*Journal of Organometallic Chemistry*, 270 (1984) 365–373
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

# ORGANOPLATINUM(IV) COMPOUNDS

## II *. PREPARATION AND CHARACTERIZATION OF TRIMETHYLPLATINUM(IV) COMPOUNDS WITH CHELATING NITROGEN DONOR LIGANDS. THE CRYSTAL AND MOLECULAR STRUCTURE OF IODOTRIMETHYL[BIS(3,5-DIMETHYL-1-PYRAZOLYL)METHANE]PLATINUM(IV)

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(Received February 1st, 1984)

## Summary

Compounds of the types $Me_3PtX(NN)$ (where X = Cl, I, OAc, $NO_3$; NN = bis(1-pyrazolyl)methane ($pz_2CH_2$), bis(3,5-dimethyl-1-pyrazolyl)methane ($(Me_2pz)_2CH_2$), or bis(2-pyridyl)methane ($py_2CH_2$)), $[Me_3Pt(NNN)][PF_6]$ (where NNN = tris(1-pyrazolyl)methane ($pz_3CH$), or tris(2-pyridyl)methane ($py_3CH$)), and $[Me_3Pt((Me_2pz)_2CH_2(py)][PF_6]$ have been prepared and characterized by elemental analyses and $^1H$ and $^{13}C$ NMR spectroscopy; the structure of $Me_3PtI[(Me_2pz)_2CH_2]$ (**1**) has also been determined by X-ray crystallography. Crystals of **1** are orthorhombic, space group *Pcmn* with four molecules in a unit cell of dimensions *a* 11.936(5), *b* 14.462(4), *c* 10.138(5) Å. The structure was solved by the heavy-atom method and refined by full-matrix least-squares calculations to $R = 0.022$ for 1719 observed data. The molecule has crystallographic mirror symmetry. The Pt atom has octahedral geometry with one methyl group *trans* to iodine and two methyl groups *trans* to the N atoms of the bidentate ligand (Pt–I 2.843(1), Pt–N, 2.236(4), Pt–C 2.077(6) (*trans* to I) and 2.032(5) Å (*trans* to N)).

## Introduction

During the last decade, there has been an increasing interest in the chemistry of platinum(IV) in general, and organoplatinum(IV) in particular [1,2]. Triorganoplatinum(IV) complexes with bidentate ligands have been reported in the last few years [3–9], and have been found to display interesting features. Dithio- and

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[*] For part I see Ref. 10.

TABLE 1

ANALYTICAL AND $^1$H NMR DATA FOR TRIMETHYLPLATINUM(IV) COMPLEXES WITH CHELATING NITROGEN DONOR LIGANDS

| Complex | M.p. [a] (°C) | Analyses (Found (calcd.) (%)) | | | Solvent | $^1$H NMR data [b] (Pt–Me resonances) | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | C | H | N | | $\delta^1$ | $J(^{195}Pt–^1H)$ (Hz) | $\delta^2$ | $J(^{195}Pt–^1H)$ (Hz) |
| [Me$_3$Pt(bis(1-pyrazolyl)methane)Cl] | 255–260 | 28.36 | 4.05 | 14.31 | $CD_2Cl_2$ | 1.38 | 72.2 | 0.75 | 73.6 |
| | | (28.34) | (4.04) | (13.22) | | | | | |
| [Me$_3$Pt(bis(1-pyrazolyl)methane)I] | 244–246 | 23.25 | 3.56 | 10.92 | $CD_2Cl_2$ | 1.55 | 72.7 | 0.84 | 72.0 |
| | | (23.31) | (3.32) | (10.87) | | | | | |
| [Me$_3$Pt(bis(3,5-dimethyl-1-pyrazolyl)methane)I] | 215–218 | 29.36 | 4.50 | 9.27 | $CDCl_3$ | 1.82 | 72.5 | 1.26 | 72.3 |
| | | (29.43) | (4.41) | (9.06) | | | | | |
| [Me$_3$Pt(bis(2-pyridyl)methane)I)] | 248–250 | 31.45 | 3.56 | 5.44 | $CD_2Cl_2$ | 1.54 | 69.5 | 1.06 | 72.0 |
| | | (31.29) | (3.56) | (5.21) | | | | | |
| [Me$_3$Pt(bis(3,5-dimethyl-1-pyrazolyl)methane)NO$_3$] | 229–232 | 33.14 | 5.17 | 14.00 | $CD_2Cl_2$ | 1.36 | 70.3 | 1.23 | 79.2 |
| | | (33.20) | (4.97) | (13.83) | | | | | |
| [Me$_3$Pt(bis(3,5-dimethyl-1-pyrazolyl)methane)OAc] | 200–203 | 38.17 | 5.85 | 11.35 | $CDCl_3$ | 1.42 | 69.0 | 1.03 | 73.0 |
| | | (38.17) | (5.60) | (11.13) | | | | | |
| [Me$_3$Pt(bis(3,5-dimethyl-1-pyrazolyl)methane)(py)][PF$_6$] | 204–208 | 34.17 | 4.71 | 10.19 | $CDCl_3$ | 1.28 | 70.6 | 1.16 | 68.9 |
| | | (33.93) | (5.09) | (10.41) | | | | | |
| [Me$_3$Pt(tris(1-pyrazolyl)methane)][PF$_6$] | 300 | 26.32 | 3.43 | 13.54 | $CDCl_3$ | 1.12 [c] | 72.2 | | |
| | | (26.04) | (3.36) | (14.02) | | | | | |
| [Me$_3$Pt(tris(2-pyridyl)methane)][PF$_6$] | 203–205 | 35.87 | 3.49 | 6.85 | $CDCl_3$ | 1.07 [c] | 67.3 | | |
| | | (36.08) | (3.51) | (6.64) | | | | | |

