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Intramolecular Coordination involving Tripodal 'N_2C^-' Ligands, including Structural Analysis of Complexes formed by Oxidative Addition of Chlorobis(1-pyrazolyl)propanes to Dimethylplatinum(II)

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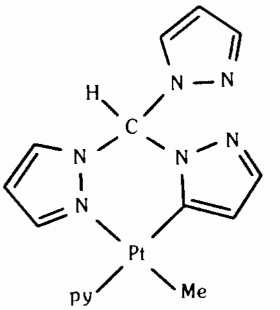
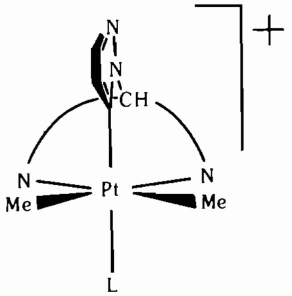
Dimethyl[tris(1-pyrazolyl)methane]platinum(II), $Me_2Pt(HCpz_3)$, undergoes a cyclometallation reaction in warm pyridine to form $MePt(HCpz_2(pzH_{-1}))$(py) involving presence of the ligand as a bidentate 'NC^-' donor, characterized by spectroscopic [1, 2] and X-ray structural analysis [2]. As this represents a new binding mode of tris(1-pyrazolyl)methane we have sought derivatives involving the metallated ligand as a tridentate 'N_2C^-' organometallic analogue of 'N_3' tris(1-pyrazolyl)methane and 'N_3^-' tris(1-pyrazolyl)borate, e.g. as in $[Me_3Pt(HCpz_3)][PF_6]$ [3] and $MePt(HBpz_3)(CF_3C_2CF_3)$ [4], and as a tripodal analogue of planar intramolecular 'N_2C^-' coordination systems, e.g. as in $Cl_3Pt[C_6H_3(CH_2NMe_2)_2$-*o,o'*] [5].



$MePt(HCpz_2(pzH_{-1}))(py)$



$[Me_2Pt(HCpz_2(pzH_{-1}))(L)]^+$

(L = py, PPh_3)

We report here the synthesis of organoplatinum(IV) cations involving metallated tris(1-pyrazolyl)methane, $[Me_2Pt(HCpz_2(pzH_{-1}))(L)]^+$ (L = py, PPh_3), and related complexes with intramolecular coordination by pyrazole groups, prior to investigation of their reactivity and further development of the organometallic chemistry of these ligands.

Platinum(II) derivatives of metallated tris(1-pyrazolyl)methane were oxidized to Pt(IV) derivatives via oxidative addition of iodomethane, since diorganoplatinum(II) complexes may be readily oxidized in this manner, e.g. $Me_2Pt(2,2'$-bipyridyl) [6–9], and characteristic octahedral geometry for Pt(IV) is expected to ensure 'N_2C^-' coordination. Thus, $MePt(HCpz_2(pzH_{-1}))$(py) reacts with a 4–5 fold excess of iodomethane in acetone under nitrogen at ambient temperature in darkness (12 h) to form a pale yellow solution, from which, after removal of excess iodomethane and some acetone followed by addition of petroleum–ether, colourless crystals were isolated. The complex has infrared and ^1H NMR spectra (in $CDCl_3$ at 300 MHz) consistent with the formulation* $[Me_2Pt(HCpz_2(pzH_{-1}))(py)]I\cdot 0.5Me_2CO$, e.g. $\nu(C{=}O)$ for solvate at 1704 cm^{-1}, appropriate relative intensities in NMR spectra, a single $Me_2Pt(IV)$ resonance at 1.51 ppm from Me_4Si with $^2J(^1H-^{195}Pt)$ 69.2 Hz, a single methine resonance at 10.45 ppm, and $^3J(^{ortho}H-^{195}Pt)$ 20.5 Hz for the pyridine group. A similar procedure, but with prior addition of a molar equivalent of triphenylphosphine, gave $[Me_2Pt(HCpz_2(pzH_{-1}))(PPh_3)]I$, which exhibited a similar NMR spectrum, e.g. $\delta[Me_2Pt(IV)]$ 1.45 with $^2J(^1H-^{195}Pt)$ 70.6 Hz and $^3J(^1H-^{31}P)$ 7.0 Hz. The PPh_3 complex is sufficiently soluble for measurement of conductance in acetone, giving a molar conductance of 100 ohm^{-1} cm^2 mol^{-1}, appropriate [10] for a 1:1 electrolyte.

