Organoplatinum(IV) Compounds. 1. Preparation and Characterization of Dimethylplatinum(IV) Compounds with Chelating Nitrogen Donor Ligands. Crystal and Molecular Structures of Dimethyl[bis(1-pyrazolyl)methane]platinum Diiodide and Dimethyl[bis(3,5-dimethyl-1-pyrazolyl)methane]platinum Diiodide

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Compounds of the type $Me_2PtX_2(\overset{\frown}{NN})$ (where X = I or NO_3 and $\overset{\frown}{NN}$ = bis(1-pyrazolyl)methane, 2,2-bis(1-pyrazolyl)propane, bis(3,5-dimethyl-1-pyrazolyl)methane, bis(2-pyridyl)methane, and 2,2′-bipyridyl) have been prepared. The crystal and molecular structures of dimethyl[bis(1-pyrazolyl)methane]platinum diiodide, 1, and dimethyl[bis(3,5-dimethyl-1-pyrazolyl)methane]platinum diiodide, 2, have been determined. Crystals of 1 are orthorhombic of space group *Pnma* with four molecules with crystallographic mirror symmetry in a cell of dimensions a = 8.218 (2) Å, b = 13.146 (2) Å, and c = 13.453 (2) Å. Crystals of 2 are monoclinic of space group $P2_1/m$ with two molecules with crystallographic mirror symmetry in a cell of dimensions a = 7.420 (1) Å, b = 14.426 (3) Å, c = 8.686 (1) Å, and β = 100.90 (1)°. The structures were solved by the heavy-atom method and refined by full-matrix least-squares calculations: for 1, R = 0.034 for 1585 observed reflections; for 2, R = 0.036 for 2226 reflections. The analyses establish that in both the structures, platinum has an octahedral geometry with Me trans to the $\overset{\frown}{NN}$ ligand and that iodine occupies the axial positions. Principal dimensions are as follows: for 1, Pt–I = 2.651 and 2.647 (1) Å, Pt–N = 2.183 (7) Å, and Pt–C = 2.081 (8) Å; for 2, Pt–I = 2.654 and 2.646 (1) Å, Pt–N = 2.236 (4) Å, and Pt–C = 2.078 (6) Å.

Introduction

Although organoplatinum compounds have been known from a long time, organoplatinum(IV) had not been explored until the work of Gilman et al.[1] in 1953. Since then, a considerable amount of work has been done, particularly in the last decade. Most of the investigations conducted so far in the field of organoplatinum(IV) chemistry, describe the chemistry of triorganoplatinum(IV);[2–6] only a few attempts have been made to investigate and develop further the chemistry of organoplatinum(IV) compounds.[7–9]

In this paper we report the preparation and properties of dimethylplatinum(IV) compounds containing chelating $\overset{\frown}{NN}$ ligands and X-ray structural analyses of dimethyl[bis(1-pyrazolyl)methane]platinum diiodide, 1, and dimethyl[bis(3,5-dimethyl-1-pyrazolyl)methane]platinum diiodide, 2.

Results and Discussion

Our attempts to replace cyclooctadiene with bis(1-pyrazolyl)methane in $Me_2Pt(COD)$ in refluxing chloroform (30 min) were unsuccessful probably due to a very slow reaction. A similar type of reaction, which involves $Me_2Pt(COD)$ and 2,2′-bipyridyl, has been found to be very slow and reached completion in 3 weeks.[10] When PtMeCl(COD) is treated with silver hexafluorophosphate in acetone and bis(1-pyrazolyl)methane is then added, the product obtained is $[(PtMe(\overset{\frown}{NN})acetone)^+(PF_6)^-]_2[COD]$ (where $\overset{\frown}{NN}$ = bis(1-pyrazolyl)methane) instead of COD-free compound as reported with tris(1-pyrazolyl)methane[11] and tris(1-pyrazolyl)borate ligands.[12,13] Cyclooctadiene, however, can be replaced with iodine with the formation of platinum(IV) compounds. Thus compounds of the type $Me_2PtI_2(\overset{\frown}{NN})$ have been isolated by the reactions of $Me_2Pt(COD)$ with iodine in the presence of chelating nitrogen donor ligands in dichloromethane

$$Me_2Pt(COD) + \overset{\frown}{NN} + I_2 \xrightarrow{CH_2Cl_2} Me_2PtI_2(\overset{\frown}{NN}) + COD$$

(where $\overset{\frown}{NN}$ = bis(1-pyrazolyl)methane, bis(3,5-dimethyl-1-pyrazolyl)methane, 2,2-bis(1-pyrazolyl)propane, bis(2-pyridyl)methane, and 2,2′-bipyridyl).

