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Structural studies of complexes containing cycloplatinated tris(pyrazol-1-yl)methane

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Abstract

Cyclometallation at the C(5) position of one ring of tris(pyrazol-1-yl)methane occurs on dissolution of $PtMe_2\{(pz)_3CH\}$ in 3,5-dimethylpyridine, to form the platinum(II) complex $PtMe\{(pz)_2(C_3H_2N_2)CH-N,C\}(3,5-Me_2py)$ (**1b**). Structural studies of **1b**, and the related complexes $PtMe\{(pz)_2(C_3H_2N_2)CH-N,C\}$(*N*-methylimidazole) (**1c**) and $PtMe\{(pz)_2(C_3H_2N_2)CH-N,C\}\{PPh_2(o\text{-}MeOC_6H_4)\}$ (**1d**) show that these complexes have square planar geometry with *cis*-organic groups, with the cyclometallated group having one pyrazole ring uncoordinated. The complexes $PtMe\{(pz)_2(C_3H_2N_2)CH-C\}(L_2)$ [L_2 = $2PPh_3$ (**2a**), $2PEtPh_2$ (**2b**), $Ph_2PCH_2CH_2PPh_2$ (**2c**)] have a similar geometry at platinum(II); the metallated ligand is present as a $[C]^-$ donor with two uncoordinated pyrazole rings. In **2a**, **2b**, and **2c**, there are short Pt···H contacts at ~ 2.7 Å for the methine proton of the cyclometallated ligand.

Introduction

The tris(pyrazol-1-yl)methane complex $PtMe_2\{(pz)_3CH\}$ undergoes a cyclometallation reaction in pyridine (py) or *N*-methylimidazole (mim), involving loss of methane to form intramolecular coordination complexes $PtMe\{(pz)_2(C_3H_2N_2)CH-N,C\}(L)$ (**1a**, **1c**) [1–4]. The cyclometallation of a pyrazole nitrogen donor ring of $(pz)_3CH$ was first reported [1] soon after the initial recognition that cyclometallation of one of the donor rings of the classical ligand 2,2′-bipyridyl is an important feature of its reactivity [5]. However, for $PtMe_2\{(pz)_3CH\}$ and similar complexes $PtMe_2(L)$ [L = $(pz)_2CH_2$, $(pz)_2CHPh$, $(pz)_2(mim)CH$] [3], the cyclometallation of a potential pyrazole donor ring can occur for polydentate ligands in which the rings are linked by a bridging group (CH, CH_2, or CHPh), rather than linked directly as for the pyridine rings of 2,2′-bipyridyl.

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Table 1

Crystal data and refinement parameters for PtMe{(pz)$_2$(C$_3$H$_2$N$_2$)CH-*N*,*C*}(L) [L = Me$_2$py (**1b**), mim (**1c**), PPh$_2$(*o*-MeOC$_6$H$_4$) (**1d**)], PtMe{(pz)$_2$(C$_3$H$_2$N$_2$)CH-*C*}(L$_2$) [L = PPh$_3$ (**2a**) [a], PPh$_2$Et (**2b**), L$_2$ = Ph$_2$PCH$_2$CH$_2$PPh$_2$ (**2c**)]

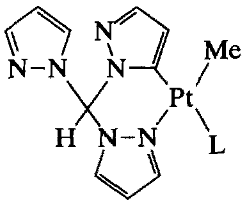
	1b	**1c**	**1d**	**2a** [b]	**2b** [c]	**2c** [d]
Formula	$C_{18}H_{21}N_7Pt$	$C_{15}H_{18}N_8Pt$	$C_{30}H_{29}N_6OPPt$	$C_{47}H_{42}N_6P_2Pt.\frac{1}{2}C_3H_6O$	$C_{39}H_{42}N_6P_2Pt$	$C_{37}H_{36}N_6P_2Pt$
Space group	$P2_1/c$	$P2_1/n$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a, Å	8.031(7)	11.884(4)	9.384(5)	17.28(2)	14.917(5)	16.224(10)
b, Å	10.641(3)	9.368(2)	14.535(5)	12.93(3)	12.178(6)	11.002(13)
c, Å	23.412(15)	15.322(7)	22.043(8)	10.78(1)	11.877(9)	10.959(5)
β, deg	108.70(6)	95.80(3)	110.58(3)	82.60(8)	69.99(5)	107.48(5)
V, Å^3	1895	1697	2815	2267	1870	1701
Z	4	4	4	2	2	2
Mol. wt.	530.5	505.5	715.7	977.0	851.8	821.8
D_{calcd}, g cm^{-3}	1.86	1.98	1.69	1.43	1.51	1.60
Cryst. size, mm	0.50×0.34×0.51	0.30×0.43×0.18	0.29×0.41×0.15	0.04×0.39×0.35	0.48×0.25×0.21	0.08×0.16×0.24
μ, cm^{-1}	71.2	79.6	49.7	30.5	36.9	48.8
$F(000)$	1024	968	1408	980	852	816
$2\theta_{max}$, deg	60	60	50	45	50	40
$A^*_{min,max}$	2.99, 4.61	2.93, 9.08	1.94, 2.52	1.70, 1.99	2.02, 4.28	1.36, 2.21
N	5500	4934	4949	5853	6068	3172
N_o	4266	3916	3812	3228	5412	2161
R	0.052	0.052	0.044	0.093	0.058	0.078
R_w	0.062	0.062	0.050	0.097	0.075	0.087

[a] Crystallizing as a hemi(acetone) solvate. [b] $\alpha = 81.16(13)°$, $\gamma = 73.11(13)°$. [c] $\alpha = 67.99(5)°$, $\gamma = 87.62(3)°$. [d] $\alpha = 112.36(6)°$, $\gamma = 91.88(7)°$.

