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Conformational studies in palladium(IV) and platinum(IV) chemistry. Crystal structure of the 1,1-bis(pyrazol-1-yl)-ethane complex *fac*-$PtIMe_3\{(pz)_2CHMe\text{-}N,N'\}$

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Abstract

The reaction of iodomethane with the 1,1-bis(pyrazol-1-yl)ethane complex $PtMe_2\{(pz)_2CHMe\text{-}N,N'\}$ gives the platinum(IV) complex *fac*-$PtIMe_3\{(pz)_2CHMe\text{-}N,N'\}$, which has been fully characterized, by, among other means, an X-ray structural study. The analogous palladium(IV) complex has also been prepared by a similar reaction in $(CD_3)_2CO$ at −30°C, and the two complexes exhibit similar ^1H NMR spectra. For the palladium(IV) species, however, reductive elimination of ethane occurs above −30°C to give $PdIMe\{(pz)_2CHMe\text{-}N,N'\}$. The ^1H NMR spectra of the platinum(IV) and palladium(IV) complexes show that they are present in one configuration in solution, and large downfield shifts of the methine $C\mathit{H}CH_3$ resonance, compared with the same proton in $MMe_2\{(pz)_2C\mathit{H}Me\text{-}N,N'\}$, are consistent with a conformation of the six-membered chelate ring that places the methine proton adjacent to the iodine atom. The octahedral platinum(IV) complex adopts this configuration in the solid state, with $I \cdots H = 3.1$ Å. The ^1H NMR and structural studies support earlier assignments of solution behaviour for platinum(IV) and palladium(IV) complexes of related ligands, *e.g.* $(pz)(py)CH_2$ and $(py)_2CHMe$ (py = pyridin-2-yl), and confirm the influence of hydrogen ··· halogen interactions on ^1H NMR spectra of octahedral complexes of this type.

Introduction

Compared with the organometallic chemistry of platinum in the tetravalent oxidation state, synthetic alkylpalladium(IV) chemistry has only recently been developed [1–4]. Further, it has been noted that for some classes of palladium(IV) complexes, stability is achieved only at low temperatures. For these complexes,

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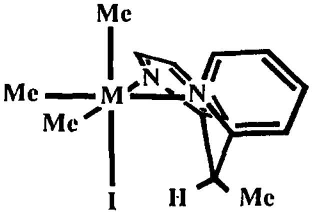

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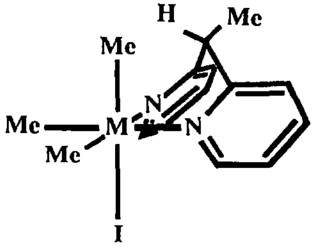

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characterization has often relied upon comparison of ^1H NMR spectra with those of robust and isolable platinum(IV) analogues. For example, for the ligand 1,1-bis(pyridin-2-yl)ethane, ^1H NMR spectra indicate that isomers I and II are formed in solution upon the *in situ* oxidative addition of iodomethane to $MMe_2\{(py)_2CHMe\}$ [5]

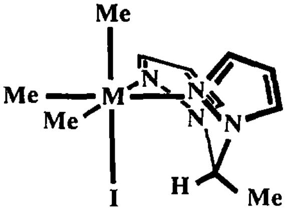
The ligand "bridgehead" methyl group is "equatorial" in both isomers, presumably to avoid Me ··· Me (isomer I) or I ··· Me (isomer II) interactions. Assignment of structure for the isomers is partly based on an expected downfield shift for the bridgehead protons (CH or CMe) when they are adjacent to iodine. We report here an extension of this work to include 1,1-bis(pyrazol-1-yl)ethane, $(pz)_2CHMe$, resulting in the formation of a single isomer in solution. The spectra show a significant downfield shift for the bridgehead proton when compared with $MMe_2\{(pz)_2CHMe\}$, suggesting structure III, and crystals of the platinum(IV) complex are of sufficient quality to allow a crystallographic confirmation of the structure.