As the complexes did not give crystals suitable for X-ray structural analysis, related pyrazole donor Pt(IV) complexes involving 'N_2C^-' coordination were sought via oxidative addition reactions of a Pt(II) substrate with haloalkane reagents containing two pyrazole groups. The new reagents 1-chloro-2,2-bis(1-pyrazolyl)propane ($ClCH_2Cpz_2CH_3$) and 1,3-dichloro-2,2-bis(1-pyrazolyl)propane [$(ClCH_2)_2Cpz_2$] were obtained in high yield by condensation reactions as shown, using anhydrous cobalt(II) chloride as catalyst in the manner described [11] for related bis(1-pyrazolyl)alkanes.

$$pz_2C{=}O + (ClCH_2)(XCH_2)C{=}O \longrightarrow ClCH_2Cpz_2CH_2X + CO_2$$

(X = H, Cl)

The complex $[Me_2Pt(SEt_2)]_2$ was chosen as a substrate because the diethylsulfide ligands are readily displaced by nitrogen donors and the complex undergoes facile oxidative addition reactions [6]. If nitro-

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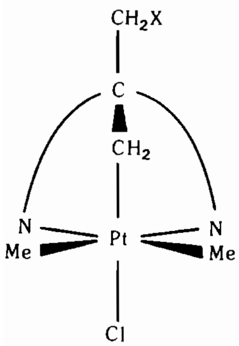
*All complexes have satisfactory microanalyses (C, H, N, P, halogen).

TABLE I. Crystal Data for Complexes $Me_2(Cl)Pt(CH_2Cpz_2CH_2X)$

Complex	X = H	X = Cl
Formula	$C_{11}H_{17}ClN_4Pt$	$C_{11}H_{16}Cl_2N_4Pt$
M	435.8	470.3
Space group	$P2_12_12_1$	$P2_1/c$
a (Å)	14.206(8)	8.407(2)
b (Å)	10.888(6)	13.836(6)
c (Å)	8.959(5)	113.139(4)
β (deg)		110.16(2)
V (Å^3)	1386(1)	1434.6(8)
D_{calc} (g cm^{-3})	2.09	2.17
Z	4	4
$F(000)$	824	888
μ_{Mo} (cm^{-1})	99	97
Crystal dimensions (mm)	0.18 × 0.16 × 0.48	0.15 × 0.40 × 0.10
$A^*_{min,max}$	4.0, 6.3	2.3, 3.4
$2\theta_{max}$ (deg)	60	60
Number of unique data	2248	4213
Number of data with $I > 3\sigma(I)$	1818	2912
R	0.032	0.032
R'	0.029 (preferred chirality)	0.033

gen donor complexes such as '$Me_2Pt(ClCH_2Cpz_2CH_2X)$' form, subsequent oxidative addition is expected in view of the proximity of chlorine atom(s) and platinum.

On heating $[Me_2Pt(SET_2)]_2$ with $ClCH_2Cpz_2CH_2X$ in benzene under nitrogen for 15 min a colourless crystalline precipitate formed, and was collected from the hot solution by filtration, washed with benzene and diethyl ether, and recrystallized by exposure of an acetone solution to diethyl ether vapour in a closed container. The complexes were characterized as $Me_2(Cl)Pt(CH_2Cpz_2CH_2X)$ by microanalysis, osmometric molecular weight determinations in chloroform at 37 °C [found 421 (X = H), 449 (Cl); calc. 435 (H), 470 (Cl)], conductance measurements (non-electrolytes in acetone), NMR spectra and X-ray structural analysis. Thus, in addition to pyrazole resonances, NMR spectra exhibit $Me_2Pt(IV)$ resonances at δ 1.30 (X = H), 1.33 (X = Cl), with $^2J(^1H-^{195}Pt)$ 73.7 Hz (H), 73.6 Hz (Cl); $PtCH_2$ resonances at δ 2.38 (H), 2.46 (Cl) with $^2J(^1H-^{195}Pt)$ 51.4 Hz (H), 54.3 Hz (Cl); and CH_2X resonances at δ 2.45 (H), 4.65 (Cl) with $J(^1H-^{195}Pt)$ 5.8 Hz (H) and 2.9 Hz (Cl).



$Me_2(Cl)Pt(CH_2Cpz_2CH_2X)$

(X = H, Cl)

Single crystal X-ray diffraction studies were undertaken for both complexes using a Syntex $P\bar{1}$ four-circle diffractometer in conventional $2\theta/\theta$ scan mode with Mo Kα radiation (Table I)*. Full matrix least-squares refinements, after analytical absorption corrections, involved anisotropic thermal parameters for the non-hydrogen atoms with hydrogen atoms included with calculated (x, y, z, U_{iso}) and constrained, with reflection weights $w = 1/\sigma^2(F)$ and $\sigma^2(I) = \sigma^2_{diff}(I) + 0.00012\sigma^4_{diff}(I)$. Neutral complex scattering factors were used [12]; computation used the XTAL 83 program system [13] implemented by Dr S. R. Hall on a Perkin–Elmer 3240 computer. Details of the coordination geometry for platinum are given in Table II, and the structure of $Me_2(Cl)Pt(CH_2Cpz_2CH_3)$ is illustrated in Fig. 1.