This method appears to be particularly convenient for the preparation of dimethylplatinum(IV) compounds compared with other methods that are difficult and give low yields.

Iodine in $Me_2PtI_2(\overset{\frown}{NN})$ can be replaced by nitrate group by the addition of silver nitrate

$$Me_2PtI_2(\overset{\frown}{NN}) + 2AgNO_3 \rightarrow Me_2Pt(NO_3)_2(\overset{\frown}{NN}) + 2AgI$$

($\overset{\frown}{NN}$) = bis(3,5-dimethyl-1-pyrazolyl)methane).

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Table I. Dimethylplatinum(IV) Compounds of the Type $Me_2Pt(\widehat{NN})X_2$ with Chelating Nitrogen Donor Ligands

X	$(\widehat{NN})$ =	color	mp,[a] °C	anal. found (calcd)			δ(Me-Pt)	$^2J(^1H-^{195}Pt)$, Hz
				C	H	N		
I	bis(1-pyrazolyl)methane	brown	160-165	17.43 (17.24)	2.41 (2.25)	8.89 (8.93)	2.58	75.4
I	bis(3,5-dimethyl-1-pyrazolyl)-methane	orange	160-163	22.58 (22.85)	3.34 (3.24)	7.90 (8.20)	2.74	76.1
NO_3	bis(3,5-dimethyl-1-pyrazolyl)-methane	yellow	144-149	28.05 (28.21)	3.92 (4.01)		2.22	67.0[b]
I	bis(2-pyridyl)methane	brown	190-200	24.37 (24.05)	2.47 (2.48)	4.17 (4.31)	2.58	71.5
I	2,2′-bipyridyl	brown	155-160	23.19 (22.69)	2.15 (2.22)	4.31 (4.41)	2.40	73.2
I	2,2-bis(1-pyrazolyl)propane	orange	159-162	20.17 (20.16)	2.94 (2.78)	8.70 (8.55)	2.63	75.2

[a] Decomposition temperature. [b] 60 MHz.

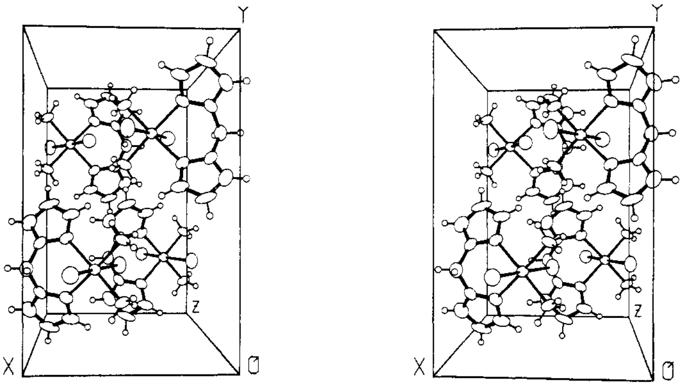
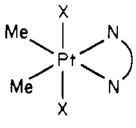


Figure 1. Stereoview of the packing of **1**.

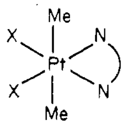
The dimethylplatinum(IV) compounds of the type $Me_2Pt_2X_2(N^\frown N)$ with chelating nitrogen donor ligands, which have now been prepared, are given in Table I along with their analytical data.

