0.187 5(7)	0.951 2(10)	0.194 2(10)
C(2)	0.222 5(9)	0.858 9(11)	0.149 3(11)
C(3)	0.311 8(10)	0.823 6(9)	0.151 7(11)
C(4)	0.370 6(9)	0.885 2(13)	0.210 2(13)
C(5)	0.334 3(12)	0.982 8(11)	0.263 2(11)
C(6)	0.242 8(11)	1.008 5(10)	0.251 8(11)
(*vi*) Solvent pyridine *b*			
N(1)	0.123 7(14)	0.858 5(14)	0.492 1(15)
C(2)	0.051 8(14)	0.802 2(12)	0.527 6(16)
C(3)	0.007 0(11)	0.834 0(12)	0.622 0(16)
C(4)	0.027 2(10)	0.921 0(12)	0.681 5(13)
C(5)	0.099 6(11)	0.981 4(12)	0.643 1(15)
C(6)	0.148 3(10)	0.950 0(12)	0.548 5(13)

ring [equation (v)]. With this formulation a molecular weight of 669 is expected, in good agreement with the experimental

$$\underset{(3)}{[\mathrm{PtMe(tpzm - H)(PPh_3)_2}]} \xrightarrow{\text{heat}} \underset{(4)}{[\mathrm{Pt(tpzm - H)\{PPh_2(C_6H_4)\}}]} + \mathrm{PPh_3} + \mathrm{MeH} \quad \text{(v)}$$

value, 688. Two sharp medium-strong absorptions appear at 1 117 and 764 cm^{-1}. The higher-frequency band is likely to be the in-plane C–H deformation associated with an *ortho*-disubstituted benzene nucleus,[12] and the lower band is in the region expected for out-of-plane C–H deformations of a benzene nucleus, as absorptions of this kind have been noted for *ortho*-metallated PPh$_3$ in other complexes.[13,14] The complex gave poor Raman spectra.

In the ^{1}H n.m.r. spectrum of complex (4) the multiplet structure of the phenyl group (7—7.5 p.p.m.) is altered from that of (3), obscuring some resonances of metallated tpzm. The presence of two doublets at 5.45 and 6.18 p.p.m. ($J \approx$ 9 Hz) may be assigned as H(3,4) or H(4,5) for a pyrazole ring metallated at C(5) or C(3), respectively, but are inconsistent with metallation at C(4). Metallation at C(5) is assumed, as for complexes (3) (coupling not resolved for resonances at 5.4 and 6.17 p.p.m.) and (2) (insufficiently soluble).

Table 2. Platinum environment geometries. The first column in the matrix is the platinum–ligand distance (Å); other entries are the angles (°) subtended at the platinum by the relevant atoms. Atoms derived from the pyrazolyl ligand units are italicized

(*a*) Compound (2)

Atom	*r*(Pt–X)	N	*C*	*N*
C	2.024(9)	88.9(3)	90.8(4)	179.1(15)
N	2.102(8)		179.0(4)	91.3(2)
C	1.969(8)			89.0(3)
N	2.100(8)			

(*b*) Compound (5)

Atom	*r*(Pt–X)	P	N	*C*
C	2.083(9)	177.9(7)	87.3(3)	86.8(3)
P	2.322(3)		94.3(2)	91.8(2)
N	2.126(7)			171.9(3)
C	1.981(6)			

For the least-squares plane defined by the platinum and the four other atoms (in the above order) σ (e.s.d of defining atoms) = 0.007 Å, deviations δ = 0.002, 0.004, 0.004, and 0.002, and δPt = −0.013 Å in complex (2); σ = 0.064 Å, δ = 0.061, 0.049, −0.066, and −0.072, and δPt = 0.028 Å in complex (5).

Table 3. Tri(1-pyrazolyl)methane non-hydrogen ligand geometries; distances in Å, angles in degrees

	Complex (2)			Complex (5)		
Ring *n*	1	2	3	1	2	3
C–N(1)	1.42(1)	1.45(1)	1.46(1)	1.45(1)	1.47(1)	1.43(1)
N(1)–N(2)	1.39(1)	1.36(1)	1.35(1)	1.38(1)	1.35(1)	1.35(1)
N(1)–C(5)	1.39(1)	1.36(1)	1.30(1)	1.37(1)	1.34(1)	1.36(1)
N(2)–C(3)	1.32(1)	1.33(1)	1.33(2)	1.33(1)	1.32(2)	1.32(2)
C(3)–C(4)	1.38(1)	1.39(1)	1.33(2)	1.39(1)	1.36(2)	1.36(2)
C(4)–C(5)	1.40(1)	1.36(1)	1.37(2)	1.38(1)	1.35(1)	1.36(2)
N(*n*)–C–N(*n* + 1)	110.3(7)	110.6(7)	111.5(7)	109.7(7)	111.7(7)	114.1(7)
N(2)–N(1)–C	117.5(7)	122.9(7)	116.1(8)	118.5(6)	118.2(7)	118.9(7)
C(5)–N(1)–C	127.8(7)	125.8(8)	131.2(8)	127.1(7)	131.0(7)	129.5(8)
N(2)–N(1)–C(5)	114.5(6)	110.7(7)	112.7(8)	114.4(6)	110.4(8)	111.5(8)
N(1)–N(2)–C(3)	102.0(7)	105.9(7)	103.0(9)	101.8(7)	104.7(8)	103.2(9)
N(2)–C(3)–C(4)	114.1(8)	110.3(8)	111.9(1)	113.5(8)	112.2(9)	114.1(11)
C(3)–C(4)–C(5)	107.0(8)	106.6(8)	106.3(1)	106.8(7)	104.7(10)	104.1(10)
C(4)–C(5)–N(1)	102.3(3)	106.6(8)	106.0(1)	103.4(7)	108.0(9)	107.0(10)
N(1)–N,C–Pt	120.6(6)	121.9(5)		126.2(6)		
C–N,C–Pt	137.1(7)	132.0(6)		130.3(6)		