[a] Decomposition temperature. [b] Chemical shifts are relative to the solvent peak ($CDCl_3$ $\delta$ 7.24 ppm, $CD_2Cl_2$ $\delta$ 5.32 ppm). [c] All the three methyl groups are *trans* to the ligand moiety.

diseleno-ethers, $MeE(CH_2)_nEMe$ (E = S or Se), for example, have been shown to react with $[Me_3PtX]_4$ to give either dinuclear complexes when $n = 0$ or 1, or mononuclear complexes when $n = 2$ or 3, and in mononuclear complexes the chalcogen atoms have been shown to be inverting essentially independently [6,8].

In the previous paper of this series [10] we have discussed the preparation, reactivity and crystal and molecular structures of dimethylplatinum(IV) complexes with chelating nitrogen donor ligands. We now describe the preparation and properties of trimethylplatinum(IV) complexes with bi- and tri-dentate nitrogen donor ligands, and the crystal and molecular structure of $Me_3PtI[(Me_2pz)_2CH_2]$ (**1**).

## Experimental

Trimethylplatinum(IV) chloride was prepared by the reaction of $K_2PtCl_6$ with an excess of MeLi in ether [11]. Trimethylplatinum(IV) iodide [12], bis(1-pyrazolyl)methane [13], bis(2-pyridyl)methane [14], and tris(2-pyridyl)methane [15], were prepared by the literature methods. Bis(3,5-dimethyl-1-pyrazolyl)methane and tris(1-pyrazolyl)methane were obtained from Columbia Organic Chemical Inc. and silver hexafluorophosphate from Strem Chemicals.

$^1H$ NMR spectra were recorded on Bruker WH-400 and WP-60 NMR spectrometers and chemical shifts are relative to internal solvent peak ($CDCl_3$ $\delta$ 7.24 ppm, $CD_2Cl_2$ $\delta$ 5.32 ppm). $^{13}C$ NMR spectra were recorded at 100.6 MHz on a Bruker WH-400 spectrometer and chemical shifts are relative to external TMS. Microanalyses were performed by Guelph Chemical Laboratories. Melting points were determined in a capillary tube and are uncorrected.

### *Preparation and characterization of iodotrimethyl[bis(3,5-dimethyl-1-pyrazolyl)-methane]platinum(IV) (1) and related derivatives*

To a hot benzene solution (~ 15 ml) of trimethylplatinum iodide (202 mg, 0.550 mmol), bis(3,5-dimethyl-1-pyrazolyl)methane (113 mg, 0.553 mmol) in benzene (~ 6 ml) was added with stirring; the resulting solution was refluxed for 5 min and a white solid product precipitated. After cooling, the benzene was reduced to its half volume (~ 10 ml). The remaining benzene was decanted, the product $Me_3PtI[(Me_2pz)_2CH_2]$ (**1**) was washed with two lots of benzene (~ 2 ml each), and dried under vacuum. Recrystallization of **1** from chloroform afforded colourless prismatic crystals in 64% yield. Similarly chloro- or iodotrimethyl[bis(1-pyrazolyl)methane]platinum(IV) and iodotrimethyl[bis(2-pyridyl)methane]-platinum(IV) were prepared. Pertinent data for these complexes are given in Table 1.

