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DIMETHYLPLATINUM(IV) COMPOUNDS

II*. SPECTRA AND REACTIONS OF THE COMPOUNDS $[Pt(CH_3)_2X_2]_n$ (X=I, Br AND Cl)

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SUMMARY

The infrared spectra of the compounds $[Pt(CH_3)_2X_2]_n$ (X=I, Br and Cl) have been recorded between 4000 and 60 cm^{-1}. The spectra indicate the presence of both bridging and terminal halogen atoms. The reactions of these compounds, and in particular of $[Pt(CH_3)_2Br_2]_n$, with a number of neutral and uninegative ligands are reported and the ^1H NMR and infrared spectra of the products are discussed.

INTRODUCTION

Although a large number of stable trimethylplatinum(IV) complexes have been prepared[1], surprisingly little work has been done on dimethyl- and monomethylplatinum(IV) complexes. Gilman *et al.*[2], in a study of the reaction of CH_3MgI with anhydrous $PtCl_4$, isolated compounds which were postulated to be $Pt(CH_3)_2I_2$, $PtCH_3I_3$ and $PtCH_3I_5$, but these were not well characterized. However, compounds of the general formulae $[Pt(CH_3)_2L_2X_2]$, $[Pt(CH_3)L_2X_3]$ where X=I, Br and Cl, L=a tertiary phosphine or arsine[3,4], and $[Pt(CH_3)_2LRX]$ where X=I, Br and Cl, R=an acyl or allyl group, L=a diarsine[5,6] have been extensively investigated.

Recently the preparations of $Pt(CH_3)_2X_2$, where X=I and Br; $[Pt(CH_3)_2L_2X_2]$ where for example, $L=C_2H_5CN$, X=Br; and $[Pt(CH_3)_2L_2(CH_3CO)Cl]$ where L=4-methylpyridine have been mentioned briefly[7]. We have reported[8] the preparations of the compounds $[Pt(CH_3)_2X_2]_n$ (X=I, Br and Cl) which are useful starting materials for the preparation of a variety of dimethylplatinum(IV) complexes. In this paper the infrared spectra of these compounds are discussed, and a number of their reactions, in particular of $[Pt(CH_3)_2Br_2]_n$, with a variety of neutral and uninegative ligands are reported. Structures for the reaction products are postulated on the basis of infrared and ^1H NMR spectral data.

RESULTS AND DISCUSSION

The compounds $[Pt(CH_3)_2X_2]_n$ (X=I, Br and Cl)

These compounds are necessarily polymeric if the usual six-coordination of

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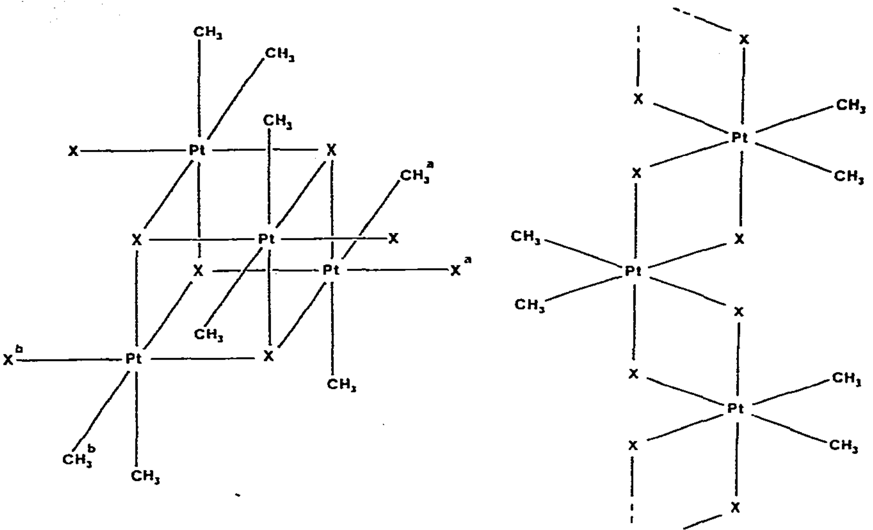
* Ref. 8 is considered to be Part I.