Experimental

The reagents $PtMe_2\{(pz)_2CHMe\}$ [6] and $PdMe_2\{(pz)_2CHMe\}$ [7] were prepared as previously described. Iodomethane was distilled in the dark and stored at −20°C. Solvents were dried and distilled. ^1H NMR spectra were recorded with a Bruker AM 300 spectrometer, with chemical shifts given in ppm relative to Me_4Si. The molecular weight of $PtIMe_3\{(pz)_2CHMe\}$ was determined with a Knauer vapor pressure osmometer for approx. $(1-3) \times 10^{-2}$ *M* solutions in chloroform at 37°C.

fac-$PtIMe_3\{(pz)_2CHMe\}$

Iodomethane (100 μl) was added to a solution of $PtMe_2\{(pz)_2CHMe\}$ (0.1 g) in acetone (10 mL) and the mixture stirred for 10 min. Hexane was added dropwise



III

until cloudiness developed, and needles separated during 30 min. The product was collected, washed with diethyl ether, and vacuum dried at 50°C for 2 h. (89% yield). Anal. Found: C, 25.1; H, 3.6. $C_{11}H_{19}IN_4Pt$ calc.: C, 25.0; H, 3.6%. Mol. wt. 513 (calc. 529). ^1H NMR [$(CD_3)_2CO$]: δ 8.55 (1H, q, CH, $^3J = 6.9$ Hz), 8.28 [2H, d, H(5), $^3J = 2.8$ Hz], 7.82 [2H, d, H(3), $^3J = 2.3$ Hz], 6.62 [2H, "t", H(4)], 2.50 (3H, d, CMe, $^3J = 6.9$ Hz), 1.55 [6H, "t", PtMe, J(HPt) = 72.9 Hz], 0.76 [3H, "t", PtMe, J(HPt) = 71.6 Hz].

Detection of fac-*$PdIMe_3\{(pz)_2CHMe\}$ in solution*

A solution of $PdMe_3\{(pz)_2CHMe\}$ in $(CD_3)_2CO$ was cooled in the variable temperature probe of the NMR spectrometer to −30°C. An excess of iodomethane in $(CD_3)_2CO$ was added, and spectra were recorded as soon as possible after addition in order to monitor the progress of the reaction. The resulting spectrum is shown in Fig. 2. δ 8.57 (1H, q, CH, $^3J = 6.9$ Hz), 8.33 [2H, d, H(5), $^3J = 2.6$ Hz], 7.96 [2H, d, H(3), $^3J = 2.0$ Hz], 6.62 [2H, "t", H(4)], 2.45 (3H, d, CMe, $^3J = 6.9$ Hz), 1.90 (6H, s, PdMe), 1.28 (3H, s, PdMe).

Structure determination

Crystals of both needle (**N**) and plate (**P**) morphologies were obtained from the sample prepared as described above. Unique data sets were measured to $2\theta_{max} = 50°$ using monochromatic Mo-K_α radiation (λ 0.7107_3) with an Enraf–Nonius CAD-4 diffractometer operating in conventional 2θ–θ scan mode. A total of N independent reflections were obtained at about 295 K, N_o 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, except for C(O2) of **P**; $(x, y, z, U_{iso})_H$ were included at estimated values. 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 [8]; computation used the XTAL 3.0 program system implemented by Hall [9]. Coordinates and equivalent isotropic thermal parameters for the non-hydrogen atoms, and the coordination geometry for the complex, are given in Tables 1 and 2 *, and a projection of the structure is shown in Fig. 1.