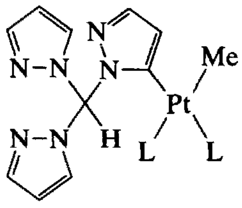
Table 2

Non-hydrogen atom coordinates and equivalent isotropic displacement parameters for $PtMe\{(pz)_2(C_3H_2N_2)CH\text{-}N,C\}(Me_2py)$ (**1b**)

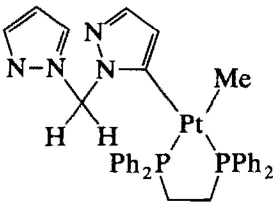
Atom	*x*	*y*	*z*	U_{eq} (Å^2)
Pt	0.31863(4)	0.31478(3)	0.66252(1)	0.0345(1)
C(0)	0.199(1)	0.467(1)	0.6848(5)	0.063(4)
C	0.200(1)	0.1397(8)	0.5398(4)	0.035(3)
N(11)	0.0705(9)	0.1720(7)	0.5654(3)	0.039(2)
N(12)	−0.1000(9)	0.1348(7)	0.5348(3)	0.042(3)
C(13)	−0.191(1)	0.1930(9)	0.5657(5)	0.046(3)
C(14)	−0.083(1)	0.2645(9)	0.6137(4)	0.042(3)
C(15)	0.086(1)	0.2517(8)	0.6132(3)	0.033(3)
N(21)	0.3587(9)	0.0927(6)	0.5847(3)	0.035(2)
N(22)	0.4368(9)	0.1574(7)	0.6376(3)	0.037(2)
C(23)	0.579(1)	0.0898(9)	0.6652(4)	0.044(3)
C(24)	0.595(1)	−0.0142(9)	0.6336(5)	0.049(4)
C(25)	0.451(1)	−0.0106(9)	0.5811(4)	0.044(3)
N(31)	0.2458(9)	0.2457(7)	0.5094(3)	0.037(2)
N(32)	0.371(1)	0.231(1)	0.4830(4)	0.061(4)
C(33)	0.376(2)	0.339(1)	0.4568(6)	0.074(6)
C(34)	0.259(2)	0.423(1)	0.4657(6)	0.077(6)
C(35)	0.176(1)	0.360(1)	0.5001(5)	0.054(4)
N(1)	0.5606(9)	0.3852(7)	0.7186(3)	0.041(3)
C(2)	0.634(1)	0.4860(9)	0.7029(4)	0.045(3)
C(3)	0.786(1)	0.5424(9)	0.7390(4)	0.046(3)
C(31)	0.856(2)	0.659(1)	0.7189(6)	0.063(5)
C(4)	0.866(1)	0.487(1)	0.7952(5)	0.050(4)
C(5)	0.795(1)	0.3842(9)	0.8140(4)	0.045(3)
C(51)	0.878(2)	0.323(1)	0.8736(6)	0.074(5)
C(6)	0.640(1)	0.3350(9)	0.7729(4)	0.046(3)



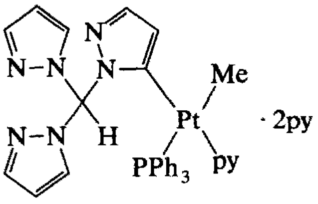
1a: L = py
1b: L = 3,5-Me_2py
1c: L = mim
1d: L = PPh_2(*o*-$MeOC_6H_4$)



2a: L = PPh_3
2b: L = $PEtPh_2$



2c



3

Several phosphine derivatives of **1a** have been reported, including **1d** and **2** [3]. An attempted crystallographic study of **2a** resulted in characterization of an artefact, PtMe{(pz)$_2$(C$_3$H$_2$N$_2$)CH-*C*}(py)(PPh$_3$) · 2py (**3**), probably a consequence of isolation of the triphenylphosphine complex from a pyridine solution [2]. The formulation of complexes **1a,c,d** and **2a–c** has been established from NMR spectroscopic studies [3]; we report here a crystallographic study of complexes **1b–d**, and of complexes containing cycloplatinated (pz)$_3$CH as a unidentate [C]$^-$ ligand (**2a–c**), including the elusive triphenylphosphine complex (**2a**).

Experimental

The complexes **1c**, **1d**, **2a**, **2b** and **2c** were prepared as previously reported [3]. The new complex **1b** was prepared by a procedure similar to that reported for **1a** (Found: C, 41.3; H, 4.0; $C_{18}H_{21}N_7Pt$ calc.: C, 40.8; H, 4.0%).

Crystallography

For each complex a unique data set was measured at 295 K using an Enraf–Nonius CAD-4 diffractometer operating in conventional 2θ-θ scan mode with

Table 3

Non-hydrogen atom coordinates and equivalent isotropic displacement parameters for PtMe{(pz)$_2$(C$_3$H$_2$N$_2$)CH-*N*,*C*}(mim) (**1c**)

Atom	x	y	z	U_{eq} (Å^2)
Pt	0.58330(3)	0.29164(4)	0.70618(2)	0.0325(1)
C(0)	0.5591(9)	0.403(1)	0.5913(6)	0.048(3)
C	0.4726(7)	0.3451(9)	0.8934(6)	0.035(3)
N(11)	0.5194(6)	0.4657(8)	0.8524(5)	0.037(2)
N(12)	0.5170(6)	0.5946(8)	0.8939(5)	0.038(2)
C(13)	0.5642(9)	0.6811(9)	0.8393(7)	0.043(3)
C(14)	0.5940(8)	0.611(1)	0.7656(6)	0.039(3)
C(15)	0.5657(7)	0.4696(9)	0.7727(5)	0.034(3)
N(21)	0.5511(6)	0.2258(8)	0.8968(5)	0.035(2)
N(22)	0.6000(6)	0.1783(8)	0.8256(5)	0.036(2)
C(23)	0.6612(8)	0.065(1)	0.8537(6)	0.042(3)
C(24)	0.6492(8)	0.038(1)	0.9411(6)	0.046(3)
C(25)	0.5791(9)	0.140(1)	0.9668(6)	0.046(3)
N(31)	0.3612(6)	0.3044(8)	0.8527(5)	0.040(2)
N(32)	0.2952(9)	0.227(1)	0.9018(7)	0.064(4)
C(33)	0.206(1)	0.199(1)	0.846(1)	0.073(5)
C(34)	0.214(1)	0.259(2)	0.7660(9)	0.076(5)
C(35)	0.3140(8)	0.321(1)	0.7703(7)	0.060(4)
N(1)	0.6033(6)	0.1056(8)	0.6353(5)	0.037(2)
C(2)	0.6663(8)	0.090(1)	0.5698(7)	0.045(3)
N(3)	0.6577(7)	−0.0431(9)	0.5369(5)	0.050(3)
C(31)	0.711(1)	−0.097(1)	0.4619(8)	0.071(5)
C(4)	0.586(1)	−0.116(1)	0.5841(8)	0.058(4)
C(5)	0.5553(9)	−0.025(1)	0.6448(7)	0.054(4)