TABLE 1

INFRARED SPECTRA OF DIMETHYLPLATINUM(IV) AND MIXED TRIMETHYL-DIMETHYLPLATINUM(IV) HALOGEN COMPOUNDS

$[Pt(CH_3)_2I_2]_n$	$[Pt(CH_3)_2Br_2]_n$	$[Pt(CH_3)_2Cl_2]_n$	$[Pt(CH_3)_2BrCl]_n$	$[Pt(CH_3)_3I \cdot Pt(CH_3)_2I_2]_n$	$[Pt(CH_3)_3Br \cdot Pt(CH_3)_2Br_2]_n$	*Assignment*
2944 w(br)[a]	3000 w(br)	3014 w(br)	3002 w(br)	2978 m(br)	2968 m(br)	ν(C–H)
2915 m	2911 m	2930 m	2919 m	2910 s	2918 w	
				2904 s	2902 m	
2790 vw	2787 vw	2800 vw	2790 vw	2800 w	2798 w	$2 \times \delta_{asym}(CH_3)$
1410 m(br)	1409 m(br)	1412 m(br)	1409 m(br)	1411 m(br)	1410 m(br)	$\delta_{asym}(CH_3)$
1241 s	1252 m	1261 m	1257 m	1262 s	1264 m	$\delta_{asym}(CH_3)$ and $\delta_{sym}(CH_3)$
	1245 w		1250 (sh)	1240 s	1247 s	
	1222 w(sh)		1224 (sh)	1222 s	1224 vs	
1212 s	1220 s	1227 vs	1221 s	1219 s	1220 (sh)	
				1214 m		
	558 w	570 (sh)		557 w	572 w	ν(Pt–C)
538 w	552 w	567 w	559 m	542 w	559 m	
171 s	255 s	332 s	320 s	175 s	250 s	ν(Pt–X) terminal
	222 s(br)		212 m			
152 m	202 s	234 s	203 m	160 m	205 s	ν(Pt–X) bridging
				148 m	175 (sh)	
					169 m	
127 m	156 s	197 s	188 m	122 m	154 s	δ(Pt–X) terminal
111 m	128 s	154 m	130 w	106 m	128 m	δ(Pt–X) bridging
				99 m	123 (sh)	
					110 m	
					85 m	
					81 m	

[a] vs, very strong; s, strong; m, medium; w, weak; vw, very weak; (br), broad; (sh), shoulder.



(a) (b)

Fig. 1. Possible structures for $[Pt(CH_3)_2X_2]_n$, (a) tetrameric and (b) polymeric forms.

platinum(IV) is to be maintained. However, they are insoluble in non-coordinating solvents and molecular weights could not be determined. The compounds may have tetrameric structures resembling those found for $[Pt(CH_3)_3X]_4$[9,10] ($X=I$ and Cl) and postulated for $[Pt(CH_2)_3X_2]_n$[11] ($X=Br$ and Cl), or polymeric structures such as that found for $[PtX_4]_n$[12] ($X=I$ and Cl) (as shown in Fig. 1 a and b). The infrared spectra reported below are more consistent with a structure of type (a)*.

Infrared spectra

The infrared spectral data of the compounds $[Pt(CH_3)_2X_2]_n$ between 4000 and 60 cm^{-1} are recorded in Table 1.

In the C–H stretching region (2800–3000 cm^{-1}) each of the compounds exhibits a pattern of three bands, similar to that observed for the compounds $[Pt(CH_3)_3X]_4$[13]. Two of these bands, assignable to ν(C–H), are at higher frequencies than those in $[Pt(CH_3)_3X]_4$ by 10–30 cm^{-1} in each case, while the third band, assigned as an overtone of the asymmetric methyl bending vibration, is at a slightly lower frequency in the dimethylplatinum(IV) compounds, as is the $\delta_{asym}(CH_3)$ mode at ~ 1410 cm^{-1}.

Between 1200 and 1300 cm^{-1} at least one pair of sharp absorption bands is observed for all three compounds. These are assigned to methyl deformation modes, including the totally symmetric type. As observed in the compounds $[Pt(CH_3)_3X]_4$[13], there is a shift of bands to higher frequency from $X=I$ to $X=Cl$.

