Synthesis of 1,1-Bis(pyrazol-1-ylmethyl)ethene and the Structure of a Trimethylplatinum(IV) Derivative containing an Eight-membered Chelate Ring*

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The bidentate pyrazole-donor ligand 1,1-bis(pyrazol-1-ylmethyl)ethene, $[(pz)CH_2]_2C{=}CH_2$, may be synthesized in high yield on reaction of the readily obtained potassium pyrazolide with commercially available $(ClCH_2)_2C{=}CH_2$. Reaction of the ligand with $[\{PtMe_2(SEt_2)\}_2]$, followed by addition of iodomethane, gives the platinum(IV) complex *fac*-$[PtIMe_3\{[(pz)CH_2]_2C{=}CH_2\text{-}N,N'\}]$. Proton NMR and X-ray structural studies show that the eight-membered chelate ring $PtNNC_3NN$ adopts a configuration in which the pyrazole rings are in different environments, forming angles of 26.0(3) and 38.2(3)° with the 'PtC_2N_2' mean plane. Thus, the four methylene protons are also in different environments, as are the PtMe groups *trans* to pyrazole groups. The eight-membered chelate ring is fluxional, undergoing inversion with $\Delta G^\ddagger \approx 15$ kcal mol^{-1} (≈ 63 kJ mol^{-1}) at 10 °C.

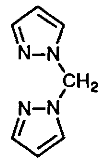
Bis(pyrazol-1-yl)alkanes, *e.g.* $(pz)_2CH_2$, form a rich organometallic chemistry with platinum(II) and platinum(IV), including co-ordination as *N,N'*-bidentate donors, and *C*- and *N,C*-cyclometallation systems involving binding of platinum at C(5) of one pyrazole ring.[1] We are now extending this chemistry to include ligands forming larger chelate rings, instead of the six-membered rings in complexes of bidentate bis(pyrazol-1-yl)alkanes.

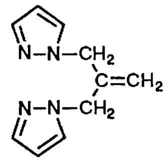
As the initial part of this work we report here the synthesis of 1,1-bis(pyrazol-1-ylmethyl)ethene, $[(pz)CH_2]_2C{=}CH_2$, and the isolation and structural study of a platinum(IV) complex containing an eight-membered chelate ring, $[PtIMe_3\{[(pz)CH_2]_2C{=}CH_2\}]$. This work has coincided with the report of the synthesis of $[(pz)CH_2]_2C{=}C[CH_2(pz)]_2$, and its application as an interesting new class of tetrapod ligand related to the porphyrin group.[2]

Experimental

The reagent $[\{PtMe_2(SEt_2)\}_2]$[3] was prepared as described, $(ClCH_2)_2C{=}CH_2$ was used as received (Aldrich), and all solvents were dried and distilled. Proton NMR spectra were recorded with a Bruker AM 300 spectrometer (^1H chemical shifts given in ppm relative to $SiMe_4$) and the molecular weight of the complex was determined with a Knauer vapour-pressure osmometer for *ca.* (1–3) × 10^{-2} mol dm^{-3} solutions at 37 °C.

1,1-Bis(pyrazol-1-ylmethyl)ethene, $[(pz)CH_2]_2C{=}CH_2$.—Pyrazole (30 g, 441 mmol) was added to a suspension of potassium (17.24 g, 441 mmol) in tetrahydrofuran (400 cm^3) under nitrogen, and the mixture was refluxed until the potassium had been consumed (*ca.* 1.5 h). 3-Chloro-2-(chloromethyl)prop-1-ene (27.5 g, 220 mmol) was added in one portion at ambient temperature under nitrogen, and after 30 min of stirring the suspension was heated under reflux for 4 h. The solution was filtered hot, and the filtrate reduced to a minimum volume under vacuum. Vacuum distillation gave the product as a viscous oil (33.1 g, 80%). ^1H NMR ($CDCl_3$): δ 7.55 [d, 2 H, H^3, $^3J(H^3H^4)$ 1.6], 7.35 [d, 2 H, H^5, $^3J(H^4H^5)$ 2.3 Hz], 6.28 ('t', 2 H, H^4), 5.13 ('t', 2 H, $=CH_2$) and 4.64 ('t', 4 H, CH_2). Mass spectrum: *m/z* 188 (*M*, 2), 121 (100) and 81 (52%).