Dimethyl[bis(1-pyrazolyl)methane]platinum diiodide when heated under vacuum at ~160 °C eliminates mainly ethane (identified by infrared spectroscopy), indicating cis elimination of the methyl groups.[14] The remaining black solid gave irreproducible analytical results and was obviously a general, thermal decomposition product. Recently, photolysis reactions of di- and trimethylplatinum(IV) compounds have been investigated, and ethane formation has been observed.[15]

Three geometrical isomers (A–C) of $Me_2PtX_2(N^\frown N)$ are possible in which $N^\frown N$ behaves as a bidentate ligand.



A



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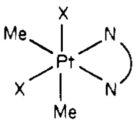

C

The ^1H NMR spectra of these compounds in CD_2Cl_2 indicate the presence of only one isomer in solution since only a single methyl–platinum resonance with ^{195}Pt satellites could be observed. Isomer C can be ruled out, since for this isomer two nonequivalent methyl–platinum resonances with different coupling constants are expected. Structure B, although symmetrical, contains two bulky iodo groups in cis positions and hence may be less likely than isomer A. The observed magnitude of coupling constant ($^2J(^{195}Pt-^1H)$) is also consistent with structure A as reported for Me_2Pt^{IV} compounds in which methyl groups are cis and halogens trans;[8,16] resonances due to ligand protons appear at higher frequencies than those of free ligands. Our X-ray analyses establish that our products have the structure of isomer A.

Table II. Interatomic Distances (Å) and Angles (deg) in $Me_2Pt(pz_2CH_2)I_2$ (**1**) and $Me_2Pt[(Me_2pz)_2CH_2]I_2$ (**2**) with Estimated Standard Deviations in Parentheses[a]

	1	2
a. Bond Distances		
Pt-I(1)	2.651 (1)	2.654 (1)
Pt-I(2)	2.647 (1)	2.646 (1)
Pt-N(1)	2.183 (7)	2.236 (4)
Pt-C(1)	2.081 (8)	2.078 (6)
N(1)-N(2)	1.332 (10)	1.358 (5)
N(1)-C(5)	1.297 (12)	1.350 (6)
N(2)-C(2)	1.467 (11)	1.430 (5)
N(2)-C(3)	1.330 (13)	1.348 (6)
C(3)-C(4)	1.361 (18)	1.383 (7)
C(4)-C(5)	1.351 (16)	1.384 (7)
C(3)-C(6)		1.489 (7)
C(5)-C(7)		1.487 (7)
b. Bond Angles		
I(1)-Pt-I(2)	174.9 (1)	175.1 (1)
I(1)-Pt-N(1)	94.6 (2)	95.0 (1)
I(1)-Pt-C(1)	87.3 (3)	85.8 (2)
I(2)-Pt-N(1)	89.2 (2)	88.6 (1)
I(2)-Pt-C(1)	89.1 (3)	90.7 (2)
N(1)-Pt-C(1)	92.7 (3)	93.7 (2)
$N(1)-Pt-N(1)^I$	84.4 (4)	85.8 (2)
$C(1)-Pt-C(1)^I$	90.2 (5)	86.8 (4)
Pt-N(1)-N(2)	123.4 (6)	119.1 (3)
Pt-N(1)-C(5)	131.1 (7)	134.8 (3)
N(2)-N(1)-C(5)	104.6 (8)	105.7 (4)
N(1)-N(2)-C(2)	119.8 (8)	120.5 (5)
N(1)-N(2)-C(3)	111.3 (8)	111.1 (4)
C(2)-N(2)-C(3)	128.9 (9)	128.3 (5)
$N(2)-C(2)-N(2)^I$	112.4 (11)	113.9 (6)
N(2)-C(3)-C(4)	106.8 (9)	107.0 (4)
N(2)-C(3)-C(6)		123.4 (5)
C(4)-C(3)-C(6)		129.5 (5)
C(3)-C(4)-C(5)	104.4 (9)	105.9 (5)
N(1)-C(5)-C(4)	112.9 (11)	110.2 (5)
N(1)-C(5)-C(7)		124.4 (5)
C(4)-C(5)-C(7)		125.3 (5)
c. van der Waals Contacts		
Molecule 1		
I(1)· · ·H(21)	2.837	
$I(2)\cdots H(22)^I$	3.155	
Molecule 2		
I(1)· · ·H(21)		2.723
$I(2)\cdots H(22)^{II}$		3.040

[a] Superscripts I and II refer to the symmetry transformations 1 + *x*, *y*, *z* and *x*, *y*, 1 + *z*, respectively.