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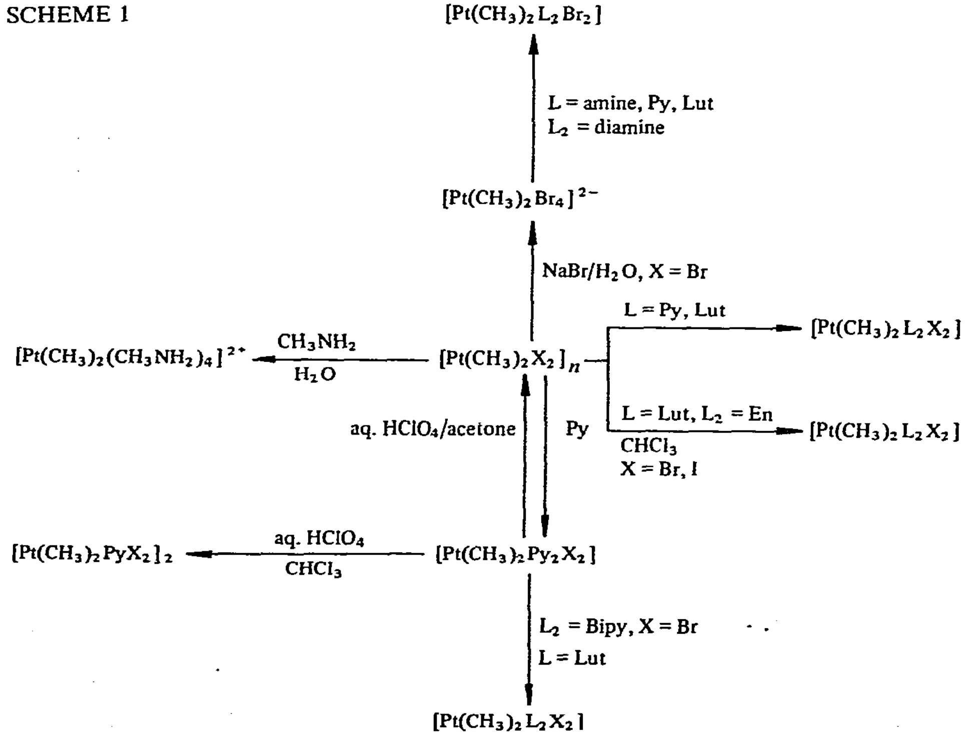
* A large number of structures of this type may be drawn but only two would produce the observed isomer of $Pt(CH_3)_2Py_2Br_2$ (see later) on reaction with pyridine, assuming symmetrical cleavage of the bromo bridges. One of the two structures is illustrated in Fig. 1a, the other would have the X and CH_3 groups interchanged within the pairs marked a and b.

In the compounds $[Pt(CH_3)_3X]_4$, a weak band was observed at ~879 cm^{-1} assignable to a methyl rocking vibration[13]. No absorption is observed in this region in the spectra of $[Pt(CH_3)_2X_2]_n$.

In the Pt–C stretching region (500–600 cm^{-1}), an asymmetric peak is observed at 538 cm^{-1} in $[Pt(CH_3)_2I_2]_n$, two peaks at 552 and 558 cm^{-1} in $[Pt(CH_3)_2Br_2]_n$, and a highly asymmetric peak at 567 cm^{-1} in $[Pt(CH_3)_2Cl_2]_n$. These features are possibly due to the symmetric and asymmetric stretching modes of a non-linear C–Pt–C unit. The increase in frequency of ν(Pt–C) from the iodo to the chloro compound parallels the behaviour of this mode in the compounds $[Pt(CH_3)_3X]_4$[13]. The frequencies are in each case some 20 cm^{-1} lower in the dimethylplatinum(IV) compounds, which may be a result of greater coupling of this mode with the Pt–X stretching modes.