monochromatic Mo-K_α radiation (λ 0.7107$_3$ Å), yielding N independent reflections; N_0 with $I > 3\sigma(I)$ were considered 'observed' and used in the full matrix least-squares refinement after analytical absorption corrections, and solution of the structures by vector methods. Residuals R and R_w are quoted on $|F|$ at convergence; statistical weights derived from $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0004\sigma^4(I_{diff})$ were employed. Neutral-atom complex scattering factors were used [6]; computation used the XTAL 3.0 program system implemented by S.R. Hall [7]. Crystal data, coordinates and equivalent isotropic thermal parameters for the nonhydrogen

Table 4

Non-hydrogen atom coordinates and equivalent isotropic displacement parameters for PtMe{(pz)$_2$-(C$_3$H$_2$N$_2$)CH-*N*,*C*}{PPh$_2$(*o*-MeOC$_6$H$_4$)} (**1d**)

Atom	x	y	z	U_{eq} (Å^2)
Pt	0.38625(4)	0.44891(3)	0.72696(2)	0.0351(1)
C(0)	0.543(1)	0.3485(8)	0.7383(5)	0.052(4)
C	0.078(1)	0.4827(7)	0.5993(4)	0.043(4)
N(11)	0.2126(8)	0.4591(5)	0.5870(3)	0.041(3)
N(12)	0.2028(9)	0.4589(6)	0.5243(4)	0.050(3)
C(13)	0.347(1)	0.4471(8)	0.5289(5)	0.051(4)
C(14)	0.445(1)	0.4401(7)	0.5932(5)	0.045(4)
C(15)	0.359(1)	0.4483(6)	0.6324(4)	0.037(3)
N(21)	0.1077(9)	0.5582(6)	0.6463(4)	0.044(3)
N(22)	0.2258(9)	0.5587(6)	0.7027(4)	0.043(3)
C(23)	0.219(1)	0.6401(7)	0.7282(5)	0.055(5)
C(24)	0.099(1)	0.6911(8)	0.6883(7)	0.074(6)
C(25)	0.031(1)	0.6385(8)	0.6365(5)	0.059(5)
N(31)	0.0168(9)	0.4031(6)	0.6241(4)	0.045(3)
N(32)	−0.126(1)	0.4105(7)	0.6244(5)	0.068(4)
C(33)	−0.152(1)	0.3298(9)	0.6462(7)	0.074(6)
C(34)	−0.030(1)	0.2717(8)	0.6599(6)	0.068(6)
C(35)	0.079(1)	0.3207(7)	0.6474(6)	0.061(5)
P(1)	0.4079(3)	0.4451(2)	0.8335(1)	0.0387(9)
C(111)	0.528(1)	0.3571(7)	0.8880(5)	0.043(4)
C(112)	0.487(1)	0.2641(7)	0.8733(5)	0.050(4)
O(112)	0.3575(9)	0.2483(5)	0.8235(4)	0.065(3)
C(1121)	0.319(2)	0.158(1)	0.8019(7)	0.092(7)
C(113)	0.582(1)	0.1969(8)	0.9118(6)	0.064(5)
C(114)	0.711(1)	0.2189(9)	0.9626(6)	0.069(6)
C(115)	0.749(1)	0.3077(9)	0.9779(5)	0.061(5)
C(116)	0.656(1)	0.3773(7)	0.9408(5)	0.048(4)
C(121)	0.231(1)	0.4396(7)	0.8510(4)	0.039(4)
C(122)	0.088(1)	0.4527(7)	0.8018(4)	0.040(3)
C(123)	−0.035(1)	0.4492(9)	0.8168(5)	0.061(5)
C(124)	−0.032(1)	0.4322(9)	0.8770(7)	0.074(6)
C(125)	0.102(1)	0.419(1)	0.9255(6)	0.081(6)
C(126)	0.233(1)	0.4224(9)	0.9125(5)	0.067(5)
C(131)	0.500(1)	0.5511(7)	0.8720(4)	0.042(4)
C(132)	0.449(1)	0.6090(8)	0.9098(5)	0.053(4)
C(133)	0.530(2)	0.6873(8)	0.9365(6)	0.066(5)
C(134)	0.668(2)	0.7070(8)	0.9290(6)	0.070(6)
C(135)	0.716(1)	0.6497(9)	0.8904(6)	0.067(5)
C(136)	0.632(1)	0.5734(7)	0.8612(5)	0.050(4)