$(pz)_2CH_2$


$[(pz)CH_2]_2C{=}CH_2$

$[PtIMe_3\{[(pz)CH_2]_2C{=}CH_2\}]$.—A solution of $[(pz)CH_2]_2C{=}CH_2$ (0.092 g, 0.49 mmol) and $[\{PtMe_2(SEt_2)\}_2]$ (0.15 g, 0.24 mmol) in acetone (20 cm^3) was refluxed under nitrogen. After 15 min the yellow solution was cooled, excess of iodomethane (*ca.* five-fold) was added and the solution stirred for 30 min. Excess of iodomethane was removed and hexane added until cloudiness developed. Microcrystals formed overnight (0.15 g, 58%) (Found: C, 27.7; H, 3.8; N, 9.4. Calc. for $C_{13}H_{21}IN_4Pt$: C, 28.1; H, 3.8; N, 10.1%). ^1H NMR [$(CD_3)_2CO$]: δ 8.15 (s, 1 H, H^3), 7.98 (br, 2 H, H^5), 7.74 (br, 1 H, H^3), 6.54 (br, 2 H, H^4), 5.61 [d, 1 H, CH_2, $^2J(HH)$ 14.7], 5.35 (s, 2 H, $=CH_2$), 4.84 [d, 1 H, CH_2, $^2J(HH)$ 14.4], 4.71 [d, 1 H, CH_2, $^2J(HH)$ 14.7], 4.45 [d, 1 H, CH_2, $^2J(HH)$ 14.4 Hz], 1.53 and 1.49 ['td', 3 H, PtMe, *trans* to pz, $^2J(HPt)$ 73.6] and 1.10 ['td', 3 H, PtMe *trans* to I, $J(HPt)$, 69.7 Hz]. Molecular weight in chloroform: 523 (calc. 555).

Crystallography.—A unique data set measured to $2\theta_{max} = 55°$ was collected with an Enraf-Nonius CAD-4 diffractometer operating in conventional 2θ–θ scan mode. A total of 3741 independent reflections were obtained at *ca.* 295 K, 2882 with $I > 3\sigma(I)$ being considered 'observed' and used in the full-matrix least-squares refinement after analytical absorption correction and solution of the structure by vector methods. Anisotropic thermal parameters were refined for non-hydrogen atoms; $(x, y, z, U_{iso})_H$ were included constrained at estimated

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* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

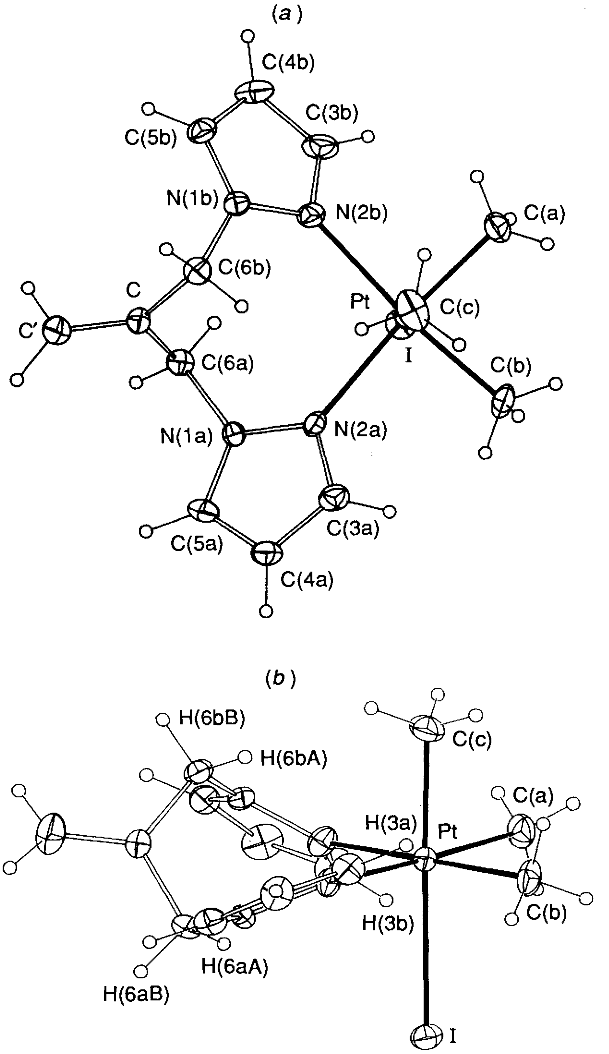

Fig. 1 The molecular structure of [PtIMe$_3${[(pz)CH$_2$]$_2$C=CH$_2$}] in two orientations to illustrate the conformation of the chelate ring, and the geometry at platinum. Hydrogen atoms are shown with an arbitrary radius of 0.1 Å, and 20% thermal ellipsoids are shown for the non-hydrogen atoms