The spectra of $[Pt(CH_3)_2X_2]_n$ below 500 cm^{-1} are consistent with the presence of both bridging and terminal halogen atoms in these compounds. $[Pt(CH_3)_2Cl_2]_n$ exhibits bands in this region at 332, 234, 197 and 154 cm^{-1}. Comparison of these values with those found in $[Pt(CH_2)_3Cl_2]_n$[11] (230 and 125 cm^{-1} assigned to bridging Cl, 330 (doublet) and 200 cm^{-1} assigned to terminal Cl) and $[Pt(CH_3)_3Cl]_4$[13] (216 and 136 cm^{-1} assigned to bridging Cl) suggests that the structures of $[Pt(CH_3)_2Cl_2]_n$ and these compounds may be related. In contrast there is little correspondence between the spectrum of $[Pt(CH_3)_2Cl_2]_n$ and the more complicated spectrum of $[PtCl_4]_n$[12b]. Therefore peaks at 234 and 154 cm^{-1} in the spectrum of $[Pt(CH_3)_2Cl_2]_n$ are tenta-

SCHEME 1



tively assigned to ν(Pt–Cl) and δ(Pt–Cl) respectively for a triply bridging Cl atom, while those at 332 and 197 cm^{-1} are assigned to the corresponding modes for a terminal Cl atom.

The spectra of $[Pt(CH_3)_2Br_2]_n$ and $[Pt(CH_2)_3Br_2]_n$ are also quite similar below 500 cm^{-1}. Peaks at 255 and 156 cm^{-1} in $[Pt(CH_3)_2Br_2]_n$ correspond to those at 252 and 144 cm^{-1} in $[Pt(CH_2)_3Br_2]_n$ and may be assigned to ν(Pt–Br) and δ(Pt–Br) respectively for a terminal Br atom, while peaks at 202 and 128 cm^{-1} in $[Pt(CH_3)_2Br_2]_n$, assigned to ν(Pt–Br) and δ(Pt–Br) for a bridging Br atom, have counterparts at 206 and 110 cm^{-1} in the spectrum of $[Pt(CH_2)_3Br_2]_n$[11].

For $[Pt(CH_3)_2I_2]_n$, peaks at 171 and 127 cm^{-1} are tentatively assigned to ν(Pt–I) and δ(Pt–I) for terminal I, and peaks at 152 and 111 cm^{-1} to the corresponding modes for bridging I.

Reactions with neutral ligands

A number of reactions of the compounds $[Pt(CH_3)_2X_2]_n$ (X=I, Br and Cl), and in particular of $[Pt(CH_3)_2Br_2]_n$, are shown in Schemes 1 and 2. In general, the compounds $[Pt(CH_3)_2X_2]_n$ react with neutral nitrogen–donor ligands to give compounds of the formulae $[Pt(CH_3)_2L_2X_2]$, where L_2 represents either one bidentate or two unidentate ligands. As indicated in Scheme 1, such compounds may be prepared by a number of different routes, but the reaction of the ligand L with $[Pt(CH_3)_2Br_4]^{2-}$ proved to be the most convenient for the preparation of a range of amine, diamine and heteroaromatic *N*-donor ligands. Where a compound *e.g.* $[Pt(CH_3)_2Lut_2Br_2]$ was prepared via all of these routes, the same isomeric form was invariably obtained.