The crystal structures of **1** and **2** (Figures 1 and 2, respectively) consist of discrete monomeric molecules (Fig-

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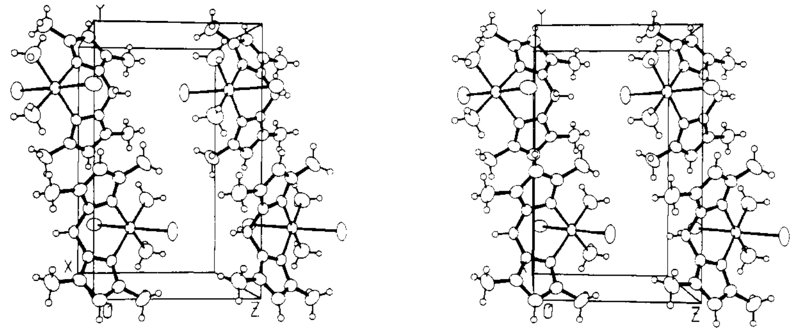

Figure 2. Stereoview of the packing of **2**.

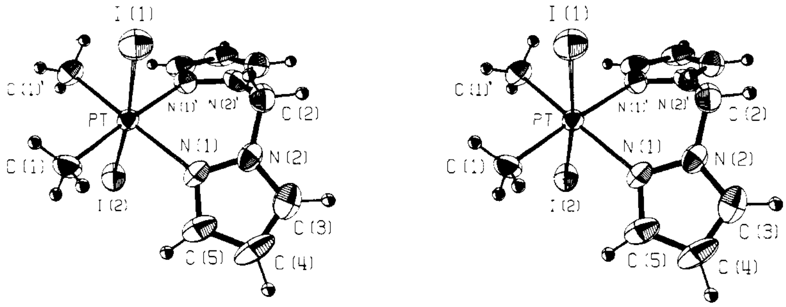

Figure 3. Stereoview of a molecule of **1**.

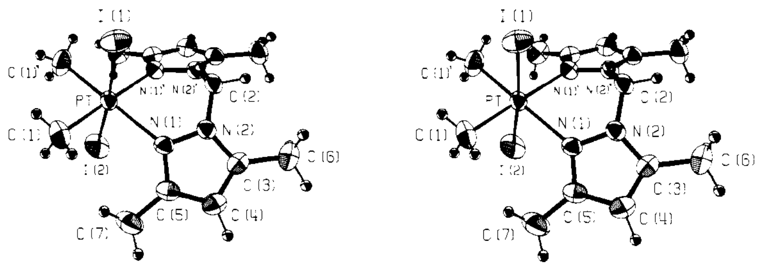

Figure 4. Stereoview of a molecule of **2**.

ures 3 and 4, respectively) with the two iodine ligands, trans octahedrally coordinated to the $\mathrm{Me_2Pt(N\frown N)}$ moiety. In both the structures, Pt, I(1), I(2), and C(2) lie on crystallographic mirror planes. The principal coordination dimensions for **1** and **2** are given in Table II. The Pt–I distances (2.651 (1), 2.647 (1), and mean 2.649 Å in **1** and 2.654 (1), 2.646 (1), and mean 2.650 Å in **2**) are essentially identical and are close to the values found for the terminal $\mathrm{Pt^{IV}}$–I bonds in $\mathrm{Pt(C_{10}H_{14}O_4)I_2}$ (2.667 (1) Å),[17] $\mathrm{Pt(phen)I_6}$ and $\mathrm{Pt(phen)I_5}$ (range 2.662–2.669 (2) Å),[18] $\mathrm{(C_5H_5NH_2)PtI_6}$ (range 2.661–2.670 (1) Å),[19] and $\mathrm{(PtI_4)_\infty}$ (2.62 Å)[20] and to the sum of the covalent radii (2.64 Å).[21] In both molecules, the Pt–I(2) bond is essentially normal to the $\mathrm{PtC_2N_2}$ coordination plan (deviations 0.0 (9) and 1.5 (6)° in **1** and **2**, respectively, whereas the Pt–I(1) bond is significantly off the plane normal (deviations 5.1 (9) and 6.4 (6)° in **1** and **2**, respectively) with N(1)–Pt–I(1) = 94.6 and 95.2°, and C(1)–Pt–I(1) = 87.3 and 85.8° in **1** and **2**, respectively. This small bending places the iodine I(1) at greater distance from the axial hydrogen on C(2) in both molecules and results in I(1)···H(21) intramolecular contacts of 2.84 and 2.72 Å in **1** and **2**, respectively, which are still less than the sum of the van der Waals radii.