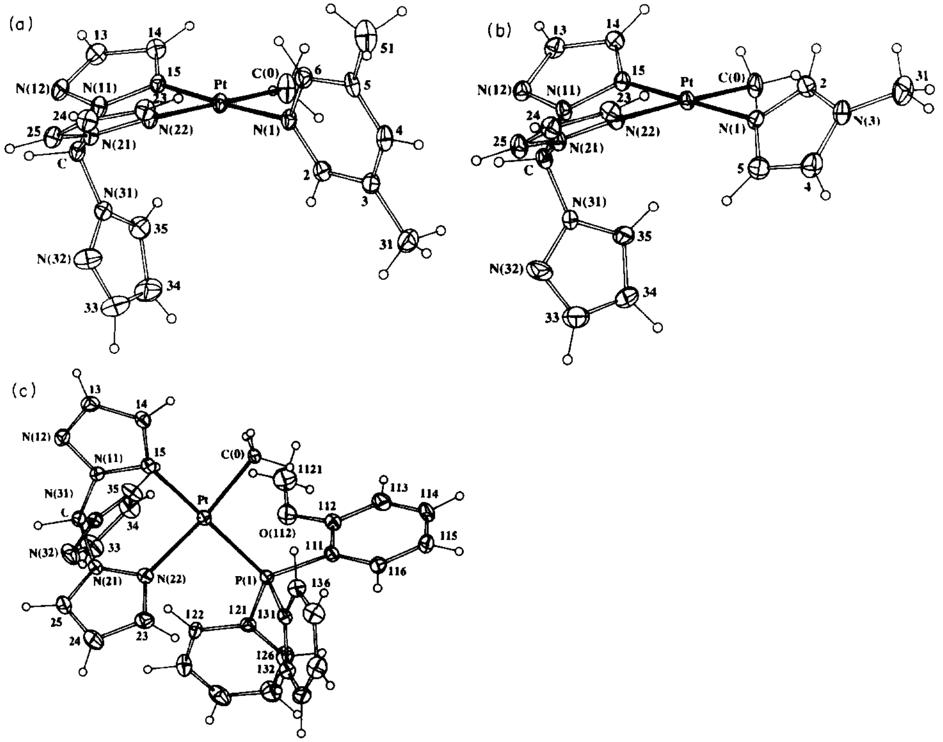


Fig. 1. The molecular structures of complexes in which cyclometallated tris(pyrazol-1-yl)methane acts as a bidentate $[C-N]^-$ group. Hydrogen atoms are shown with an arbitrary radius of 0.1 Å, and 20% thermal ellipsoids are shown for the non-hydrogen atoms. (a) $PtMe\{(pz)_2(C_3H_2N_2)CH-$*N*,*C*$\}(3,5\text{-}Me_2py)$ (**1b**). (b) $PtMe\{(pz)_2(C_3H_2N_2)CH-$*N*,*C*$\}(mim)$ (**1c**), Pt ··· H(35) ~ 2.9 Å. (c) $PtMe\{(pz)_2(C_3H_2N_2)CH-$*N*,*C*$\}\{PPh_2(o\text{-}MeOC_6H_4)\}$ (**1d**), Pt ··· H(35) ~ 3.0 Å.

atoms, and geometries of the cations are given in Tables 1–8, and views of the complexes are shown in Figs. 1 and 2. *

Abnormal features and variations in procedure

The present series of complexes presented collectively an abnormal array of difficulties, some crystals being small, others badly formed and many twinned. Accordingly, suitable caution should be exercised in the use and interpretation of detailed results.

Complex 1c: A significant difference map residue was located ~ 2.5 Å from the platinum atom in the direction of ring 3; when modelled as a nitrogen atom with variable population, the latter refined to a value of ~ 0.3, reducing *R* to 0.046. In view of its implausibility it was not included in the final refinement cycles;

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* Tables of thermal parameters and calculated hydrogen atom positions, and details of ligand geometry, will be deposited at the Cambridge Crystallographic Data Centre, Department of Chemistry, Cambridge CB2 1EW (UK). Any request should be accompanied by a full literature citation for this article. A list of structure factors is available from the authors.

Table 5

Non-hydrogen atom coordinates and isotropic displacement parameters for $PtMe\{(pz)_2(C_3H_2N_2)CH\text{-}C\}(PPh_3)_2 \cdot \frac{1}{2}Me_2CO$ (**2a**)

Atom	x	y	z	U_{iso} (Å^2)
Pt	0.2204(1)	0.2502(1)	0.1178(1)	0.0549(6) [b]
C(0)	0.283(2)	0.182(3)	−0.033(3)	0.11(1)
C	0.164(2)	0.022(2)	0.107(3)	0.065(9)
N(11)	0.113(1)	0.123(2)	0.060(2)	0.057(7)
N(12)	0.045(2)	0.122(2)	0.006(2)	0.073(8)
C(13)	0.012(2)	0.225(3)	−0.031(3)	0.09(1)
C(14)	0.061(2)	0.288(2)	−0.002(3)	0.059(8)
C(15)	0.127(2)	0.227(2)	0.060(2)	0.048(8)
N(21)	0.121(2)	−0.024(2)	0.224(2)	0.075(8)
N(22)	0.153(2)	−0.040(2)	0.333(3)	0.11(1)
C(23)	0.095(3)	−0.073(3)	0.405(4)	0.12(1)
C(24)	0.030(2)	−0.082(3)	0.358(4)	0.11(1)
C(25)	0.044(2)	−0.043(3)	0.230(3)	0.09(1)
N(31)	0.201(2)	−0.061(2)	0.028(2)	0.064(7)
N(32)	0.281(2)	−0.109(3)	0.033(3)	0.13(1)
C(33)	0.298(3)	−0.175(4)	−0.065(4)	0.14(2)
C(34)	0.227(2)	−0.166(3)	−0.114(3)	0.09(1)
C(35)	0.164(2)	−0.095(3)	−0.055(3)	0.09(1)
P(1)	0.3428(6)	0.2632(7)	0.1630(8)	0.073(5)
C(111)	0.417(3)	0.136(3)	0.184(4)	0.12(1)
C(112)	0.399(3)	0.046(4)	0.163(4)	0.14(2)
C(113)	0.454(4)	−0.061(4)	0.182(5)	0.16(2)
C(114)	0.523(3)	−0.065(4)	0.227(4)	0.15(2)
C(115)	0.542(3)	0.019(5)	0.263(5)	0.18(2)
C(116)	0.481(4)	0.123(5)	0.246(5)	0.17(2)
C(121)	0.395(2)	0.337(3)	0.035(3)	0.08(1)
C(122)	0.478(3)	0.306(3)	0.010(4)	0.14(2)
C(123)	0.511(3)	0.371(4)	−0.100(5)	0.15(2)
C(124)	0.457(3)	0.457(3)	−0.161(4)	0.13(1)
C(125)	0.375(3)	0.491(3)	−0.141(4)	0.12(1)
C(126)	0.348(2)	0.421(3)	−0.036(4)	0.11(1)
C(131)	0.352(2)	0.328(3)	0.299(4)	0.10(1)
C(132)	0.350(2)	0.271(3)	0.427(4)	0.12(1)
C(133)	0.348(3)	0.327(4)	0.525(4)	0.13(2)
C(134)	0.358(3)	0.426(4)	0.511(4)	0.14(2)
C(135)	0.362(3)	0.486(4)	0.391(5)	0.14(2)
C(136)	0.359(2)	0.436(3)	0.278(4)	0.12(1)
P(2)	0.1400(5)	0.3262(6)	0.2844(7)	0.056(4) [b]
C(211)	0.149(1)	0.459(2)	0.292(2)	0.031(6)
C(212)	0.161(2)	0.519(3)	0.165(3)	0.08(1)
C(213)	0.176(2)	0.624(3)	0.158(3)	0.08(1)
C(214)	0.170(2)	0.671(3)	0.263(4)	0.11(1)
C(215)	0.153(2)	0.614(3)	0.385(3)	0.10(1)
C(216)	0.147(2)	0.512(3)	0.387(3)	0.08(1)
C(221)	0.034(2)	0.352(2)	0.278(2)	0.045(7)
C(222)	−0.020(2)	0.452(2)	0.251(3)	0.07(1)
C(223)	−0.101(2)	0.469(3)	0.241(3)	0.09(1)
C(224)	−0.135(2)	0.380(3)	0.258(3)	0.09(1)
C(225)	−0.086(2)	0.279(3)	0.284(3)	0.070(9)
C(226)	−0.002(2)	0.264(2)	0.297(3)	0.064(9)
C(231)	0.150(2)	0.248(2)	0.446(3)	0.064(9)
C(232)	0.102(2)	0.293(3)	0.552(3)	0.09(1)