Table 1 Non-hydrogen atom coordinates for [PtIMe$_3${[(pz)-CH$_2$]$_2$C=CH$_2$}]

Atom	*x*	*y*	*z*
Pt	0.447 91(5)	0.405 61(2)	0.705 61(2)
I	0.172 60(9)	0.270 69(5)	0.614 74(4)
C(a)	0.436(2)	0.470 3(7)	0.592 9(7)
C(b)	0.643(1)	0.316 4(8)	0.692 2(6)
C(c)	0.651(2)	0.504 0(9)	0.769 0(7)
N(1a)	0.379 6(9)	0.3163(5)	0.876 0(4)
N(2a)	0.494 3(9)	0.333 1(5)	0.833 2(4)
C(3a)	0.651(1)	0.288 7(7)	0.883 1(6)
C(4a)	0.637(1)	0.245 4(7)	0.956 4(6)
C(5a)	0.465(1)	0.265 9(6)	0.951 0(6)
C(6a)	0.201(1)	0.367 5(6)	0.853 1(5)
N(1b)	0.205 3(9)	0.559 6(5)	0.768 7(4)
N(2b)	0.225(1)	0.506 0(5)	0.703 5(5)
C(3b)	0.086(1)	0.533 0(8)	0.631 9(6)
C(4b)	−0.024(1)	0.601 2(7)	0.648 8(7)
C(5b)	0.055(1)	0.615 5(6)	0.736 4(6)
C(6b)	0.319(1)	0.540 3(6)	0.860 3(5)
C	0.229(1)	0.464 9(6)	0.896 8(5)
C′	0.183(2)	0.481 0(8)	0.964 0(7)

Table 2 Co-ordination and ligand geometry for [PtIMe$_3${[(pz)-CH$_2$]$_2$C=CH$_2$}]

Co-ordination geometry			
Pt–C(a)	2.03(1)	Pt–N(2a)	2.227(7)
Pt–C(b)	2.04(1)	Pt–N(2b)	2.214(8)
Pt–C(c)	2.04(1)	Pt–I	2.803(1)
C(a)–Pt–C(b,c)	86.5(5), 85.8(4)		
C(b)–Pt–C(c)	89.6(5)		
C(a)–Pt–N(2a,2b)	173.7(4), 87.3(4)		
C(b)–Pt–N(2a,2b)	88.5(4), 173.3(3)		
C(c)–Pt–N(2a,2b)	90.3(4), 92.3(4)		
N(2a)–Pt–N(2b)	97.9(3)		
I–Pt–C(a,b,c)	92.8(3), 89.6(3), 178.5(4)		
I–Pt–N(2a,2b)	91.0(2), 88.4(2)		
Pt–N(2a)–N(1a)	131.9(4)		
Pt–N(2a)–C(3a)	124.4(7)		
Pt–N(2b)–N(1b)	131.0(5)		
Pt–N(2b)–C(3b)	124.5(7)		
Ligand geometry			
N(1a)–N(2a)	1.36(1)	N(1b)–N(2b)	1.36(1)
N(1a)–C(6a)	1.48(1)	N(1b)–C(6b)	1.45(1)
C–C(6a)	1.50(1)	C–C(6b)	1.50(1)
C–C′	1.31(2)		
N(1a)–C(5a)	1.35(1)	N(1b)–C(5b)	1.33(1)
N(2a)–C(3a)	1.33(1)	N(2b)–C(3b)	1.31(1)
C(3a)–C(4a)	1.39(2)	C(3b)–C(4b)	1.38(2)
C(4a)–C(5a)	1.35(2)	C(4b)–C(5b)	1.35(1)
N(2a)–N(1a)–C(6a)	122.2(6)	N(2b)–N(1b)–C(6b)	120.7(7)
N(2a)–N(1a)–C(5a)	111.8(7)	N(2b)–N(1b)–C(5b)	110.6(7)
C(5a)–N(1a)–C(6a)	124.5(8)	C(5b)–N(1b)–C(6b)	127.8(8)
N(1a)–C(6a)–C	111.0(6)	N(1b)–C(6b)–C	110.6(6)
C(6a)–C–C′	121.5(9)	C(6b)–C–C′	122.9(9)
C(6a)–C–C(6b)	115.6(8)		
N(1a)–N(2a)–C(3a)	103.6(7)	N(1b)–N(2b)–C(3b)	104.3(8)
N(2a)–C(3a)–C(4a)	111.9(9)	N(2b)–C(3b)–C(4b)	112.3(9)
C(3a)–C(4a)–C(5a)	105.3(8)	C(3b)–C(4b)–C(5b)	104.6(8)
N(1a)–C(5a)–C(4a)	107.4(9)	N(1b)–C(5b)–C(4b)	108.2(9)