The complexes have very similar structures, based on distorted octahedral geometry for Pt(IV), with the 'N_2C^-' ligands confirmed as tripodal (*facial*) tridentates. The main distortion from regular octahedral geometry results from the small bite angles of the tridentate, with C(1)–Pt–N and N–Pt–N angles 78.5(2)–82.5(4)°. The chlorine atom is

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*Further information is available, see Supplementary Material.

TABLE II. Bond Distances (Å) and Angles (°) for Platinum in $Me_2(Cl)Pt(CH_2Cpz_2CH_2X)$

Atoms	X = H	X = Cl	Atoms	X = H	X = Cl
Distances					
Pt–C(1)	2.06(1)	2.030(6)	Pt–Cl	2.421(3)	2.443(2)
Pt–C(A)	2.05(1)	2.043(7)	Pt–N(a1)	2.129(8)	2.166(4)
Pt–C(B)	2.00(1)	2.035(9)	Pt–N(1b)	2.145(7)	2.163(6)
Angles					
C(A)–Pt–C(B)	89.2(5)	88.1(3)	C(B)–Pt–Cl	91.3(3)	90.8(2)
C(1)–Pt–C(A)	93.8(5)	94.3(3)	N(a1)–Pt–N(b1)	82.5(4)	81.4(2)
C(1)–Pt–C(B)	94.7(4)	93.6(3)	N(a1)–Pt–Cl	94.5(3)	96.6(1)
C(1)–Pt–N(a1)	78.7(4)	78.5(2)	N(b1)–Pt–Cl	95.9(2)	96.4(1)
C(1)–Pt–N(b1)	77.9(3)	79.1(2)	C(1)–Pt–Cl	171.2(3)	173.6(2)
C(A)–Pt–N(b1)	93.6(4)	93.7(3)	C(A)–Pt–N(a1)	172.1(4)	171.9(2)
C(A)–Pt–Cl	92.8(4)	90.4(2)	C(B)–Pt–N(b1)	172.1(4)	172.5(2)
C(B)–Pt–N(a1)	93.8(5)	95.9(2)			
Pt–C(1)–C(2)	101.4(6)	102.2(4)	Pt–N(a1)–C(a5)	143.4(8)	143.4(4)
Pt–N(a1)–N(a2)	108.8(6)	108.8(9)	Pt–N(b1)–C(b5)	144.3(7)	144.6(5)
Pt–N(b1)–N(b2)	109.1(5)	109.5(4)			

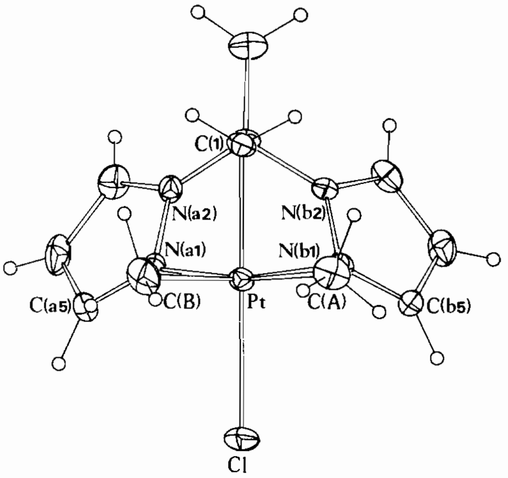

Fig. 1. Projection of $Me_2(Cl)Pt(CH_2Cpz_2CH_3)$ with selected atom numbering; 20% thermal ellipsoids are shown for the non-hydrogen atoms, and hydrogen atoms have been given an arbitrary radius of 0.1 Å.

trans to the CH_2 group, and the three carbon atoms are in a *facial* 'C_3Pt' orientation.

Although metallated tris(1-pyrazolyl)methane acts as a tripodal, 'N_2C^-' ligand with Pt(IV), the new chloro-bis(1-pyrazolyl)propane reagents may be of more general interest as sources of tripodal 'N_2C^-' coordination because they are readily synthesized and the presence of halogen should allow the synthesis of derivatives for a wider range of metal species, e.g. $R_2Sn(IV)$ [14], Pd(II) and Pt(II) [15], Pt(IV) [5], and Ni(II) [16] recently studied with the planar 'N_2C^-' ligand $[C_6H_3(CH_2NMe_2)_2\text{-}o,o']^-$.

Supplementary Material

The atomic coordinates, ligand geometries, least squares planes for pyrazole rings, thermal parameters, and diagrams of both structures are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW, U.K. Any request should be accompanied by the full literature citation for this Letter.

Acknowledgements

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