Table 5 (continued)

Atom	x	y	z	U_{iso} (Å^2)
C(233)	0.117(2)	0.226(3)	0.672(3)	0.10(1)
C(234)	0.178(3)	0.135(3)	0.673(4)	0.11(1)
C(235)	0.223(2)	0.084(3)	0.582(4)	0.12(1)
C(236)	0.213(2)	0.146(3)	0.452(3)	0.08(1)
O(01) [a]	0.336(4)	−0.308(6)	0.624(6)	0.23(3)
C(01) [a]	0.367(4)	−0.255(5)	0.552(8)	0.13(3)
C(1) [a]	0.327(5)	−0.195(6)	0.436(7)	0.14(3)
C(2) [a]	0.454(5)	−0.294(8)	0.52(1)	0.23(5)

[a] Site occupancy factor = 0.5. [b] U_{eq}.

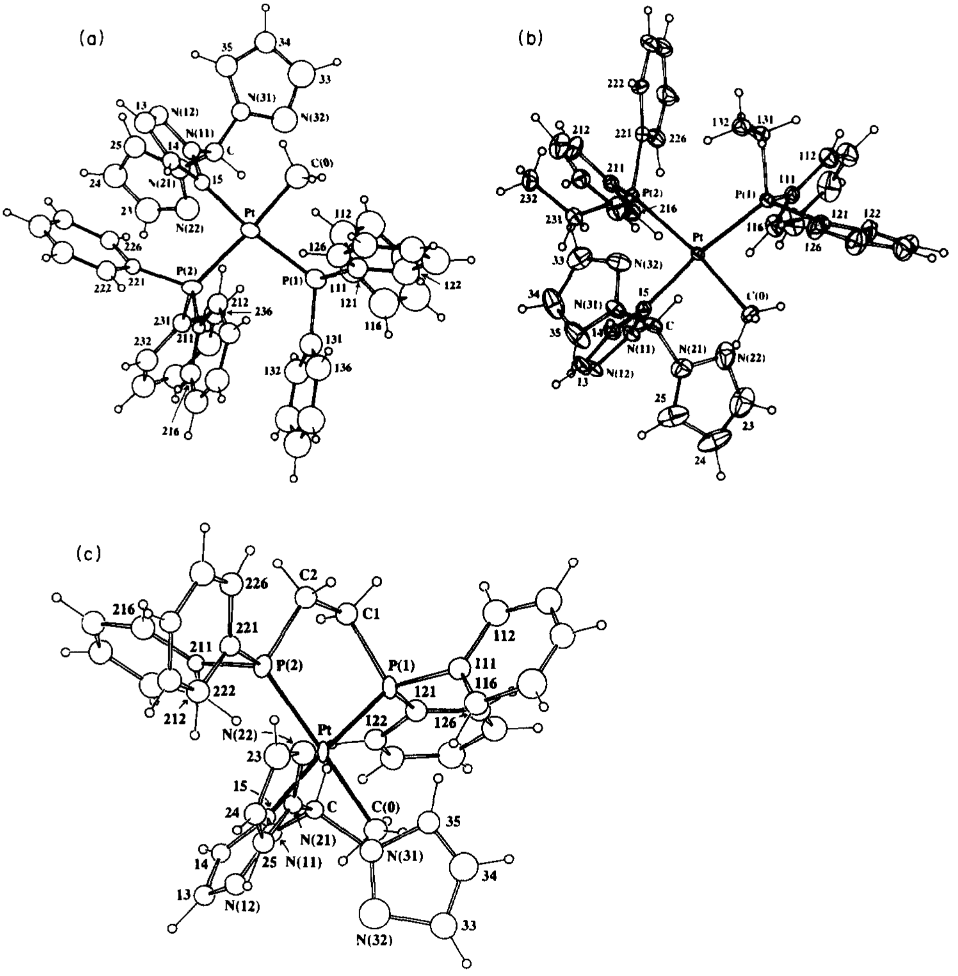

Fig. 2. The molecular structures of complexes in which cyclometallated tris(pyrazol-1-yl)methane acts as a [C]$^-$ group. (a) PtMe{(pz)$_2$(C$_3$H$_2$N$_2$)CH-*C*}(PPh$_3$)$_2$ (**2a**), Pt···HC ~2.7, Pt···H(112) ~2.8, Pt···H(126) ~3.1, Pt···H(212) ~2.9, Pt···H(236) ~3.0 Å. (b) PtMe{(pz)$_2$(C$_3$H$_2$N$_2$)CH-*C*}(PEtPh$_2$)$_2$ (**2b**), Pt···HC ~2.7, Pt···H(116) ~2.9, Pt···H(216) ~2.8 Å. (c) PtMe{(pz)$_2$(C$_3$H$_2$N$_2$)CH-*C*}(PPh$_2$CH$_2$CH$_2$PPh$_2$) (**2c**), Pt···HC ~2.7, Pt···H(116) ~3.1, Pt···H(212) ~3.0 Å.