The Pt–C distances 2.081 (8) Å in **1** and 2.078 (6) Å in **2** are not significantly different and agree with the sum of the covalent radii (2.08 Å).[21]

The major difference between **1** and **2** is in the overcrowding in the $\mathrm{Me_2PtN_2}$ moiety, caused by the presence of additional methyl groups, which leads to interactions between the C(1) and C(7) methyl groups in **2**. This manifests itself in significant bond length extension and bond angle changes to overcome overcrowding. Thus, the Pt–N distance in **2** (2.236 (4) Å) is 0.053 Å longer than the distance in **1** (2.183 (3) Å). Both distances are somewhat longer than the Pt–N distances reported for a number of Pt(IV) complexes, e.g., $\mathrm{Pt(NH_3)_2(2,4\text{-}pentanediiminate)_2(ClO_4)_2}$ (2.002 (4) Å),[22] $\mathrm{Pt[(en)_2Cl_2](CuCl_4)\cdot H_2O}$ (2.074 and 2.087 (12) Å),[23] and $\mathrm{Pt(phen)I_6}$ and $\mathrm{Pt(phen)I_5}$ (range 2.06–2.12 (2) Å).[18] Concomitant with the bond length extension on going from **1** to **2**, there is a 3.4° decrease in the Me–Pt–Me angle, a 4.3° decrease in the Pt–N(1)–N(2) angle, and a 3.7° increase in the Pt–N(1)–C(5) angle, which all have the effect of minimizing C(1)···C(7) interactions. There is also some out-of-plane bending in **2**, C(7) is 0.08 Å out of the N(1), N(2), C(3), C(4), C(5) plane away from

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Table III. Deviations of Atoms from the Least-squares Planes

atom[b]	dev, Å 1	dev, Å 2
(a) PtN_2C_2 Plane		
equation[a] for molecule 1: $4.0486X + 0.0Y + 11.7072Z = 0.7479$		
equation for molecule 2: $5.3277X + 0.0Y - 7.115\,92Z = -1.0682$		
Pt	0.026	0.011
C(1)	−0.007	−0.003
$C(1)^I$	−0.007	−0.003
N(1)	−0.006	−0.003
$N(1)^I$	−0.006	−0.003
I(1)[c]	2.666	2.649
I(2)[c]	−2.620	−2.634
(b) N(1), N(2), C(3), C(4), C(5) Plane		
equation for molecule 1: $-1.8200X + 6.3150Y - 11.4167Z = 0.8663$		
equation for molecule 2: $-5.9208X + 6.3361Y + 4.8312Z = 1.8073$		
N(1)	0.001	0.002
N(2)	−0.003	−0.004
C(3)	0.003	0.005
C(4)	−0.003	−0.003
C(5)	0.001	0.001
C(6)[c]		0.004
C(7)[c]		0.080
Pt[c]	0.313	0.235

[a] In the plane equation, X, Y, and Z are the fractional coordinates given in Table IV. [b] Superscript I refers to the symmetry transformation x, $^1/_2 - y$, z. [c] Atoms not included in the mean-planes calculations.

the C(1) methyl group (Table III), whereas C(6), which is not affected by overcrowding, lies in the ring plane. Interestingly, the six-membered PtN_4C ring has essentially the same boat conformation in both molecules, the Pt···C(2) fold angle being 131.1° in **1** and 130.3° in **2**.