### *Crystal structure analysis of $Me_3PtI[(Me_2pz)_2CH_2]$ (1)*

*Crystal data.* $C_{14}H_{25}IN_4Pt$, $M_r = 571.4$, orthorhombic, $a$ 11.936(5), $b$ 14.462(4), $c$ 10.138(5) Å, $U$ 1750.0 Å$^3$, $Z = 4$, $D_c$ 2.17 g cm$^{-3}$, $F(000) = 1072$, Mo-$K_\alpha$ radiation, $\lambda$ 0.70926 Å, $\mu$(Mo-$K_\alpha$) 89.5 cm$^{-1}$. Space group *Pcmn* (alternate setting of *Pnma*, with equivalent positions: $\pm[x, y, z]$; $\pm[1/2 - x, y, 1/2 + z]$; $\pm[x, 1/2 - y, z]$; $\pm[1/2 - x, 1/2 - y, 1/2 + z]$) or $P2_1cn$ from the systematic absences ($hk0$ absent if $h + k = 2n + 1$, $0kl$ absent if $l = 2n + 1$). Our analysis of the $E$-statistics and successful refinement in the centrosymmetric space group (see below) confirms our choice of *Pcmn* over $P2_1cn$.

### *Data collection, solution and refinement of the structure*

Data were collected to a maximum $\theta$ of 27° on an Enraf Nonius CAD-4 diffractometer by the $\omega/2\theta$ scan technique using monochromatized Mo-$K_\alpha$ radiation. Following machine location and centering of 25 reflections with $\theta$ in the range to $10 < \theta < 15°$, accurate cell constants and the orientation matrix were obtained by a least-squares refinement. A total of 1975 unique reflections were collected, of which 1719 had $I > 3\sigma(I)$ and were used in structure solution and refinement. The intensities of three standard reflections monitored at regular intervals did not change significantly over the period of data collection. The data were corrected for Lorentz and polarization factors, and for absorption. Maximum and minimum values of the transmission coefficients are 0.3345 and 0.0551 respectively.

The structure was solved by the heavy-atom method. Initial refinement [16] by full-matrix least-squares calculations with isotropic temperature factors for the non-hydrogen atoms lowered $R$ to 0.079, which further dropped to 0.027 after six cycles of anisotropic refinement. A difference map calculated at this stage revealed maxima (0.7–0.3 eÅ$^{-3}$) corresponding to the anticipated hydrogen atom positions, these were included in the subsequent refinement in geometrically idealized positions (C–H 0.95 Å), and in addition overall isotropic thermal parameters were refined for the various types of hydrogen atoms. In the final cycles of refinement, weights were derived from the counting statistics. Scattering factors used in the structure factor calculations were taken from ref. 17 for non-hydrogen atoms and ref. 18 for hydrogen atoms, allowance was made for anomalous dispersion [19]. Refinement converged with $R = 0.022$ and $R_w = [\Sigma w\Delta^2/\Sigma wF_0^2]^{1/2} = 0.025$. A difference map calculated at the conclusion of the refinement was essentially featureless. Final fractional coordinates with estimated standard deviations are in Table 2 and anisotropic thermal parameters are in Table 3. Calculated hydrogen coordinates and structure factor listings are available from the authors on request.

### *Preparation of acetato- and nitrato-trimethyl[bis(3,5-dimethyl-1-pyrazolyl)methane]platinum(IV)*

To a chloroform solution (~ 15 ml) of **1** (62 mg, 0.109 mmol) excess of silver

TABLE 2

FINAL FRACTIONAL COORDINATES (×10$^5$ for Pt and I, ×10$^4$ for remainder) WITH E.S.D.'S IN PARENTHESES

| Atom | $x$ | $y$ | $z$ |
|---|---|---|---|
| Pt | 8557(2) | 25000 | 14538(2) |
| I | −14542(4) | 25000 | 21366(5) |
| N(1) | 703(3) | 1458(3) | −166(4) |
| N(2) | 97(3) | 1672(3) | −1260(3) |
| C(3) | 203(4) | 1036(4) | −2223(4) |
| C(31) | −391(5) | 1093(5) | −3516(4) |
| C(4) | 917(4) | 381(4) | −1716(6) |
| C(5) | 1216(3) | 661(3) | −446(4) |
| C(51) | 1997(4) | 167(4) | 422(5) |
| C(6) | −597(5) | 2500 | −1260(6) |
| C(7) | 2576(5) | 2500 | 1147(7) |
| C(8) | 1063(4) | 1545(4) | 2904(5) |