SCHEME 2

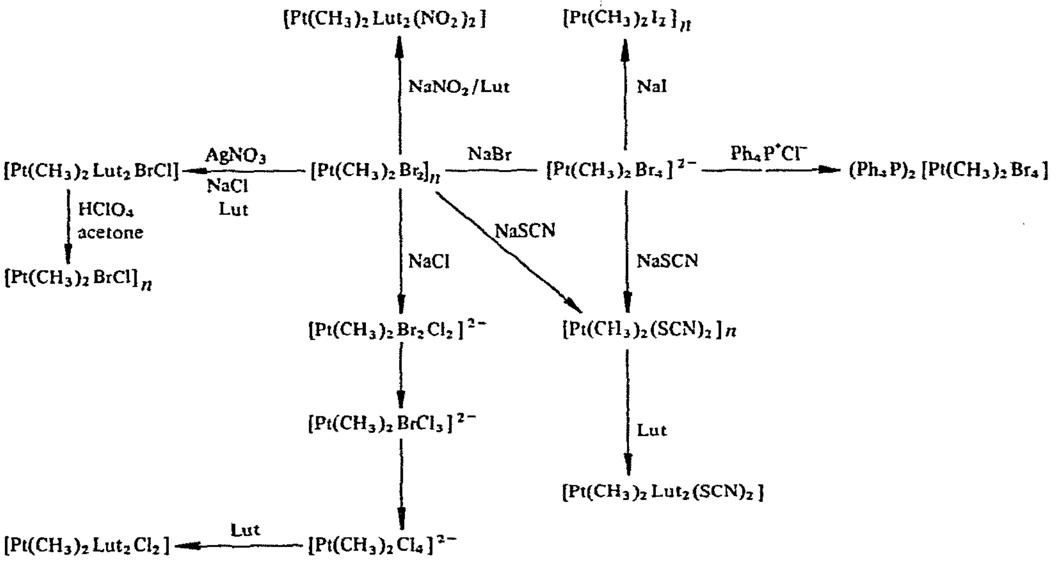


TABLE 2

^{1}H NMR SPECTRA OF DIMETHYLPLATINUM(IV) COMPOUNDS

Compound	τ	$^2J(^{195}Pt\text{-}CH_3)$	$\tau(CH_3\text{-}Lig)$	$^3J(^{195}Pt\text{-}N\text{-}C\text{-}H)$	$\tau(H_\alpha\text{-}Lut)$	$\tau(H\gamma\text{-}Lut)$	pK_a
In $CDCl_3$ solution referenced with TMS							
$[Pt(CH_3)_2(CH_3NH_2)_2Br_2]$	8.30	71.3	7.72	14.5			10.66
$[Pt(CH_3)_2(C_2H_5NH_2)_2Br_2]$	8.29	71.4		[a]			10.81
$[Pt(CH_3)_2(C_6H_5CH_2NH_2)_2Br_2]$	8.21	71.7		[a]			9.33
$[Pt(CH_3)_2(C_6H_5NH_2)_2Br_2]$	8.34	74.2		[a]			4.63
$[Pt(CH_3)_2(o\text{-}ClC_6H_4NH_2)_2Br_2]$	8.16	75.1		[a]			2.65
$[Pt(CH_3)_2N\text{-}MeenBr_2]$[b]	8.26	71.5	7.26	[a]			
	8.34	72.5					
$[Pt(CH_3)_2N,N\text{-}DimeenBr_2]$[b]	8.16	71.5	7.21	12.5			
	8.40	71.3					
$[Pt(CH_3)_2N,N'\text{-}DimeenBr_2]$[b]	8.30	71.2	7.28	[a]			
$[Pt(CH_3)_2N,N,N',N'\text{-}TetrameenBr_2]$[b]	8.12	70.7	7.20	13.0			
$[Pt(CH_3)_2Py_2I_2]$	7.46	72.7					
$[Pt(CH_3)_2Py_2Br_2]$	7.90	71.5					
$[Pt(CH_3)_2Py_2BrCl]$	8.01	70.5					
$[Pt(CH_3)_2Py_2Cl_2]$	8.11	69.8					
$[Pt(CH_3)_2Lut_2I_2]$[c]	7.51	72.3	7.70	13.5	1.34	2.55	
$[Pt(CH_3)_2Lut_2Br_2]$	7.94	70.2	7.70	13.0	1.46	2.55	
$[Pt(CH_3)_2Lut_2Cl_2]$	8.15	69.8	7.69	13.0	1.47	2.56	
$[Pt(CH_3)_2Lut_2(NO_2)_2]$	7.99	69.2	7.65	12.5	1.67	2.50	
$[Pt(CH_3)_2Lut_2(SCN)_2]$	8.42	67.3	7.64	12.0	1.86	2.43	
in D_2O solution referenced with DSS							
$[Pt(CH_3)_2(CH_3NH_2)_4]Br_2$	8.71	66.5	7.48, 7.64	15.0, 49.0			
$[Pt(CH_3)_2Br_4]^{2-}$	7.73	76.5					
$[Pt(CH_3)_2Cl_4]^{2-}$	8.00	76.2					
$[Pt(CH_3)_2BrCl_3]^{2-}$	7.93	76.8					
$[Pt(CH_3)_2Br_2Cl_2]^{2-}$	7.86	77.5					
$[Pt(CH_3)_2Br_2]_n + AgNO_3$	8.00	75.7					

[a] Region complex. [b] *N*-Meen = *N*-methylethylenediamine; *N,N*-Dimeen = *N,N*-dimethylethylenediamine; *N,N'*-Dimeen = *N,N'*-dimethylethylenediamine; *N,N,N',N'*-Tetrameen = *N,N,N',N'*-Tetramethylethylenediamine. [c] Lut = 3,5-dimethylpyridine.