values. Residuals *R* and *R′* on $|F|$ at convergence were 0.037 and 0.040; statistical weights derived from $\sigma^2(I) = \sigma^2(I_{\text{diff}}) + 0.0004\ \sigma^4(I_{\text{diff}})$ were employed. Neutral atom complex scattering factors were used;[4] computation used the XTAL 3.0 program system implemented by S. R. Hall.[5] Coordinates for the non-hydrogen atoms, and the co-ordination geometry for the complex, are given in Tables 1 and 2, and projections of the structure are shown in Fig. 1.

Crystal data. $C_{13}H_{21}IN_4Pt$, *M* 555.3, monoclinic, space group $P2_1/c$ (C_{2h}^5), *a* 7.813(4), *b* 13.807(3), *c* 16.471(6) Å, β 112.67(3)°, *U* 1640 Å^3, D_c ($Z = 4$) 2.25 g cm^{-3}, *F*(000) 1032. Specimen size: pale yellow plate, 0.28 × 0.18 × 0.12 mm. Monochromatic Mo-Kα radiation, λ 0.7107$_3$ Å, μ 99.9 cm^{-1}; $A^*_{\text{min,max}}$ 2.89, 6.22.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates and thermal parameters.

Results and Discussion

Reaction of 3-chloro-2-(chloromethyl)prop-1-ene with potassium pyrazolide in the manner reported for the synthesis of (pz)$_3$CH[6] gave the required ligand in 80% yield [equation (1)].

$$(ClCH_2)_2C{=}CH_2 + 2K(pz) \longrightarrow [(pz)CH_2]_2C{=}CH_2 + 2KCl \quad (1)$$

The ligand reacts with [{PtMe$_2$(SEt$_2$)}$_2$] in refluxing acetone to

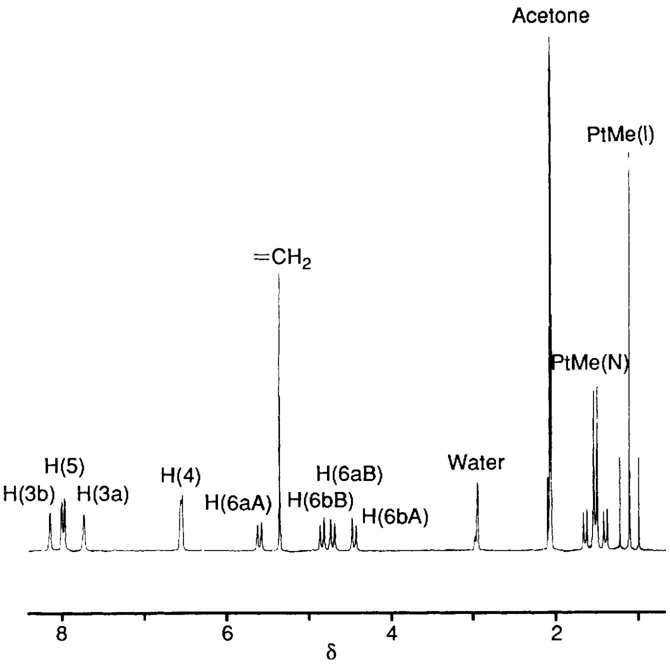

Fig. 2 Proton NMR spectrum of $[PtIMe_3\{[(pz)CH_2]_2C{=}CH_2\}]$ in $(CD_3)_2CO$, illustrating the presence of two pz environments, three PtMe environments, and four environments for the methine protons of the ligand. The atoms *trans* to the PtMe groups are indicated in parentheses

produce a dark oil on removal of acetone which proved difficult to purify or characterize. However, the product does react readily with iodomethane, by an oxidative-addition reaction, to form crystalline $[PtIMe_3\{[(pz)CH_2]_2C{=}CH_2\}]$ [equation (2)].