Table 6

Non-hydrogen atom coordinates and equivalent isotropic displacement parameters for PtMe{(pz)$_2$(C$_3$H$_2$N$_2$)CH–*C*}(PPh$_2$Et)$_2$ (**2b**)

Atom	x	y	z	U_{eq} (Å^2)
Pt	0.19370(3)	0.16257(3)	0.24374(4)	0.0320(2)
C(0)	0.0801(9)	0.194(1)	0.173(1)	0.053(6)
C	0.1398(9)	0.425(1)	0.265(1)	0.050(6)
N(11)	0.0935(7)	0.3215(8)	0.3797(9)	0.046(4)
N(12)	0.0334(8)	0.335(1)	0.489(1)	0.059(5)
C(13)	0.0058(9)	0.223(1)	0.571(1)	0.061(7)
C(14)	0.0454(8)	0.142(1)	0.518(1)	0.048(6)
C(15)	0.1048(7)	0.2066(9)	0.391(1)	0.039(5)
N(21)	0.0741(9)	0.494(1)	0.208(1)	0.068(7)
N(22)	0.109(1)	0.543(1)	0.075(2)	0.11(1)
C(23)	0.036(2)	0.602(2)	0.050(2)	0.12(2)
C(24)	−0.042(2)	0.587(2)	0.156(3)	0.13(1)
C(25)	−0.011(1)	0.521(2)	0.259(2)	0.11(1)
N(31)	0.1983(8)	0.5000(9)	0.290(1)	0.056(5)
N(32)	0.2935(8)	0.511(1)	0.230(1)	0.071(6)
C(33)	0.326(1)	0.581(2)	0.273(2)	0.086(9)
C(34)	0.251(2)	0.616(2)	0.355(2)	0.10(1)
C(35)	0.171(1)	0.563(2)	0.364(2)	0.11(1)
P(1)	0.2806(2)	0.1303(3)	0.0593(3)	0.037(1)
C(111)	0.3330(8)	0.271(1)	−0.079(1)	0.045(5)
C(112)	0.401(1)	0.272(1)	−0.195(1)	0.065(7)
C(113)	0.439(1)	0.381(2)	−0.299(1)	0.079(8)
C(114)	0.410(2)	0.485(2)	−0.285(2)	0.11(1) [a]
C(115)	0.345(1)	0.484(1)	−0.171(2)	0.09(1)
C(116)	0.306(1)	0.376(1)	−0.068(1)	0.065(7)
C(121)	0.2090(8)	0.057(1)	0.001(1)	0.045(6)
C(122)	0.203(1)	0.107(1)	−0.118(1)	0.069(8)
C(123)	0.153(1)	0.044(2)	−0.158(2)	0.08(1)
C(124)	0.111(1)	−0.067(2)	−0.077(2)	0.09(1)
C(125)	0.115(1)	−0.116(2)	0.043(2)	0.09(1)
C(126)	0.164(1)	−0.053(1)	0.083(1)	0.068(8)
C(131)	0.3833(8)	0.042(1)	0.054(1)	0.047(6)
C(132)	0.3618(9)	−0.082(1)	0.160(1)	0.058(6)
P(2)	0.3025(2)	0.1236(2)	0.3510(3)	0.036(1)
C(211)	0.2816(8)	−0.029(1)	0.469(1)	0.044(5)
C(212)	0.337(1)	−0.081(1)	0.544(1)	0.068(8)
C(213)	0.307(1)	−0.198(1)	0.637(2)	0.083(9)
C(214)	0.2199(9)	−0.266(1)	0.662(1)	0.056(3)
C(215)	0.175(1)	−0.211(1)	0.582(1)	0.070(7)
C(216)	0.2012(9)	−0.096(1)	0.490(1)	0.049(6)
C(221)	0.4301(8)	0.155(1)	0.252(1)	0.042(5)
C(222)	0.4982(9)	0.074(1)	0.253(1)	0.052(6)
C(223)	0.594(1)	0.114(2)	0.168(2)	0.076(9)
C(224)	0.620(1)	0.229(2)	0.082(2)	0.074(8)
C(225)	0.550(1)	0.306(1)	0.077(1)	0.072(8)
C(226)	0.4568(9)	0.272(1)	0.161(1)	0.056(6)
C(231)	0.2947(8)	0.215(1)	0.446(1)	0.047(5)
C(232)	0.368(1)	0.208(1)	0.510(1)	0.069(8)

[a] U_{iso}.

Table 7

Non-hydrogen atom coordinates and isotropic displacement parameters for $\mathrm{PtMe\{(pz)_2(C_3H_2N_2)CH}$–$\mathit{C}\mathrm{\}(PPh_2CH_2CH_2PPh_2)}$ (**2c**)

