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FORMATION OF DIMETHYLAMINE COMPLEXES OF TRIMETHYLPLATINUM(IV) FROM REACTIONS WITH *N,N,N′,N′*-TETRAMETHYLDIAMINOMETHANE

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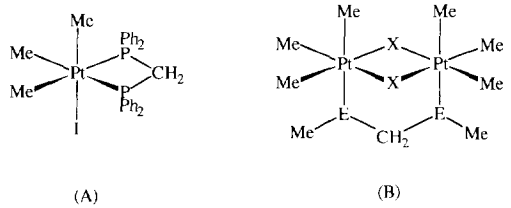
Abstract—Attempts to prepare complexes of trimethylplatinum(IV) with *N,N,N′,N′*-tetramethyldiaminomethane (TMDM) as either a chelating or bridging ligand gave only the complexes of dimethylamine $[PtMe_3X(HNMe_2)]_2$ (X = Cl, Br and I; **1–3** and $[PtMe_3(2,2'\text{-bipyridyl})(HNMe_2)]^+[BF_4]^-$ (**4**). ^1H NMR evidence showed that only one of the two possible isomers was formed for **1–3**.

Trimethylplatinum(IV) halide complexes containing the bidentate ligands $Y_nECH_2EY_n$ can be either mononuclear with a chelated ligand (E = P; Y = Ph; $n = 2$)[1] (Fig. 1, **A**), or binuclear with a bridged ligand (E = S, Se; Y = Me; $n = 1$)[2] (Fig. 1, **B**). We are unaware of any examples of such a ligand giving both types of complex. However, 1,2-diaminoethane (en) does exhibit both modes[3] in $[(PtMe_3)_2(en)_3]^{2+}$. It was therefore of interest to investigate the trimethylplatinum(IV) complexes of the analogous ligand *N,N,N′,N′*-tetramethyldiaminomethane ($Me_2NCH_2NMe_2$, TMDM), which usually forms carbene[4] complexes. However, there is evidence[5,6] that it acts as an N—N bidentate chelate in $MCl_4 \cdot TMDM$ (M = Ti, Sn) and Ni $(TMDM)_2(ClO_4)_2$, and possibly has a bridging role in $[(Me_3M)_2TMDM]$ (M = Al, Ga, In).[7]



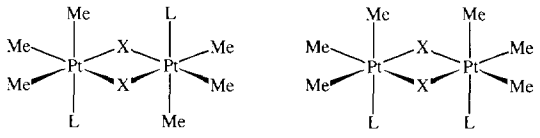
(A) (B)

Fig. 1. Chelate (**A**) and bridged (**B**) trimethylplatinum(IV) halide complexes of the bidentate ligands $Y_nECH_2EY_n$ (E = P; Y = Ph; $n = 2$: E = S, Se; Y = Me; $n = 1$).

RESULTS AND DISCUSSION

The reactions between the trimethylplatinum(IV) halides and either a stoichiometric or excess amount of TMDM in chloroform gave only a single, unexpected dinuclear product $[PtMe_3X(Me_2NH)]_2$ **1–3**; X = Cl, Br, I) similar to the dinuclear complexes $[PtMe_3IL]_2$, L = NH_3, $MeNH_2$, 3,5-lutidine and pyridine[8] (**A** or **B** in Fig. 2). When the reaction was carried out in benzene under nitrogen with rigorous exclusion of moisture, the trimethylplatinum(IV) halide was recovered unchanged.

A product identical to that formed from $[PtMe_3I]_4$ and tetramethyldiaminomethane was prepared from the reaction between $[PtMe_3I]_4$ and dimethylamine (IR and NMR data). From this



(A) (B)

Fig. 2. *Trans* (**A**) and *cis* (**B**) isomers of the halide-bridged complexes $[PtMe_3XL]_2$ (X = Cl, Br, I; L = NH_3, $MeNH_2$, 3,5-lutidine and pyridine).

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reaction also, NMR evidence showed that only one of the two possible isomeric products (Fig. 2) was obtained. An indication of the stability of the dinuclear halide-bridged complexes with amine ligands is given by the reaction of $[PtMe_3I]_4$ with an ethanolic solution of methylamine,[8] which gives a mixture of $[PtMe_3(MeNH_2)_3]^+$ and $[PtMe_3X(MeNH_2)]_2$, the mononuclear bis complex $[PtMe_3X(MeNH_2)_2]$ being inaccessible by this procedure.