TABLE 3

ANISOTROPIC TEMPERATURE FACTORS$^a$ (Å$^2$ ×10$^3$)

| Atom | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|
| Pt | 28(1) | 35(1) | 29(1) | 0 | 0(1) | 0 |
| I | 36(1) | 66(1) | 66(1) | 0 | 16(1) | 0 |
| N(1) | 33(2) | 38(2) | 36(2) | 1(2) | −1(1) | −2(2) |
| N(2) | 39(2) | 40(2) | 35(2) | −3(1) | −4(1) | −2(2) |
| C(3) | 49(3) | 40(3) | 46(2) | −7(2) | 3(2) | −16(2) |
| C(31) | 76(4) | 62(4) | 41(3) | −11(2) | −4(2) | −16(3) |
| C(4) | 47(3) | 40(3) | 56(3) | −11(2) | 9(2) | −10(2) |
| C(5) | 33(2) | 35(2) | 47(2) | 1(2) | 8(2) | −5(2) |
| C(51) | 46(3) | 49(3) | 64(3) | 8(2) | 6(2) | 9(2) |
| C(6) | 34(3) | 47(4) | 44(3) | 0 | −16(3) | 0 |
| C(7) | 32(3) | 58(4) | 52(4) | 0 | −8(3) | 0 |
| C(8) | 53(3) | 54(3) | 39(3) | 13(2) | −3(2) | 1(2) |

Overall isotropic temperature factors $U_{iso}$ for secondary and methyl-H atoms refined to 0.069(12) and 0.080(7) Å$^2$, respectively.

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[a] Anisotropic thermal parameters $U_{ij}$ (Å$^2$ ×10$^3$) in the expression: $\exp[-2\pi^2(U_{11}h^2a^{\star 2}+U_{22}k^2b^{\star 2}+U_{33}l^2c^{\star 2}+2U_{12}hka^{\star}b^{\star}+2U_{13}hla^{\star}c^{\star}+2U_{23}klb^{\star}c^{\star})]$.

acetate (~ 100 mg, 0.599 mmol) was added and the whole heated under reflux for 1 h under a nitrogen atmosphere. Silver iodide and unreacted silver acetate were filtered off. The filtrate was evaporated to dryness and recrystallized from chloroform to give a white crystalline solid (yield 33 mg, 60%). The corresponding nitrate derivative was prepared in an analogous manner.

### *Preparation of trimethyl[bis(3,5-dimethyl-1-pyrazolyl)methane](pyridine)platinum(IV) hexafluorophosphate*

A suspension of **1** (147 mg, 0.257 mmol) in acetone (5 ml) was added with stirring to an acetone solution of $AgPF_6$ (64 mg, 0.253 mmol), and the stirring continued for 30 min. Precipitated AgI was filtered off, pyridine (0.1 ml) was added to the filtrate (a solution of $[Me_3Pt[(Me_2pz)_2CH_2](acetone)][PF_6]$) and stirring continued for an additional 30 min. Acetone was evaporated off under vacuum and the residue was passed through a Florisil column, eluting with acetone. The solvent was reduced to 3 ml and benzene (3 ml) was slowly added. The solution was kept for a few hours at room temperature and $[Me_3Pt[(Me_2pz)_2CH_2](Py)][PF_6]$ (yield 148 mg, 86%) crystallized out.

### *Preparation of trimethyl[tris(2-pyridyl)methane]platinum(IV) and trimethyl[tris(1-pyrazolyl)methane]platinum(IV) hexafluorophosphates*

To an acetone solution (~ 20 ml) of $AgPF_6$ (232 mg, 0.917 mmol), trimethylplatinum(IV) iodide (338 mg, 0.921 mmol) was added with stirring at room temperature. The reactants were stirred for 15 min to ensure completion of the reaction. Silver iodide was filtered off and to the filtrate (a solution of $[Me_3Pt(acetone)_3][PF_6]$) an acetone solution (~ 5 ml) of tris(2-pyridyl)methane (227 mg, 0.919 mmol) was added with stirring, and stirring was continued for further 30 min. The solvent was pumped off leaving a white solid which was recrystallized from a chloroform/hexane mixture to yield $[Me_3Pt(py_3CH)][PF_6]$, a white crystalline solid (yield 500 mg, 86%). In a similar fashion $[Me_3Pt(pz_3CH)][PF_6]$ was prepared. Analytical data and $^1H$ NMR data of these complexes are given in Table 1.