Atom	x	y	z	U_{iso} (Å^2)
Pt	0.2022(1)	0.1510(1)	0.4565(2)	0.0390(6) [a]
C(0)	0.130(2)	0.276(3)	0.385(4)	0.06(1)
C	0.262(2)	0.082(3)	0.175(3)	0.042(9)
N(11)	0.182(2)	0.013(2)	0.153(3)	0.046(7)
N(12)	0.126(2)	−0.065(3)	0.013(3)	0.057(8)
C(13)	0.055(2)	−0.108(3)	0.034(3)	0.05(1)
C(14)	0.067(2)	−0.061(3)	0.176(3)	0.045(9)
C(15)	0.145(2)	0.023(3)	0.249(3)	0.036(9)
N(21)	0.310(2)	0.013(2)	0.093(3)	0.042(7)
N(22)	0.394(2)	0.018(3)	0.154(3)	0.07(1)
C(23)	0.426(3)	−0.058(4)	0.062(4)	0.09(1)
C(24)	0.363(2)	−0.103(3)	−0.066(4)	0.06(1)
C(25)	0.290(2)	−0.060(3)	−0.043(4)	0.06(1)
N(31)	0.247(2)	0.206(3)	0.146(3)	0.065(9)
N(32)	0.176(3)	0.223(4)	0.050(4)	0.12(1)
C(33)	0.200(3)	0.370(4)	0.079(4)	0.09(1)
C(34)	0.274(3)	0.403(5)	0.190(5)	0.10(2)
C(35)	0.305(2)	0.322(4)	0.238(4)	0.06(1)
P(1)	0.2552(6)	0.3023(8)	0.681(1)	0.046(5) [a]
C(111)	0.346(2)	0.430(3)	0.714(4)	0.06(1)
C(112)	0.401(3)	0.509(4)	0.864(4)	0.08(1)
C(113)	0.470(3)	0.603(4)	0.880(4)	0.09(1)
C(114)	0.482(3)	0.617(4)	0.774(4)	0.08(1)
C(115)	0.438(3)	0.550(5)	0.639(5)	0.11(2)
C(116)	0.361(2)	0.450(4)	0.608(4)	0.07(1)
C(121)	0.180(2)	0.390(3)	0.752(3)	0.06(1)
C(122)	0.096(2)	0.323(3)	0.718(3)	0.06(1)
C(123)	0.035(2)	0.384(4)	0.772(4)	0.07(1)
C(124)	0.048(3)	0.517(4)	0.850(4)	0.09(1)
C(125)	0.128(3)	0.588(4)	0.881(4)	0.08(1)
C(126)	0.191(2)	0.531(3)	0.829(3)	0.06(1)
C(1)	0.300(2)	0.209(3)	0.786(3)	0.06(1)
C(2)	0.345(2)	0.100(3)	0.716(3)	0.06(1)
P(2)	0.2749(6)	0.0073(9)	0.536(1)	0.049(5) [a]
C(211)	0.200(2)	−0.112(3)	0.555(3)	0.034(8)
C(212)	0.123(2)	−0.079(3)	0.577(3)	0.05(1)
C(213)	0.071(3)	−0.160(4)	0.606(4)	0.08(1)
C(214)	0.096(2)	−0.280(4)	0.600(4)	0.07(1)
C(215)	0.168(3)	−0.319(4)	0.580(4)	0.07(1)
C(216)	0.227(2)	−0.231(4)	0.554(4)	0.07(1)
C(221)	0.344(2)	−0.094(3)	0.453(4)	0.05(1)
C(222)	0.312(2)	−0.167(3)	0.313(4)	0.06(1)
C(223)	0.361(3)	−0.250(4)	0.238(4)	0.07(1)
C(224)	0.439(2)	−0.263(3)	0.312(4)	0.06(1)
C(225)	0.475(3)	−0.192(4)	0.456(4)	0.07(1)
C(226)	0.427(2)	−0.107(3)	0.531(4)	0.06(1)

[a] U_{eq}.

Table 8

Coordination geometry for the complexes (distances in Å, angles in degrees)

$\mathrm{PtMe\{(pz)_2(C_3H_2N_2)CH\text{-}}N,C\}(\mathrm{L})$	L = 3,5-$\mathrm{Me_2py}$ (**1b**)	L = mim (**1c**)
Pt–C(0.15)	2.03(1), 1.973(7)	2.041(9), 1.975(9)
Pt–N(1,22)	2.104(7), 2.099(7)	2.080(8), 2.108(7)
C(0)–Pt–C(15)	89.0(4)	90.0(4)
C(0)–Pt–N(1,22)	88.6(4), 178.5(3)	89.5(3), 177.3(4)
C(15)–Pt–N(22)	89.6(3)	89.0(3)
N(1)–Pt–N(22)	92.8(3)	91.5(3)
Pt–C(15)–N(11), C(14)	120.5(6), 135.8(7)	120.2(6), 137.2(7)
Pt–N(22)–N(21), C(23)	122.2(5), 133.7(6)	121.3(5), 133.0(7)
Pt–N(1)–C(2,6)	121.2(5), 121.0(6)	
Pt–N(1)–C(2,5)		126.4(6), 128.7(7)

$\mathrm{PtMe\{(pz)_2(C_3H_2N_2)CH\text{-}}N,C\}\{\mathrm{PPh_2(o\text{-}MeOC_6H_4)}\}$ (**1d**)	
Pt–C(0,15), N(22), P(1)	2.03(1), 2.01(1), 2.129(8), 2.284(3)
C(0)–Pt–C(15), N(22), P(1)	86.9(4), 172.0(4), 93.3(3)
C(15)–Pt–N(22), P(1)	85.5(3), 177.4(3)
N(22)–Pt–P(1)	94.3(2)
Pt–C(15)–N(11), C(14)	118.5(7), 139.7(6)
Pt–N(22)–N(21), C(23)	120.6(6), 134.5(6)
Pt–P(1)–C(111, 21, 31)	120.1(4), 117.2(3), 108.4(4)

$\mathrm{PtMe\{(pz)_2(C_3H_2N_2)CH\text{-}}C\}(\mathrm{L_2})$	$\mathrm{L_2 = 2PPh_3}$ (**2a**)	$\mathrm{L_2 = 2PEtPh_2}$ (**2b**)	$\mathrm{L_2 = PPh_2CH_2CH_2PPh_2}$ (**2c**)
Pt–C(0, 15)	2.00(4), 1.92(3)	2.10(2), 2.04(1)	2.07(4), 2.05(3)
Pt–P(1, 2)	2.29(1), 2.286(8)	2.300(4), 2.319(4)	2.253(8), 2.29(1)
C(0)–Pt–C(15)	86(1)	85.0(6)	80(1)
C(0)–Pt–P(1, 2)	85(1), 175(1)	87.2(4), 171.6(4)	94.7(9), 177(1)
C(15)–Pt–P(1, 2)	171.3(8), 89.4(8)	171.3(3), 87.2(4)	175(1), 99(1)
P(1)–Pt–P(2)	99.3(3)	100.8(1)	85.8(3)
Pt–C(15)–N(11), C(14)	126(2), 138(2)	122.6(6), 134.5(9)	122(2), 133(3)
Pt–P(1)–C(111, 121, 131)	114(2), 114(1), 122(1)	111.2(5), 114.5(4), 121.2(5)	
Pt–P(2)–C(211, 221, 231)	111.2(8), 116(1), 118.7(9)	115.5(5), 117.5(5), 113.6(4)	
Pt–P(1)—C(1, 111, 121)			106.2(9), 113(1), 117(1)
Pt–P(2)–C(2, 211, 221)			109(1), 112(1), 123(1)

its most probable origin may be partial inclusion of a solvent fragment, minor disorder, or impurity.