The identity of products **1** and **2** as adducts of dimethylamine was confirmed by microanalyses, molar mass measurements in chloroform solution (Table 1), and by IR and NMR data. Poor analytical figures for the iodide (**3**) suggest that it slowly loses the amine ligand on standing, but its molar mass (found : 830; required : 836) and spectroscopic properties show that it has a bridged structure analogous to that of the chloride and bromide. The instability of the iodide complex, with reversion to tetrameric $[PtMe_3I]_4$, is consistent with the relative strengths of the metal to halide bonds[2] in $Pt^{IV}Me_3$ halide complexes (Cl < Br < I) revealed by the ^2J(PtH) coupling constants for the *trans* methyl groups. The complexes are air-stable (except the iodide), white or creamy-white crystalline solids, which do not melt but decompose above *ca* 230°C. All are soluble in common organic solvents.

The IR spectra of the complexes contain fewer bands than other trimethyplatinum(IV) diamino complexes,[9] and remain essentially unchanged above 600 cm^{-1} on varying the halide. The two N—H stretching modes seen at 3284 and 3250 cm^{-1} in the case of the bromide move to lower wavenumbers on deuteriation [ν(N—H)/ν(N—D) = 1.36]. The other bands in the spectra are readily attributable to ligand and platinum–methyl vibrations but are not diagnostically useful.

A stretching mode at 572, 567 and 563 cm^{-1} for the chloride, bromide and iodide respectively may be tentatively assigned to a Pt—C stretch, the frequency decreasing from X = Cl to X = I, i.e. increasing *trans* influence[10] of the halide.

The ^1H NMR data (Table 2) are consistent with the proposed structure for compounds **1–3**. Each methyl platinum signal in trimethylplatinum(IV) compounds consists of a two overlapping subspectra in a 2 : 1 intensity ratio. These subspectra result from methyls bound to NMR-inactive platinum nuclides (66.2%) and methyl groups bound to ^{195}Pt ($I = 1/2$) (33.8%), respectively. The ^{195}Pt–^1H scalar coupling constants (^2J) are strongly dependent on the nature of the *trans* atom.[11] Only two platinum–methyl signals are observed in the intensity ratio 2 : 1, which suggests that only one of the two possible isomers distinguishable by NMR spectroscopy (Fig. 2) is present.

The most intense, high field resonance in the NMR spectra of **1–3** is assigned to a methyl group *trans* to the bridging halide. With the single exception of complexes of pyridazines,[12] methyls *trans* to halide invariably resonate at lowest frequency in adducts of the trimethylplatinum(IV) halides with nitrogen donor ligands.[1] The $^2J(^{195}Pt$–$^1H)$ values for the equatorial platinum methyl groups are typical for methyls *trans* to bridging halides, and are higher than those observed in complexes with terminal halides, e.g. $[PtMe_3Ipy]_2$ and $[PtMe_3Ipy_2]$ have $^2J = 75.5$ and 69.6 Hz respectively for methyls *trans* to iodine.[8]

Table 1. Analytical data for the trimethylplatinum(IV) dimethylamine complexes **1–4**

Complex	Yield (%)	Melting point (°C)	Elemental analysis[a] C	H	N	X	Molar mass[b]
$[PtMe_3Cl(Me_2NH)]_2$ (**1**)	60	228[c]	18.7 (18.7)	5.0 (5.0)	4.4 (4.4)	11.3 (11.1)	624 (641)
$[PtMe_3Br(Me_2NH)]_2$ (**2**)	59	235[c]	16.4 (16.4)	4.4 (4.4)	3.8 (3.8)	21.2 (21.9)	725 (730)
$[PtMe_3I(Me_2NH)]_2$ (**3**)[d]	54	240[e]	12.5 (14.6)	3.4 (3.4)	1.8 (3.4)		830 (836)
$[PtMe_3(2,2'\text{-bipy})(HNMe_2)]^+[BF_4]^+$ (**4**)	79	185–186[e]	34.2 (34.1)	4.6 (4.6)	7.9 (8.0)		

[a] Calculated values in parenthesis.
[b] Osmometrically in chloroform solution at 28°C.
[c] Decomposition temperature without melting.
[d] Loses dimethylamine on standing (see text).
[e] Melts with decomposition.