## Results and discussion

Trimethylplatinum(IV) halides, $[Me_3PtX]_4$, react with chelating nitrogen donor ligands in hot benzene to give white, monomeric, six-coordinate trimethylplatinum(IV) complexes, $[Me_3PtX(NN)]$ (where X = Cl, NN = bis(1-pyrazolyl)methane ($pz_2CH_2$); X = I, NN = $pz_2CH_2$, bis(3,5-dimethyl-1-pyrazolyl)methane $[(Me_2pz)_2CH_2]$, bis(2-pyridyl)methane ($py_2CH_2$)). The iodine atom in $Me_3PtI[Me_2pz)_2CH_2]$ [**1**] may be removed easily in solution, as silver iodide, by the addition of AgX (X = OAc, $NO_3$).

$$Me_3PtI[(Me_2pz)_2CH_2] + AgX \rightarrow Me_3PtX[(Me_2pz)_2CH_2] + AgI$$

The reaction of **1** with $AgPF_6$ in acetone and subsequent addition of pyridine proceeds as shown:

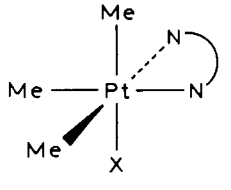
$$\begin{array}{l}Me_3PtI[(Me_2pz)_2CH_2] + AgPF_6 \xrightarrow{\text{acetone}} [Me_3Pt[(Me_2pz)_2CH_2](\text{acetone})][PF_6] + AgI \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \downarrow \text{pyridine (py)} \\ \qquad\qquad\qquad\qquad\qquad\qquad [Me_3Pt[(Me_2pz)_2CH_2](py)][PF_6]\end{array}$$

The $[Me_3Pt(acetone)_3]^+$ cation, obtained from $[Me_3PtI]_4$ and $AgPF_6$ in acetone, reacts with tris(1-pyrazolyl)methane ($pz_3CH$) or tris(2-pyridyl)methane ($py_3CH$) to give white crystalline complexes of the type $[Me_3Pt(NNN)][PF_6]$. Trimethylplatinum(IV) compounds prepared during the course of the present investigation are shown in Table 1 along with their analytical and $^1H$ NMR data.

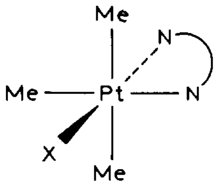
We have been interested in preparing and investigating complexes of the type $[MePt(NN)L]^+$ (L = CO, olefins or acetylenes and NN = neutral dinitrogen ligands) [10]. It is well known that certain $Me_3Pt^{IV}$ complexes (e.g. $Me_3Pt(PMe_2Ph)_2X$, X = Cl or I) on pyrolysis yield cleanly the corresponding monomethylplatinum(II) complexes with elimination of ethane [20–23]. We investigated a similar pyrolysis of the $Me_3Pt^{IV}$ complexes reported here containing neutral dinitrogen ligands, in the anticipation that they might give rise to corresponding monomethylplatinum(II) complexes, but this was shown not to be the case. Thus, when $Me_3PtI[py_2CH_2]$ was heated at 180–190 °C/0.1 mmHg for 1 h, no weight loss could be detected, but when it was heated at ~ 240 °C/0.1 mmHg it decomposed. Similarly, when the complex $[Me_3Pt[(Me_2pz)_2CH_2](acetone)][PF_6]$ was heated at ~ 100 °C, either as the solid or in 3-pentanone solution, no disproportionation could be observed, but on increasing the temperature in the range 120–140 °C, decomposition of the material also occurred. It is tempting to conclude that such general decomposition rather than clean reductive elimination is somehow associated with the presence of the chelating ligand.

There are two possible configurations, **A** and **B**, for the complex of the type $[Me_3Pt(NN)X]$ in which NN behaves as a bidentate ligand.