Crystal data

$PtIMe_3\{(pz)_2CHMe\}$, $C_{11}H_{19}IN_4Pt$, $M = 529.3$. **N**: monoclinic, space group $P2_1/C$, $a = 7.543(2)$, $b = 13.685(1)$, $c = 16.145(5)$ Å, $\beta = 112.43(2)°$, $U = 1540.5$ Å^3, D_c (Z = 4) 2.28 g cm^{-3}, $F(000) = 976$, $\mu = 106$ cm^{-1}, $N = 2700$, $N_o = 1681$, $R = 0.037$, $R_w = 0.035$. Specimen size: $0.15 \times 0.08 \times 0.06$ mm^3. Minimum and maximum transmission factors 1.82, 2.72. **P**: monoclinic, space group $P2_1/c$, $a = 13.939(7)$, $b = 8.202(5)$, $c = 13.768(7)$ Å, $\beta = 97.95(4)°$, $U = 1.558.8$ Å^3, D_c (Z = 4) 2.26 g cm^{-3}, $F(000) = 976$, $\mu = 105$ cm^{-1}, $N = 2750$, $N_o = 1768$, $R = 0.063$, $R_w = 0.072$.

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* Tables of thermal parameters and calculated hydrogen atom positions, and details of the ligand geometry, will be deposited with the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ (UK). Any request should be accompanied by a full literature citation for this article.

Table 1

Non-hydrogen atom coordinates for $PtIMe_3\{(pz)_2CHMe\}$

Atom	Needles (N)			Plates (P)		
	x	*y*	*z*	*x*	*y*	*z*
Pt	0.26273(8)	0.45035(4)	0.72177(3)	0.22206(8)	0.1995(1)	0.30454(7)
I	0.0390(2)	0.28395(7)	0.65028(6)	0.3350(2)	0.3929(2)	0.4452(1)
C(01)	0.300(2)	0.463(1)	0.6029(9)	0.103(3)	0.340(4)	0.312(3)
C(02)	0.426(2)	0.5730(9)	0.7644(9)	0.141(2)	0.070(3)	0.193(2)
C(03)	0.025(2)	0.537(1)	0.664(1)	0.253(2)	0.344(3)	0.196(2)
C	0.385(2)	0.2866(9)	0.8838(8)	0.338(2)	−0.049(3)	0.471(2)
C(1)	0.431(2)	0.207(1)	0.955(1)	0.391(2)	−0.155(3)	0.552(2)
N(11)	0.547(1)	0.3097(7)	0.8603(7)	0.234(2)	−0.083(2)	0.458(2)
N(12)	0.518(1)	0.3640(7)	0.7872(7)	0.168(2)	0.022(3)	0.405(2)
C(13)	0.684(2)	0.367(1)	0.778(1)	0.084(2)	−0.035(4)	0.408(2)
C(14)	0.821(2)	0.316(1)	0.847(1)	0.080(2)	−0.172(5)	0.462(2)
C(15)	0.728(2)	0.2780(9)	0.8974(9)	0.169(4)	−0.205(4)	0.481(3)
N(21)	0.313(1)	0.3736(7)	0.9111(6)	0.376(2)	−0.070(2)	0.378(1)
N(22)	0.232(1)	0.4458(8)	0.8489(7)	0.342(2)	0.032(2)	0.300(1)
C(23)	0.174(2)	0.513(1)	0.893(1)	0.395(2)	−0.007(3)	0.232(2)
C(24)	0.221(2)	0.484(1)	0.9818(9)	0.457(2)	−0.128(3)	0.258(2)
C(25)	0.308(2)	0.397(1)	0.9916(8)	0.440(2)	−0.171(3)	0.351(2)

Specimen size: $0.10 \times 0.17 \times 0.38$ mm^3. Minimum and maximum transmission factors 2.75, 5.25.

Results and discussion

Reaction of iodomethane with $PtMe_2\{(pz)_2CHMe\}$ in acetone at ambient temperature gave the crystalline platinum(IV) complex $PtIMe_3\{(pz)_2CHMe\}$ in high yield. The ^1H NMR spectra of the platinum(IV) complex in both $CDCl_3$ and $(CD_3)_2CO$ are readily interpretable in terms of the presence of a single species. The palladium(IV) analogue could not be isolated, but, on reaction of iodomethane with $PdMe_2\{(pz)_2CHMe\}$ in $(CD_3)_2CO$ at −30°C, a ^1H NMR spectrum very similar to that of the platinum complex was obtained (Fig. 2). Resonances for the ligand protons are within 0.14 ppm of those for the platinum complex, and, as for the platinum complex, methyl resonances for the $Pd^{IV}Me_3$ group occur in the ratio 2 : 1, and occur downfield from $PdMe_2\{(pz)_2CHMe\}$. On warming above about −30°C, reductive elimination of ethane [0.84 ppm in $(CD_3)_2CO$] occurs to give the spectrum reported previously for $PdIMe\{(pz)_2CHMe\}$ [7].