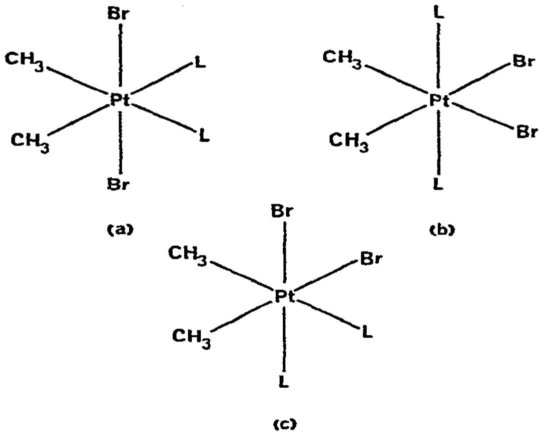


Fig. 2. Possible structures for $[Pt(CH_3)_2L_2X_2]$.

The ^1H NMR data for a number of complexes of the type $[Pt(CH_3)_2L_2X_2]$ are shown in Table 2. Where L_2 represents a bidentate ligand, two geometric isomers are possible, neglecting those isomers with *trans* methyl groups. Structures (a) and (c) of Fig. 2 indicate the distribution of groups about the platinum atom for these isomers. In methylplatinum(IV) compounds, both chemical shifts and coupling constants of the methyl-platinum protons have been found to be dependent on the nature of the ligand in the position *trans* to the methyl group[14,15]. Thus if the compounds have structure (a), a single methylplatinum triplet (^{195}Pt, $I = \frac{1}{2}$, 34% abundance) would be predicted when the L_2 ligand is symmetrical, and two such triplets should be observed for isomer (c). Although the compounds $[Pt(CH_3)_2BipyBr_2]$ and $[Pt(CH_3)_2EnBr_2]$ proved to be too insoluble to give useful NMR spectra, $[Pt(CH_3)_2$*N,N'*-DimeenBr$_2]$ and $[Pt(CH_3)_2$*N,N,N',N'*-TetrameenBr$_2]$ both exhibit only a single methylplatinum triplet, so that these compounds must have structure (a) of Fig. 1. As expected, those compounds containing unsymmetrical bidentate ligands, such as $[Pt(CH_3)_2$*N*-MeenBr$_2]$ and $[Pt(CH_3)_2$*N,N*-DimeenBr$_2]$ exhibit two non-equivalent triplets in the NMR.

Compounds of the type $[Pt(CH_3)_2L_2X_2]$ with L_2 representing two unidentate ligands may have any of structures (a), (b), or (c) of Fig. 2. As shown in Table 2, all such complexes examined show only a single methylplatinum triplet in the NMR, so that isomer (c) may be eliminated as a possible structure for these compounds. The values of $^2J(^{195}Pt\text{–}CH_3)$ range from 67.3 to 75.1 Hz for a variety of primary amine and heterocyclic *N*-donor ligands. From previous work[15] these values could be interpreted in terms of CH_3 groups *trans* to either L (isomer (a)) or Br (isomer (b)), but as indicated in the following discussion, the NMR spectra are more consistent with the compounds having structure (a) of Fig. 2.