Table 2. ^{1}H NMR data[a] for the diethylamine complexes **1–4**

Complex	Relative intensity	*Trans* atom	$\delta(PtCH_3)$	$^2J(PtCH_3)$ (Hz)	$\delta(NCH_3)$	$^3J(PtNCH_3)$ (Hz)	$^3J(HNCH_3)$ (Hz)
1[b]	2	Cl	0.95	77.8	2.64	14.7	6.3
	1	N	1.20	68.7			
2[b]	2	Br	1.04	77.2	2.69	14.9	6.1
	1	N	1.39	69.3			
3[b]	2	I	1.19	75.9	2.78	14.7	6.0
	1	N	1.73	70.4			
4[c]	1	N[d]	0.29	68.7	2.02	13.5	6.2
	2	N[e]	1.08	67.7			

[a] ^{1}H NMR spectra recorded at ambient temperature; chemical shifts quoted relative to TMS as an internal standard.
[b] Spectrum run in $CDCl_3$.
[c] Spectrum run in CD_3OD; signals from 2,2′-bipyridyl: H^6, 8.92, $^3J(HH^5)$ 6.3 Hz, $^3J(PtH) \approx 18$ Hz; H^3, 8.71, $^3J(HH^4)$ 8.16 Hz; H^4, 8.36, $^3J(HH^5)$ 7.9 Hz; H^5, 7.90, $^3J(HH^5)$ 7.9 Hz, $^3J(HH^6) \approx 6.3$ Hz.
[d] *Trans* to $HNMe_2$.
[e] *Trans* to bipyridyl.

The ligand N-methyl resonances of **1–3** appear as two overlapping 'triplets' owing to coupling to both ^{195}Pt and ^{1}H. The pattern changes on addition of D_2O to a single *ca* 1:4:1 'triplet' and therefore the N-methyl groups must be equivalent. This observation is consistent with free rotation of the diamine ligand around the Pt—N bond, or a fixed conformation in which the methyl groups are equivalent, as reported for the compounds *trans*-$[Pt(HNMe_2)_2(NH_3)_2]Cl_2$[13] and *cis*-$[Pt(HNMe_2)_2Cl_2]$[14] in the solid state. This also helps to confirm that the complexes are binuclear, as in the mononuclear bis-complex $[PtMe_3X(Me_2NH)_2]$, the N-methyl groups are not related by a plane of symmetry, and would be non-equivalent whatever the conformation about the Pt—N bond.

^{1}H NMR spectra[8] of the dinuclear species $[PtMe_3IL]_2$, where L = pyridine and 3,5-lutidine, showed that both of the possible isomers were present, with the *trans* species (Fig. 2, **A**) predominating. There was also evidence for an additional equilibrium of these isomers with both $[PtMe_3IL_2]$ and $[PtMe_3I]_4$. Such equilibria are not observed here, and the complexes **1–3** are stereochemically rigid in solution. This was demonstrated by a variable-temperature study on the complex $[PtMe_3Br(HNMe_2)]_2$ in $CDCl_3$ (−72 to +51°C) which showed no change in the spectrum over this temperature range. The absence of a similar equilibrium in the case of compounds **1–3** would suggest that they have configuration **B**, the reaction stopping before complete disruption of the tetramer can take place.

A related observation was made in an attempt to bridge the complex ion $[PtMe_3(2,2'\text{-bipyridyl})]^+$ with TMDM. When THF was used as solvent, only platinum black resulted. In methanol, however, the dimethylamine complex $[PtMe_3(2,2'\text{-bipyridyl})(HNMe_2)]^+$ was isolated as the $[BF_4]^-$ salt (**4**). Analytical and spectroscopic data are consistent with the formulation of **4** as an ionic salt containing monodentate dimethylamine. Bands in the IR of **4** at 3285 (N—H stretch), 2867, 2900, 2820 (PtC—H stretch) and 578 cm^{-1} (Pt—C stretch) are similar to those of **1–3**. In addition, two Pt—N stretching modes can be tentatively assigned at 424 and 369 cm^{-1}.

The ^{1}H NMR spectrum of **4** in CD_3OD shows one set of signals due to the trimethylplatinum groups in a 2:1 intensity ratio with $^2J(^{195}Pt\text{–}H)$ values of 67.7 Hz (*trans* to bipyridyl) and 68.7 Hz (*trans* to $HNMe_2$), respectively. The N-methyl resonance again consisted of two overlapping signals due to coupling to ^{195}Pt ($^3J = 13.5$ Hz) and ^{1}H ($^3J = 6.2$ Hz), the latter coupling being lost on treatment of the sample with D_2O. The NH signal appeared as a broad band at *ca* δ3.8. The spectrum of the bipyridyl ligand could be completely assigned (Table 2).