$$\tfrac{1}{2}[\{PtMe_2(SEt_2)\}_2] + [(pz)CH_2]_2C{=}CH_2 \xrightarrow{MeI} [PtIMe_3\{[(pz)CH_2]_2C{=}CH_2\}] + SEt_2 \quad (2)$$

Results of the structural determination for $[PtIMe_3\{[(pz)CH_2]_2C{=}CH_2\}]$ are shown in Fig. 1 and Tables 1 and 2. The complex has a '$PtIC_3$' geometry very similar to that of closely related $[PtIMe_3\{(pz)_2CHMe\}]$,[7] *e.g.* bond lengths are within 3σ. However, the 'PtN_2' geometry for the chelate ring is different, as the N–Pt–N angle [97.9(3)°] is *ca.* 13° larger in the present complex and the Pt–N bonds [2.214(8), 2.227(7) Å] are *ca.* 0.06 Å longer. In the six-membered chelate ring of $[PtIMe_3\{(pz)_2CHMe\}]$ the angles formed at the nitrogen-donor atoms are Pt–N–N 123.3(9), 122.6(8)° and Pt–N–C 129.3(9), 131.8(9)°; these are reversed in the expanded eight-membered chelate system with the larger angles formed within the chelate ring [Pt–N–N 131.9(4), 131.0(5)°; Pt–N–C 124.4(7), 124.5(7)°]. Torsion angles outward from the platinum atom (sections a, b) for this ring are 28.4(7), 41.2(8); −16(1), −15(1); −82.9(9), −88.1(10); and 71.9(9), 61.5(9)°, showing that the overall symmetry of the molecule, disregarding the *trans* Me, I groups, is quasi-2.

The planar pyrazole rings form angles of 26.0(3) (ring a) and 38.2(3)° (ring b) with the 'PtC_2N_2' mean plane, and 51.1(4)° between themselves, compared with corresponding angles of 30.4(5), 31.2(5) and 57.1(6)° for $[PtIMe_3\{(pz)_2CHMe\}]$. The alkene group, 'CC′C(6a),C(6b)' is planar and forms angles of 79.9(4) and 80.0(4)° with the pz rings a and b, respectively.

Disorder in the structure of the cobalt(II) complex of $[(pz)CH_2]_2C{=}C[CH_2(pz)]_2$[2] prevents a detailed comparison of ligand geometry with that of the platinum(IV) complex of $[(pz)CH_2]_2C{=}CH_2$.

The pyrazole rings in the complex are in different environments, *e.g.* Fig. 1(*b*) indicates that H(3a) is 'above' the 'PtC_2N_2' plane and H(3b) is 'below' this plane. Similarly, there are two environments for the methylene carbon atoms, with C(6b) above and C(6a) below the plane, and thus four methylene proton environments. The asymmetry in the structure is indicated also by the ^1H NMR spectrum of the complex in $(CD_3)_2CO$, shown in Fig. 2. The connectivity of the methylene protons is readily revealed by shift correlation spectroscopy (COSY), indicating that H(6aA) is coupled with H(6aB) and that H(6bA) is coupled with H(6bB). The doublet furthest downfield has been assigned to the proton adjacent to the iodine atom, and the proton furthest upfield to the proton adjacent to the methyl group, in accord with assignments in related complexes.[7,8] Resonances for H(3a) and H(3b) are assigned similarly.

Proton NMR spectra obtained in $CDCl_3$ as solvent give poorer separation of the four methylene resonances, but allow better variable-temperature spectra (268–288 K) showing coalescence of the two PtMe resonances for methyl groups *trans* to the pyrazole donor rings. Broadening of resonances for the ligand protons also occurs on warming, but resonances assigned to the PtMe group *trans* to iodine remain sharp. Thus, the variable-temperature behaviour is most readily interpreted as resulting from fluxional behaviour of the chelate ring, most likely inversion of conformation, and the simple approach of Cramer and Mrowca[9] gives $\Delta G^\ddagger \approx 15$ kcal mol^{-1} (≈ 63 kJ mol^{-1}) at 283 K for this process ($\Delta\nu$ 6.8 Hz).

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