As shown in Table 2, the compound $[Pt(CH_3)_2Py_2BrCl]$ exhibits only a single methylplatinum triplet, which provides unequivocal evidence for this compound having structure (a). Both the chemical shift (τ 8.01) and coupling constant (70.5 Hz) values of the methyl protons in this compound are intermediate between those of the methyl protons in $[Pt(CH_3)_2Py_2Br_2]$ (τ 7.90, J 71.5 Hz) and $[Pt(CH_3)_2Py_2Cl_2]$ (τ 8.11, J 69.8 Hz), which would be anticipated if their structures are related. Moreover, the magnitudes of the coupling constants $^2J(^{195}Pt{-}CH_3)$ in the two series $[Pt(CH_3)_2L_2X_2]$ (L = Py, Lut; X = I, Br and Cl) are consistent with CH_3 groups *trans* to L since the coupling constants increase from the chloro compound to the iodo compound, as was found for CH_3 *trans* to L in the compounds $[Pt(CH_3)_3L_2X]$[15]. In the latter compounds the value of the coupling constant for CH_3 *trans* to X decreased in the same order[15].

For the compounds $[Pt(CH_3)_2L_2Br_2]$ where L is a primary amine, there is a good correlation between $^2J(^{195}Pt{-}CH_3)$ and the pK_a of the ligand L, with the coupling constant decreasing as the pK_a value increases. A similar dependence on pK_a has been observed for the coupling constants of CH_3 *trans* to L in compounds of the type $[Pt(CH_3)_3BipyL]ClO_4$[15].

As noted earlier, the magnitude of $^2J(^{195}Pt{-}CH_3)$ is strongly dependent on the nature of the ligand *trans* to the $Pt{-}CH_3$ bond. A similar effect would be expected for coupling between ^{195}Pt and protons on the L ligands, so that values of $^3J(^{195}Pt{-}N{-}CH)$ for ligands such as CH_3NH_2 and heteroaromatics with α-protons should be quite different in the two isomers (a) (where L is *trans* to CH_3) and (b) (where L is *trans* to L) of Fig. 2. For the former isomer, the magnitude of such coupling constants would be expected to be similar to those found in trimethylplatinum(IV) complexes, while for the latter isomer they would be substantially larger since the *N*-donor ligands have a much weaker *trans* influence than CH_3 groups[15]. Couplings between ^{195}Pt and the α-protons of lutidine (3,5-dimethylpyridine) in the complexes $[Pt(CH_3)_2Lut_2X_2]$ (12.0 to 13.5 Hz, Table 2) are of the same order as those found in the compounds $[Pt(CH_3)_3Lut_2X]$[15] (11.0–12.0 Hz) as are the couplings $^3J(^{195}Pt{-}N{-}CH_3)$ in $[Pt(CH_3)_2(CH_3NH_2)_2Br_2]$ (14.5 Hz) and $[Pt(CH_3)_3(CH_3NH_2)_3]^+$ (15.0 Hz)* indicating that in each case the CH_3 groups are *trans* to L.

Chemical shift values of the methyl-platinum protons in the compounds $[Pt(CH_3)_2L_2X_2]$ also support the assignment of structure (a). For those compounds with L = a primary amine, there is little variation in the chemical shift values between those containing aliphatic and aromatic amines (Table 2) as expected for isomer (a) whereas for structure (b) the shielding effect of the aromatic rings on the amine ligands would cause a shift upfield of the methyl-platinum protons. Larger effects of this type should be observed in compounds with structure (b) containing heterocyclic *N*-donor ligands. As seen from Table 2, however, there is in fact some deshielding of methyl-platinum protons in the compounds $[Pt(CH_3)_2L_2X_2]$ with such ligands. Some deshielding of the protons would be expected in compounds with structure (a), since the axes of the methyl groups lie in the plane of the Pt–N bonds.

The formation of isomer (a) for each of the compounds $[Pt(CH_3)_2L_2X_2]$ is quite consistent with *trans* influence theory, which would predict that the bonds *trans* to CH_3 should be weakened sufficiently to allow attack by incoming ligands.

Reaction of $[Pt(CH_3)_2Br_2]_n$ with aqueous methylamine gives a water-soluble product which is apparently $[Pt(CH_3)_2(CH_3NH_2)_4]Br_2$. The NMR spectrum of this compound in D_2O is of some interest. A single methylplatinum triplet is observed with $^2J(^{195}Pt{-}CH_3)$ 66.5 Hz, as well as two non-equivalent methylamine methyl resonances, each of which exhibits coupling with ^{195}Pt. One resonance, at τ 7.48 has a coupling constant of 15.0 Hz, and this may be assigned to the methyl protons of the

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* Unpublished results.