Comparisons of the ^1H NMR spectrum of $MMe_2\{(pz)_2CHMe\}$, also obtained at −30°C in $(CD_3)_2CO$ [7,8], with those of $MIMe_3\{(pz)_2CHMe\}$ indicate that resonances for the $(pz)_2CHMe$ group are only slightly altered on oxidative addition, except for the methine proton $C\mathit{H}CH_3$. The spectra of $M^{II}Me_2\{(pz)_2CHMe\}$ show that two conformers are present, with the methine proton or methyl group positioned near the metal atom. On oxidative addition, H(3,4,5) for the pyrazole rings are shifted by $< \sim 0.3$ ppm, $CHC\mathit{H}_3$ is shifted by 0.01–0.09 ppm, but the $C\mathit{H}CH_3$ resonance is shifted downfield by 1.28–1.54 ppm. The large downfield shift is attributed to the proximity of the $C\mathit{H}CH_3$ proton to the iodine atom in

Table 2

Coordination and chelate ring geometry for PtIMe$_3${(pz)$_2$CHMe} (needles N): distances in Å, angles in degrees

Coordination geometry			
Pt-C(01)	2.05(2)	Pt-N(12)	2.16(1)
Pt-C(02)	2.04(1)	Pt-N(22)	2.15(1)
Pt-C(03)	2.05(1)	Pt-I	2.807(1)
C(01)-Pt-C(02)	88.0(6)	C(03)-Pt-N(22)	93.4(5)
C(01)-Pt-C(03)	86.2(7)	C(03)-Pt-I	89.7(4)
C(02)-Pt-C(03)	89.5(5)	N(12)-Pt-N(22)	85.3(4)
C(01)-Pt-N(12)	95.0(6)	N(12)-Pt-I	92.4(3)
C(01)-Pt-N(22)	176.4(5)	N(22)-Pt-I	95.9(3)
C(01)-Pt-I	87.7(4)	Pt-N(12)-N(11)	123.3(9)
C(02)-Pt-N(12)	88.5(4)	Pt-N(12)-C(13)	129.3(9)
C(02)-Pt-N(22)	88.4(5)	Pt-N(22)-N(21)	122.6(8)
C(02)-Pt-I	175.7(4)	Pt-N(22)-C(23)	131.8(9)
C(03)-Pt-N(12)	177.6(5)		
Ligand geometry			
N(11)-N(12)	1.34(1)	N(21)-N(22)	1.37(1)
N(11)-C(15)	1.34(2)	N(21)-C(25)	1.35(2)
N(12)-C(13)	1.32(2)	N(22)-C(23)	1.34(2)
C(13)-C(14)	1.39(2)	C(23)-C(24)	1.39(2)
C(14)-C(15)	1.36(3)	C(24)-C(25)	1.34(2)
C-N(11)	1.45(2)	C-N(21)	1.44(2)
C-C(1)	1.53(2)		
C-N(11)-N(12)	118.8(9)	C-N(21)-N(22)	119(1)
C-N(11)-C(15)	129(1)	C-N(21)-C(25)	130(1)
N(12)-N(11)-C(15)	112(1)	N(22)-N(21)-C(25)	111(1)
N(11)-N(12)-C(13)	106(1)	N(21)-N(22)-C(23)	104(1)
N(12)-C(13)-C(14)	110(2)	N(22)-C(23)-C(24)	110(1)
C(13)-C(14)-C(15)	106(1)	C(23)-C(24)-C(25)	107(1)
N(11)-C(15)-C(14)	106(1)	N(21)-C(25)-C(24)	107(1)
N(11)-C-C(1)	112(1)	N(21)-C-C(1)	111(1)
N(11)-C-N(21)	111(1)		

configuration III; an NMR effect assumed in assignment of resonances for the mixture of isomers observed in the ^{1}H NMR spectra of MIMe$_3${(py)$_2$CHMe} (I and II).