In both molecules the individual pyrazolyl rings are planar to within 0.004 and 0.005 Å in **1** and **2**, respectively (Table III), with N–N = 1.332 and 1.358 (5) Å, N–C(mean) = 1.365 and 1.379 (6) Å, and C–C(mean) = 1.356 and 1.384 (7) Å in **1** and **2**, respectively, in accord with accepted values.

Although the crystals have different space groups, their crystal packing share certain common features; there are intermolecular contacts between iodine and the hydrogen atom H(22) of the pyrazolylmethane carbon C(2) (3.16 and 3.04 Å in **1** and **2**, respectively, Table II) that are just less than the sum of the H and I van der Waals radii (3.35 Å),[21], and the pyrazolyl rings pack about inversion centers with plane-to-plane separation of 3.55 and 3.61 Å for **1** and **2**, respectively.

Experimental Section

(π-1,5-Cyclooctadiene)dimethylplatinum(II) was prepared by the method reported by Clark and Manzer;[24] bis(1-pyrazolyl)methane[25] and bis(2-pyridyl)methane[26,27] were prepared by the literature methods. Bis(3,5-dimethyl-1-pyrazolyl)methane and 2,2-bis(1-pyrazolyl)propane were obtained from Columbia Organic Chemical Inc., and 2,2′-bipyridyl was obtained from Aldrich. Infrared spectra were recorded on Perkin-Elmer 180 spectrophotometer using KBr cells. ^1H NMR spectra were recorded on Bruker WH-400 and WP-60 NMR spectrometers. Chemical shifts in CD_2Cl_2 were measured relative to external Me_4Si. Microanalyses were performed by Guelph Chemical Laboratories. Melting points were determined in a capillary tube and are uncorrected.

Preparation of Dimethyl[bis(1-pyrazolyl)methane]platinum Diiodide. To the dichloromethane solution (~3 ml) of $Me_2Pt(COD)$ (84 mg) and bis(1-pyrazolyl)methane (44 mg) was added a dilute solution of iodine (75 mg of iodine in ~10 mL of dichloromethane) dropwise with stirring at room temperature until the violet color of iodine persisted. The reactants were stirred for 30 min to ensure the completion of the reaction. The solvent was removed under vacuum; the residue was washed thoroughly with hexane and then recrystallized from dichloromethane as a brown crystalline solid (yield 133 mg, 70%).

Similarly, other diiodides were prepared and were recrystallized from dichloromethane in 55–80% yield. Pertinent data for these complexes are given in Table I.

Preparation of Dimethyl[bis(3,5-dimethyl-1-pyrazolyl)methane]platinum Dinitrate. To the dichloromethane solution (~15 mL) of dimethyl[bis(3,5-dimethyl-1-pyrazolyl)methane]platinum diiodide (103 mg) was added excess silver nitrate (150 mg) aqueous solution (~5 mL). Reactants were stirred for 90 min. The dichloromethane layer was separated from water, filtered, and then evaporated under vacuum, leaving a yellow solid which was recrystallized from a dichloromethane–hexane mixture (yield 65 mg, 78%).

Pyrolysis of Dimethyl[bis(1-pyrazolyl)methane]platinum Diiodide. Dimethyl[bis(1-pyrazolyl)methane]platinum diiodide (107.2 mg) was placed in a 25-mL round-bottom flask. The flask was evacuated and placed in an oil bath that was then heated to ~160 °C for about 30 min. The gases evolved were trapped at liquid-nitrogen temperature and then condensed in an infrared cell. A blackish solid residue (84.4 mg) was left in the flask, the composition of which varied from sample to sample (typical anal.: C, 15.99; H, 1.52; N, 9.84). From this blackish residue, a small amount of yellowish product could be extracted with dichloromethane (found: C, 22.71; H, 2.79; N, 12.14).