Compounds **1–4** are the first trimethylplatinum(IV) complexes containing the ligand dimethylamine. The values of $^2J(^{195}Pt\text{–}H)$ for methyls *trans* to the amine (68.7–70.4 Hz) suggest that this ligand is a comparable σ-donor to primary amines for which values in the range 67.1–71.8 Hz have been observed.[9]

The formation of dimethylamine from TMDM in these syntheses implies the ready cleavage of the C—N bond expected for an aminal, which is known to occur in acid solution[15] and in the Mannich reac-

Table 3.

Run	Atmosphere	Ethanol	Water	Product
1	air	✓	✓	✓
2	air	×	✓	✓
3	air	×	×	✓
4	N_2	×	✓	×
5	N_2	✓	✓	×

tion[16] of carbonyl compounds using TMDM as a base. In an attempt to identify the other product from the cleavage reaction, experiments were carried out in which $[PtMe_3I]_4$ was treated with TMDM in chloroform solution, in sealed Carius tubes, under the conditions summarized in Table 3.

A product with IR absorption bands at 1749, 1707 and 1670 cm^{-1} in chloroform solution was shown to be formic acid by comparison with the IR spectrum of a genuine sample (bands at 1750, 1707 and 1676 cm^{-1}). The source of oxygen in the product could be either air, ethanol added as stabilizer in the chloroform or water present in the solvent. It is unlikely to be water, as TMDM is prepared from dimethylamine and formaldehyde in aqueous solution[17] (run 3 confirms), and runs 4 and 5 exclude ethanol. Runs conducted under nitrogen show that the only necessary component is air, which must therefore supply the oxygen required to generate formic acid.

EXPERIMENTAL

Preparation of $[PtMe_3X(Me_2NH)]_2$ **(1–3)** *from* N,N,N′,N′*-tetramethyldiaminomethane*

A solution of $[PtMe_3X]_4$ (0.75 mmol) in chloroform (30 cm^3) was refluxed with a stoichiometric quantity of tetramethyldiaminomethane (0.375 mmol) for 4 h. After removal of the solvent, the residue was taken up in warm acetone, filtered and the filtrate evaporated to dryness. The crude product was recrystallized from acetone–light petroleum (b.p. 60–80°C) (chloride and bromide) or from *n*-hexane (iodide) to give the product in 54–60% yield.

Preparation of $[PtMe_3IMe_2NH)]_2$ **(3)** *from dimethylamine*

Trimethylplatinum(IV) iodide (150 mg, 0.41 mmol) in chloroform (15 cm^3) was treated with dimethylamine (55 mg of a 25/30% w/v aqueous solution, *ca* 0.4 mmol) in acetone (7 cm^3) and the mixture refluxed for 2 h. The solvent was removed under reduced pressure, and the pale yellow residue was extracted into acetone and filtered. Evaporation of the acetone and recrystallization from *n*-hexane gave cream coloured needles (125 mg, 61%) identical (IR and NMR spectra) to the product obtained from tetramethylmethylenediamine.

Preparation of $[PtMe_3(2,2'\text{-bipyridyl})(HNMe_2)]^+[BF_4]^-$ **(4)**

$[PtMe_3I(2,2'\text{-bipyridyl})]$[10] (1.0 g, 1.92 mmol) and $AgBF_4$ (0.5 g, 2.56 mmol) in methanol (40 cm^3) were stirred for 30 min protected from light, and then TMDM (0.5 g, 4.89 mmol) was added. The mixture was refluxed for 8 h and then filtered while hot. The solvent was removed, and ether (60 cm^3) added. The resultant pale yellow solid was filtered off, washed with diethyl ether and light petroleum (b.p. 40–60°C) and recrystallized from hot methanol. Yield 0.80 g, 71%. The product melts with decomposition on heating.

For compounds **1–3**, ^1H NMR spectra were recorded on a JEOL MH100 operating at 100 MHz and IR spectra in KBr discs on a Perkin–Elmer 357 grating spectrophotometer. For compound **4**, ^1H NMR spectra were recorded on a Bruker AM250 operating at 250.13 MHz and IR spectra on a Nicolet Magna 550 FT-IR spectrometer in a CsI disc.

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