In view of the novel features present in complexes (2)—(4), in particular the metallation of tpzm, presence of various modes of co-ordination of metallated tpzm involving co-ordinated and unco-ordinated pyrazole rings, and the potential ability of metallated tpzm to encourage five-co-ordination for platinum with a *cis*-PtC_2 moiety, crystallographic studies of suitably crystalline complexes were undertaken.

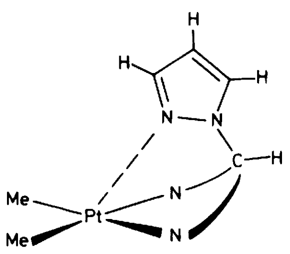
Structures in the Solid State.—A crystal of [PtMe(tpzm − H)(py)] (2) has the expected structure (see diagram above). A suitable crystal from a sample of [PtMe(tpzm − H)-$(PPh_3)_2$] (3) has the constitution [PtMe(tpzm − H)(py)-(PPh_3)]·2py, designated as complex (5), involving 2 mol of pyridine of crystallization per mol of platinum; the solvent molecules have no significant close contacts to the complex.

Aspects of the molecular geometry of complexes (2) and (5) are given in Tables 1—3, and views of the complexes are given in Figures 1 and 2. In both complexes the platinum atom has essentially square-planar geometry with angles 86.8(3)—94.3(2)°, and with atom deviations from the mean planes *cis*-PtC_2N_2 (2) and *cis*-PtC_2NP (5) in the range 0.002—0.0722Å (Table 2). There are one (2) and two (5) unco-ordinated pyrazolyl rings, respectively. This is most clearly seen in Figures 1(*b*) and 2(*a*).

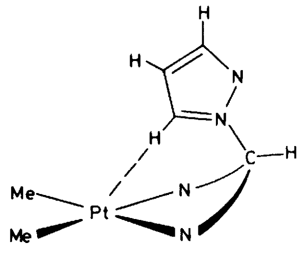
For the metallated pyrazolyl rings in both (2) and (5) the platinum atom is 0.005 Å from the mean plane of the ring, for the pyrazolyl ring co-ordinated *via* N(2) in (2) the platinum atom is 0.107 Å from the mean plane of the ring, and for co-ordinated pyridines the platinum atom is 0.026 [complex (2)] and 0.162 Å [complex (5)] from the mean planes of the rings. The pyrazolyl, pyridine, and phenyl rings are planar in both complexes, with all ring atoms within 0.02 Å of their mean planes.

Discussion

The structural studies confirm that metallation of tri(1-pyrazolyl)methane occurs at C(5) and illustrate the flexibility in co-ordination behaviour of metallated tpzm. In complex (5) two pyrazolyl groups are unco-ordinated, and in (2) intramolecular co-ordination of a pyrazolyl group gives a six-membered ring $\overline{\mathrm{PtCNCNN}}$. *ortho*-Metallation usually results in five-membered ring systems,[13,15] and as for other six-membered ring systems the structure of the ligand precludes five-membered ring formation.[16] Weak axial Pt ··· N interaction similar to that in [$AuMe_2$(tpzm)]NO_3 is not achieved, and hence complexes (1), (3), and (4) are assumed to be square planar [as depicted above for (3) and (4)].



(A)



(B)

Complex (5) was isolated as an impurity crystal in a sample of (3), and its formulation as [PtMe(tpzm − H)(py)(PPh_3)]·

2py suggests that it may be an intermediate in the formation of [PtMe(tpzm − H)(PPh_3)$_2$] (3) from [PtMe(tpzm − H)(py)] (2), involving displacement of a co-ordinated pyrazolyl group *trans* to the methyl group of (2).

Metallation of a pyrazolyl group may occur because co-ordination of two pyrazolyl groups in [$PtMe_2$(tpzm)] (1) allows the third pyrazolyl group to be either weakly axially co-ordinated (A), as in isoelectronic [$AuMe_2$(tpzm)]$^+$,[2] unco-ordinated, or in conformation (B) with the C(5)–H bond adjacent to platinum and thus possibly activated toward metallation with release of methane. Alternatively, an intermediate such as [$PtMe_2$(tpzm)(py)] with two unco-ordinated pyrazolyl groups may react similarly, since the reaction occurs in hot pyridine.

Acknowledgements

We thank the Australian Research Grants Committee for financial support, the University of Tasmania for an honours scholarship (to N. J. M.), and the Education Department of Tasmania for leave of absence (N. J. M.).

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Received 29*th July* 1982; *Paper* 2/1316