The $^1H$ NMR spectra of neutral complexes, $[Me_3Pt(NN)X]$ (X = Cl, I, $NO_3$, OAc) consist of two principal methyl–platinum resonances in the integral ratio of 2/1, each with satellites due to coupling between the methyl protons and the $^{195}Pt$ nuclei (Table 1). The peak at the lower frequency with relative integration 1 is due to



(A)



(B)

the methyl group *trans* to halogen and the resonance at higher frequency is due to the two methyl groups *trans* to the bidentate nitrogen ligand. Such a pattern has been observed for many trimethylplatinum(IV) complexes and configuration **A** has been indicated [4,22–25]. Our X-ray analysis of $Me_3PtI[(Me_2pz)_2CH_2]$ (**1**) establishes the structure as the isomer **A** type. Since the values of $^2J(^{195}Pt-^1H)$ for all of the neutral complexes are close to the values for **1**, it can be deduced that all of them also have the structure of isomer **A**. Resonances due to ligand protons appear at higher frequencies than those of free ligands.

The crystal structure of **1** consists of discrete monomeric molecules with a crystallographic mirror plane passing through the Pt, I, C(6) and C(7) atoms (Fig. 1). The Pt–I distance in **1** (2.843(1) Å) is one of the longest $Pt^{IV}$–I bond distances yet reported. Shorter $Pt^{IV}$–I distances have been observed in several octahedral $Pt^{IV}$ complexes where I is *trans* to ligands other than a methyl group. Previously reported values include: Pt–I 2.624(1) Å (I *trans* to O) in $Me_2PtI(O_2C_3H_7)(C_{12}H_8N_2)$ [9]; 2.646–2.654(1) Å (I *trans* to I) in $Me_2PtI_2[(Me_2pz)_2CH_2]$ (2.646 and 2.654(1) Å) [10], in $Me_2PtI_2[(pz_2CH_2)]$ (2.647 and 2.651(1) Å [10], in $PtI_6(phen)$ (2.662 and 2.677(2) Å) [26], in $PtI_5(phen)$ (2.667–2.669(2) Å [26] and in $PtI_2(en)_2 \cdot I_2 \cdot 2H_2O$ (2.681(1) Å) [27]. This long Pt–I bond distance provides the best illustration to date of the strong *trans*-influence [28] of the methyl group in $Pt^{IV}$ compounds.

The unique Pt–N distance in **1** 2.364(4) Å is exactly the same length (2.364(4) Å) found in the closely related complex $Me_2PtI_2[(Me_2pz)_2CH_2]$ [10] and is longer than that reported in the less crowded $Me_2PtI_2(pz_2CH_2)$ [10] system (2.183(3) Å). The Pt–C distance *trans* to I in **1** (2.077(6) Å) is significantly longer than the Pt–C distance *trans* to N (2.032(5) Å). Significantly longer Pt–C distances *trans* to N have been reported, e.g., 2.078(6) Å in $Me_2PtI_2[(Me_2pz)_2CH_2]$ [10], and 2.081(8) Å in $Me_2PtI_2(pz_2CH_2)$ [10].

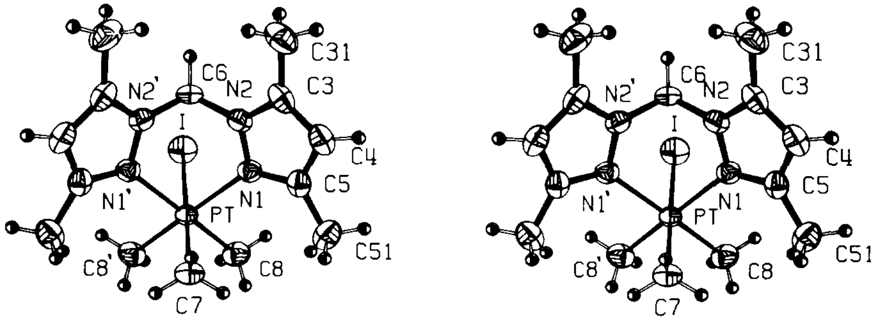


Fig. 1. A stereoview of the $Me_3PtI[(Me_2pz)_2CH_2]$ complex with the crystallographic numbering scheme.

The unique pyrazolyl ring is planar to within 0.002 Å with deviations of atoms not included in the mean-plane calculation: Pt 0.287, methylene C(6) − 0.044, methyl C(31) − 0.024 and methyl C(51) 0.044 Å. The molecular dimensions in the pyrazolyl ring are in accord with accepted values (N–N 1.359(5), N–C(mean) 1.341(6) and C–C(mean) 1.385(7) Å) (Table 4). The six membered ring, $PtN_4C$, has a boat conformation with the Pt...C(6) fold angle 119.7°.