Crystal Structure Analyses. (a) $Me_2PtI_2(pz)_2CH_2$ (1). Crystal Data: $C_9H_{14}I_2N_4Pt$; $M_r = 636.1$; orthorhombic; $a = 8.218$ (2) Å, $b = 13.146$ (2) Å, $c = 13.453$ (2) Å; $U = 1453.4$ Å^3; $Z = 4$, D(calcd) = 2.91 g cm^{-3}; $F(000) = 1104$; Mo Kα radiation, $\lambda = 0.710\,69$ Å; μ(Mo Kα) = 144.4 cm^{-1}; space group $Pnma$ or $Pn2_1a$ from systematic absences $0kl$ if $k + l = 2n + 1$ and $hk0$ if $h = 2n + 1$; the former was chosen and confirmed by the analysis.

(b) $Me_2PtI_2(Me_2pz)_2CH_2$ (2). Crystal Data: $C_{13}H_{22}I_2N_4Pt$; $M_r = 683.2$; monoclinic; $a = 7.420$ (1) Å, $b = 14.426$ (3) Å, $c = 8.686$ (1) Å; $\beta = 100.90$ (2)°; $U = 913.0$ Å^3, $Z = 2$, D(calcd) = 2.49 g cm^{-3}; $F(000) = 616$; Mo Kα radiation, $\lambda = 0.710\,69$ Å; μ(Mo Kα) = 115.0 cm^{-1}; space group $P2_1/m$ or $P2_1$ from systematic absences $0k0$ if $k = 2n + 1$; the former was chosen and confirmed by the analysis.

For both structures, accurate cell parameters were obtained by a least-squares refinement of the setting angles of 25 reflection (with θ in the range 10–15°) measured on an Enraf-Nonius CAD4 diffractometer. Intensity data were collected by the $\omega/2\theta$ scan method using monochromatic Mo K_α radiation. In each case, the intensities of three reflections, chosen as standards, were monitored every hour of exposure time and showed no significant variation. Intensity data were collected to a maximum θ of 30°; 2200 unique data were collected for **1** and 2755 for **2**. After corrections for Lorentz, polarization, and absorption effects, the data with $I > 3\sigma(I)$ (1585 for **1**, 2226 for **2**) were labeled observed and used in structure solution and refinement. Minimum and maximum values of the transmission coefficients are 0.057 and 0.154 for **1** and 0.031 and 0.122 for **2**, respectively.

Both structures were solved by the heavy-atom method, and Fourier maps based on platinum phases revealed the complete structures.[28] Refinement by full-matrix least-squares calculations with anisotropic thermal parameters for the non-hydrogen atoms lowered R to 0.082 for **1** and 0.066 for **2**. Difference maps then

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Table IV. Final Fractional Coordinates (×10⁵ for Pt and I, ×10⁴ for Others) with Estimated Standard Deviations in Parentheses

atom	*x*	*y*	*z*
		$Me_2Pt(pz_2CH_2)I_2$ (1)	
Pt	16712 (5)	25000	832 (3)
I(1)	30046 (12)	25000	18774 (6)
I(2)	840 (11)	25000	−16285 (6)
N(1)	3364 (8)	1384 (6)	−530 (5)
N(2)	4939 (9)	1572 (6)	−674 (6)
C(1)	96 (11)	1379 (6)	600 (7)
C(2)	5670 (17)	2500	−264 (11)
C(3)	5640 (13)	835 (9)	−1199 (7)
C(4)	4464 (18)	134 (7)	−1394 (8)
C(5)	3109 (14)	520 (7)	−968 (7)
		$Me_2Pt[(Me_2pz)_2CH_2]I_2$ (2)	
Pt	11279 (4)	25000	23304 (3)
I(1)	35340 (9)	25000	4249 (8)
I(2)	−10304 (13)	25000	44310 (7)
N(1)	−725 (6)	1445 (3)	962 (4)
N(2)	−1658 (6)	1669 (3)	−489 (4)
C(1)	2815 (9)	1511 (5)	3612 (7)
C(2)	−1231 (11)	2500	−1244 (8)
C(3)	−2862 (7)	999 (4)	−1067 (6)
C(4)	−2686 (8)	303 (4)	46 (7)
C(5)	−1359 (8)	604 (4)	1284 (6)
C(6)	−4085 (8)	1050 (5)	−2635 (6)
C(7)	−789 (9)	107 (5)	2798 (7)