Complex 2a: A small, poorly formed plate was used, yielding weak and limited data, and supporting meaningful anisotropic thermal parameter refinement for Pt and P only. Difference map residues were plausibly modelled and refined in terms of a lattice acetone solvent molecule with population 0.5.

Complex 2b: A twinned specimen was used, data for the larger component being deconvoluted and measured. Forty five reflections seemed to be conspicuously affected by profile overlap, and they were removed from the data set. Anisotropic thermal parameters refined for C(114) were not meaningful and the isotropic form was used.

Complex 2c: A small twinned specimen was used, yielding weak and limited data, and supporting meaningful anisotropic thermal parameter refinement for Pt and P only.

Results and discussion

Three of the complexes examined (**1b–d**) have the cyclometallated ligand present as a $[C-N]^-$ donor (Fig. 1), and the other complexes (**2a**, **2b**, **2c**) involve the ligand as a $[C]^-$ donor (Fig. 2). The coordination geometries are square planar, with the organic groups *cis* to each other in the configurations "*cis*-PtC_2N_2" (**1b**, **1c**), "*cis*-PtC_2NP" (**1d**), or "*cis*-PtC_2P_2" (**2a**, **2b**, **2c**). The Pt–C(Me) bond distance is longer than the Pt–C(pz) distance in each complex, as reported for **1a** and **3** [2], although for the present determinations lower precision gives differences in Pt–C distances that are generally within ca. 3σ.

The $[C-N]^-$ coordinated ligands adopt a boat conformation for the chelate ring, most clearly illustrated in Fig. 1(a) and 1(b). The chelate angle, C(15)–Pt–N(22), in the mim complex and the previously reported py complex are identical, 89.0(3)°; this value is within 1σ of that for the 3,5-Me_2py complex, 89.6(3)°, although these values are significant larger than that found for the phosphine complex **1d**, 86.9(4)°. The uncoordinated ring in these complexes adopts an orientation above the coordination plane ('axial'), rather than directly opposite the platinum atom ('equatorial'). This orientation is also a characteristic feature of square planar complexes containing three rings acting as *N,N'*-bidentate ligands [8,9], *e.g.* $[Pd\{(pz)_3CH\text{-}N,N'\}_2][BF_4]_2$ [9], and is attributed to greater steric congestion in the equatorial position. In complexes **1b** and **1c** the 3,5-dimethylpyridine and *N*-methylimidazole planes form angles of 74.7(3) and 38.8(4)°, respectively, with the coordination plane "PtC_2N_2"; the orientation of the mim group is similar to that reported earlier for the pyridine analogue **1a** (68.1°) [2].

For the complexes containing metallated $(pz)_3CH$ as a $[C]^-$ donor, the metallated ring forms angles of 72(1)° (**2a**), 77.4(4)° (**2b**), and 90(1)° (**2c**) with the coordination plane "*cis*-PtC_2P_2".

The methoxy oxygen of the phosphine ligand in **1d** does not interact with the platinum atom, and the uncoordinated pyrazole rings in all of the structures are not involved in Pt · · · N interactions. However, in all of the complexes except for the 3,5-Me_2py complex (**1b**), there are contacts between the platinum atom and calculated positions of hydrogen atoms that are less than ~ 3.0 Å, and these are indicated in the captions to Figs. 1 and 2. The mim (**1c**) and $PPh_2(o\text{-}MeOC_6H_4)$ (**1d**) complexes have distances of ~ 2.9 and ~ 3.0 Å between the Pt atom and H(35) of the uncoordinated rings, respectively. Similar contacts occur between the Pt atom and *ortho*-hydrogen atoms of phenyl groups in the PPh_3 complex (**2a**) (four contacts), the $PtEtPh_2$ complex (**2b**) (two contacts), and the $Ph_2CH_2CH_2PPh_2$ complex (**2c**) (two contacts).

The shortest Pt · · · H distances occur for the methine proton of metallated $(pz)_3CH$ in those complexes (**2a,b,c**) where it is present as a unidentate $[C]^-$ group, at ~ 2.7 Å. The projections in Fig. 2 have been chosen to illustrate the orientation of these Pt · · · H contacts, involving approximately planar "Pt–C(15)–N(11)–C-H" groups. The Pt · · · H distances may indicate the presence of agostic [10] interactions, as the distances and orientation appear similar to related complexes where agostic interactions are documented [10], *e.g.* Pd ··· H 2.8 Å for the ortho-hydrogen of one phenyl group in *trans*-$PdI_2(PMe_2Ph)_2$ [10,11]. Orientation of the metallated ligand to give Pt ··· H contacts may also be assisted by steric effects, *e.g.* complexes **2a,b,c** have bulky phosphine ligands that may influence the conformation of the "$(pz)_2CH$" group. A clear demonstration of the presence or absence of agostic interactions in these complexes has not been obtained. For example, ^1H NMR spectra of the complexes in $CDCl_3$ show $^4J(^1H-^{195}Pt)$ coupling for the resonance of the methine proton at δ 9.35 ($J(HPt) = 9.0$ Hz) (**2a**), 9.25 (8.6 Hz) (**2b**), and 8.84 (8.2 Hz) (**2c**), in contrast to **1a–d** which do not exhibit coupling for the methine singlets at δ 8.37–8.39. Although coupling could be attributed to agostic interactions, it may also result from other factors, *e.g.* the quite different configuration of the "planar" "Pt–C(15)–N(11)–C–H" group compared with the boat configuration for the chelate rings of **1a–d**. ^{31}P NMR spectra do not exhibit $^1H-^{31}P$ coupling for the methine group.

The crystallographic results confirm the structures proposed from spectroscopic and physical data [3]. The structures illustrate the flexibility of metallated $(pz)_3CH$ to act as $[C-N]^-$ and $[C]^-$ donors, in addition to the $[N-C-N]^-$ mode found in platinum(IV) derivatives [3].

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