The $^1H$ NMR spectra of the complexes, $[Me_3Pt(NNN)][PF_6]$ (NNN (all-*cis* ligands) = $pz_3CH$ or $py_3CH$), as anticipated, display only one platinum–methyl resonance with platinum satellites, and remain unchanged from room temperature down to −60 °C. Similarly, in the $^{13}C$ NMR spectra of these complexes only one Pt–C resonance is observed with $^1J(^{195}Pt-^{13}C)$ 688 ± 1Hz. The $\delta$(Pt–Me) and $^2J(^{195}Pt-^1H)$ values (Table 1) of $[Me_3Pt(NNN)][PF_6]$ are comparable to those observed in the analogous trimethylplatinum tris(1-pyrazolyl)borate [3].

The $^1H$ and $^{13}C$ NMR spectra of the cation $[Me_3Pt\{Me_2pz)_2CH_2\}(py)]^+$ can be compared with those from complexes of the type $[Me_3PtXL_2]$ or $[Me_3PtL_2L']^+$ [23,29,30]. Thus, two platinum–methyl resonances are observed in 2/1 ratio; in the $^1H$ NMR spectrum (Table 1) one maximum corresponds to two methyl groups *trans* to $(Me_2pz)_2CH_2$ ligand and the other to one methyl group *trans* to the pyridine ligand. Similarly in the $^{13}C$ NMR spectrum the resonance *trans* to the pyridine ligand appears at $\delta$ −8.7 with $^1J(^{195}Pt-^{13}C)$ 669 Hz and one *trans* to the $(Me_2pz)_2CH_2$ ligand appears at $\delta$ −2.9 with $^1J(^{195}Pt-^{13}C)$ 698 Hz. These data are only consistent with all-*cis* formulation for the methyl groups in $[Me_3Pt(Me_2pz)_2CH_2)(py)][PF_6]$.

## Acknowledgement

H.C. Clark and G. Ferguson are grateful to NSERC Canada for grants in aid of research.

TABLE 4

BOND DISTANCES (Å) AND ANGLES (°)

| | | | |
|---|---|---|---|
| Pt–I | 2.843(1) | N(2)–C(3) | 1.347(6) |
| Pt–N(1) | 2.236(4) | N(2)–C(6) | 1.457(5) |
| Pt–C(7) | 2.077(6) | C(3)–C(4) | 1.374(7) |
| Pt–C(8) | 2.032(5) | C(3)–C(31) | 1.493(6) |
| N(1)–N(2) | 1.359(5) | C(4)–C(5) | 1.396(7) |
| N(1)–C(5) | 1.336(6) | C(5)–C(51) | 1.468(7) |
| I–Pt–N(1) | 95.7(1) | N(1)–N(2)–C(3) | 112.7(4) |
| I–Pt–C(7) | 174.5(2) | N(1)–N(2)–C(6) | 119.3(4) |
| I–Pt–C(8) | 86.7(1) | C(3)–N(2)–C(6) | 128.0(4) |
| N(1)–Pt–C(7) | 88.3(2) | N(2)–C(3)–C(4) | 105.0(4) |
| N(1)–Pt–C(8) | 94.8(2) | N(2)–C(3)–C(31) | 123.6(5) |
| N(1)–Pt–C(8) [a] | 177.6(2) | C(4)–C(3)–C(31) | 131.4(5) |
| C(7)–Pt–C(8) | 89.3(2) | C(3)–C(4)–C(5) | 107.6(5) |
| N(1)–Pt–N(1) [a] | 84.7(2) | N(1)–C(5)–C(4) | 109.3(4) |
| C(8)–Pt–C(8) [a] | 85.6(3) | N(1)–C(5)–C(5) | 125.7(4) |
| Pt–N(1)–N(2) | 119.3(3) | C(4)–C(5)–C(51) | 125.0(5) |
| Pt–N(1)–C(5) | 134.4(3) | N(2)–C(6)–N(2) | 110.7(5) |
| N(2)–N(1)–C(5) | 105.5(4) | | |

[a] Primed atoms are related to the unprimed atoms by the transformation $x$, $1/2 - y$, $z$

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