revealed all hydrogen atoms; these were allowed for (in geometrically idealized positions with C–H = 0.95 Å and an overall U_{iso} was refined in each case) in subsequent calculations. For 1, refinement converged at $R = 0.034$ and $R_\omega = (\sum\omega\Delta^2/\sum\omega F_o^2)^{1/2} = 0.043$; for 2, the final R and R_ω values were 0.036 and 0.038 respectively. In the least-squares calculations, scattering factors for Pt, I, N, and C were taken from ref 29; those for hydrogen were from ref 30, and allowance was made for anomalous dispersion.[31] Weights in the refinement were based on counting statistics [$\omega = 1/\sigma^2(F)$], and final difference syntheses were devoid of any significant features.

Final fractional coordinates for 1 and 2 are in Table IV. Thermal parameters, calculated hydrogen coordinates, and structure factor listings are available as supplementary material.

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Registry No. 1, 84987-14-4; 2, 84987-15-5; $Me_2Pt[(Me_2pz)_2CH_2]_2(NO_3)_2$, 84987-16-6; $Me_2P(\overset{\frown}{N\,N})I_2$ ($\overset{\frown}{N\,N}$ = bis(2-pyridyl)methane), 84987-17-7; $Me_2Pt(\overset{\frown}{N\,N})I_2$ ($\overset{\frown}{N\,N}$ = 2,2′-bipyridyl), 85027-40-3; $Me_2Pt(\overset{\frown}{N\,N})I_2$ ($\overset{\frown}{N\,N}$ = 2,2-bis(1-pyrazolyl)propane), 84987-18-8.

Supplementary Material Available: Tables of thermal parameters, calculated hydrogen coordinates, and structure factors (9 pages). Ordering information is given on any current masthead page.

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(α-Haloethyl)silanes Optically Active at Carbon and at Silicon. Synthesis and Absolute Configuration

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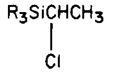
A synthetic sequence that is stereospecific at silicon was utilized to prepare 1-naphthylphenylmethyl(1-chloroethyl)silane, 1, and 1-naphthylphenylmethyl(1-bromoethyl)silane, 2, as a mixture of diastereomers. Crystallization from hexane gave 1 and 2 as pure diastereomers, the structures of which were determined by X-ray analysis.

Introduction

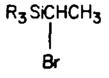
The interest in α-halo organosilanes has come from the synthetic organic chemists due to their being precursors to α-metalated organosilanes, useful in the Peterson olefination reaction[2] and more recently as synthons for aldehydes or ketones as shown by the Magnus group.[3] In addition the mechanistic organosilicon chemists have studied the intramolecular rearrangements in these systems under a variety of conditions in order to better understand these processes, which, although they have synthetic potential, have not been exploited in this way as yet.

We have recently become interested in the possibility of utilizing carbofunctional organosilanes optically active at silicon in order to better understand the mechanistic routes of certain reactions of carbofunctional organosilanes and to be able to investigate the potential of a chiral silyl group in asymmetric induction. We wish to report herein on the preparation of (*S*)-Si(*S*)-1-naphthylphenylmethyl-(α-chloroethyl)silane, **1a** (*R*)-Si(*R*)-1-naphthylphenylmethyl-(α-chloroethyl)silane, **1b**, and (*R*)-Si(*R*)-1-naphthylphenylmethyl(α-bromoethyl)silane, **2**, and their absolute configurations.



$\mathrm{R_3Si}\underset{\substack{|\\ \mathrm{Cl}}}{\mathrm{C}}\mathrm{HCH_3}$

1a (*S*,*S*)
1b (*R*,*R*)



$\mathrm{R_3Si}\underset{\substack{|\\ \mathrm{Br}}}{\mathrm{C}}\mathrm{HCH_3}$

2 (*R*,*R*)

R_3Si = 1-NpPhMeSi

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