Results of the structural determination for PtIMe$_3${(pz)$_2$CHMe} are shown in Fig. 1 and Tables 1 and 2. The molecular structures in the "needle" (**N**) and "plate" (**P**) forms of the crystals are essentially identical, and since the data from a crystal of form **N** resulted in a higher precision determination, geometrical parameters for this form only are presented in Table 2, and discussed below.

The coordination geometry, based on an octahedral *fac*-PtIC$_3$N$_2$ moiety, is similar to that reported for the closely related complex PtIMe$_3${(3,5-Me$_2$pz)$_2$CH$_2$}, although it does not possess the crystallographic mirror plane of the latter complex [10]. The bidentate ligands adopt a boat form in both complexes, and the Pt-I distance in the present complex [2.807(1) Å] is similar to that in the (3,5-Me$_2$pz)$_2$CH$_2$ complex [2.843(1) Å]. The planar pyrazole rings form angles of 30.4(5)° (ring 1) and 31.2(5)° (ring 2) with the mean PtC$_2$N$_2$ plane, and 57.1(6)°

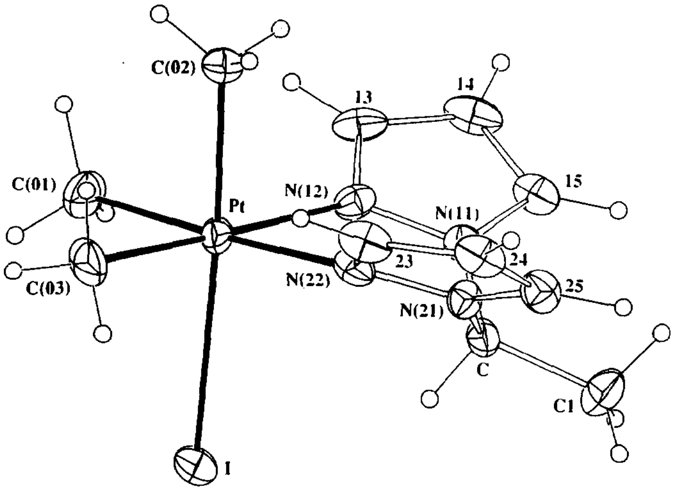

Fig. 1. The molecular structure of $PtIMe_3\{(pz)_2CHMe\}$ (needles). Hydrogen atoms are shown with an arbitrary radius of 0.1 Å, and 20% thermal ellipsoids for the non-hydrogen atoms.

between themselves. Substitution in the 3- and 5-positions of the pyrazole rings of $(pz)_2CH_2$ is known to result in minor changes in coordination geometry, attributed to steric interactions between the group in the 3-position and ligands trans to

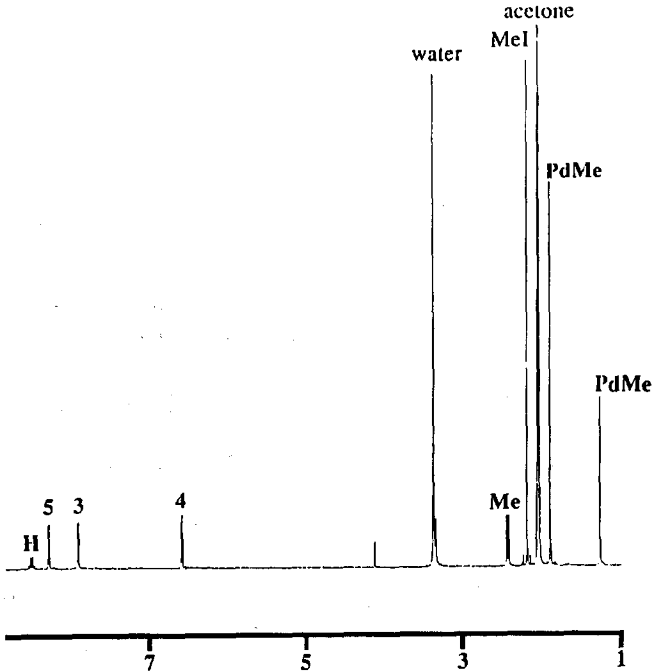

Fig. 2. ^1H NMR spectrum obtained after addition of excess MeI to $PdMe_2\{(pz)_2CHMe\}$ at −30°C. The isolated platinum(IV) complex $PtIMe_3\{pz)_2CHMe\}$ exhibits a similar spectrum.

nitrogen, e.g. for $PtI_2Me_2\{(pz)_2CH_2\}$ and $PtI_2Me_2\{(3,5\text{-}Me_2pz)_2CH_2\}$, the latter complex has longer Pt–N distances [2.236(4) compared with 2.183(7) Å] resulting in variations in Pt–N–N and Pt–N–C angles for the chelate ring [11]. Similar effects are noted on comparing $PtIMe_3\{(pz)_2CHMe\}$ with $PtIMe_3\{(3,5\text{-}Me_2pz)_2CH_2\}$, since the latter complex has a Pt–N bond length of 2.236(4) Å, compared with 2.15(1), 2.16(1) Å for the former complex.

The calculated position for the methine proton is 3.1 Å from the iodine atom, approx. 0.25 Å less than the sum of the van der Waals radii of hydrogen and iodine (3.35 Å) [12], perhaps rather longer than the values obtained by Clark *et al.* for $PtI_2Me_2\{(pz)_2CH_2\}$ (2.8 Å) and $PtI_2Me_2\{(3,5\text{-}Me_2pz)_2CH_2\}$ (2.7 Å) [11].

Crystallization of $PtIMe_3\{(pz)_2CHMe\}$ in a form suitable for X-ray diffraction has allowed confirmation of the proposed structure for this complex, and provides additional confidence in NMR assignments, for related complexes, that are based on downfield shifts as an indication that protons are adjacent to halogen atoms [5].

Acknowledgements

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References

1 P.K. Byers, A.J. Canty, B.W. Skelton and A.H. White, J. Chem. Soc., Chem. Commun., (1986) 1722.
2 A.J. Canty, Acc. Chem. Res., 25 (1992) 83.
3 W. de Graaf, J. Boersma, W.J.J. Smeets, A.L. Spek and G. van Koten, Organometallics, 8 (1989) 2907; W. de Graaf, J. Boersma and G. van Koten, Organometallics, 9 (1990) 1479.
4 M. Catellani and G.P. Chiusoli, J. Organomet. Chem., 346 (1988) C27; M. Catellani and B.E. Mann, J. Organomet. Chem., 390 (1990) 251.
5 P.K. Byers, A.J. Canty, R.T. Honeyman and A.A. Watson, J. Organomet. Chem., 385 (1990) 429.
6 A.J. Canty and R.T. Honeyman, J. Organomet. Chem., 387 (1990) 247.
7 P.K. Byers and A.J. Canty, Organometallics, 9 (1990) 210.
8 J.A. Ibers and W.C. Hamilton (Eds.), International Tables for X-ray Crystallography, Vol. 4, Kynoch Press, Birmingham, 1974.
9 S.R. Hall and J.M. Stewart, The XTAL Users Manual – Version 3.0, Universities of Western Australia and Maryland, 1990.
10 H.C. Clark, G. Ferguson, V.K. Jain and M. Parvez, J. Organomet. Chem., 270 (1984) 365.
11 H.C. Clark, G. Ferguson, V.K. Jain and M. Parvez, Organometallics, 2 (1983) 806.
12 L. Pauling, The Nature of the Chemical Bond, 3rd edition, Cornell University Press, Ithaca, 1960, p. 260.