CH_3NH_2 groups *trans* to CH_3, while the other, at τ 7.64 exhibits a coupling of 49.0 Hz. Comparison of these values with those for the methyl-platinum protons (J 68.8 Hz) and methylamine methyl protons (J 15.0 Hz) in $[Pt(CH_3)_3(CH_3NH_2)_3]^+$ shows that a CH_3 group must weaken the *trans* bond and strengthen the *cis* bonds to a greater extent than does CH_3NH_2.

Reactions with uninegative ligands

The compound $[Pt(CH_3)_2I_2]_n$ is insoluble in water and is apparently unaffected by aqueous solutions containing a variety of anions capable of coordination. On the other hand, the water-insoluble $[Pt(CH_3)_2Br_2]_n$ and $[Pt(CH_3)_2Cl_2]_n$ do dissolve in hot aqueous solutions containing coordinating anions and continued heating of such solutions leads to complete substitution of the halogen atoms. In some cases the products remain in solution, while in others, where the anion is capable of bridging, precipitates are formed. A variety of these reactions is shown in Scheme 2.

$[Pt(CH_3)_2Br_2]_n$ dissolves in hot aqueous sodium bromide and ^1H NMR spectra of the resultant solutions indicate the presence of only one species (Table 2). This species is apparently $[Pt(CH_3)_2Br_4]^{2-}$, since addition of a solution of tetraphenylphosphonium chloride to the solution gives an immediate precipitate of $(Ph_4P)_2[Pt(CH_3)_2Br_4]$. The coupling constant for the methyl protons in $[Pt(CH_3)_2Br_4]^{2-}$ is 76.5 Hz, which is slightly higher than that found for methyl groups *trans* to Br in trimethylplatinum(IV) complexes (69.6–74.6 Hz)[15].

$[Pt(CH_3)_2Br_2]_n$ also dissolves in hot aqueous sodium chloride and NMR spectra of these solutions indicate that the species present are dependent on the concentration of NaCl. At low concentrations (mole ratio of NaCl to $[Pt(CH_3)_2Br_2]_n$ $\sim 5/1$) two major species are present as evidenced by the observation of two methyl-platinum triplets in the NMR. One resonance, at τ 7.86, has $^2J(^{195}Pt-CH_3)$ 77.5 Hz, and the other, at τ 7.93, a coupling constant of 76.8 Hz. On continued heating of the solution, the intensity of the latter peak increases at the expense of the former. Addition of pyridine to such solutions precipitates a mixture of $[Pt(CH_3)_2Py_2Br_2]$ and $[Pt(CH_3)_2Py_2BrCl]$ as identified by NMR spectra. From the relative amounts of these pyridine derivatives, it is apparent that $[Pt(CH_3)_2Py_2Br_2]$ is formed from the species at τ7.86, and $[Pt(CH_3)_2Py_2BrCl]$ from the species at τ 7.93. These species are probably $[Pt(CH_3)_2Br_2Cl_2]^{2-}$ (with CH_3 *trans* to Cl) and $[Pt(CH_3)_2BrCl_3]^{2-}$. At greater concentrations of NaCl (mole ratio of NaCl to $[Pt(CH_3)_2Br_2]_n \sim 40/1$) two species are again present, with methyl proton resonances at τ 7.93 and τ 8.00. Continued heating of such solutions leads to the formation of the latter species almost exclusively, and addition of pyridine to this solution precipitates almost pure $[Pt(CH_3)_2Py_2Cl_2]$ as identified by NMR. This latter species is thus probably $[Pt(CH_3)_2Cl_4]^{2-}$.

$[Pt(CH_3)_2Br_2]_n$ dissolves readily in aqueous $NaNO_2$, but the NMR spectra of such solutions are complex and not readily interpretable. However, addition of lutidine to solutions containing a large excess of $NaNO_2$ precipitates $[Pt(CH_3)_2Lut_2(NO_2)_2]$, and the NMR spectrum of this compound is listed in Table 2. The infrared spectrum confirms the presence of N-bonded nitro groups, with bands at 1428 cm^{-1} (assignable to $\nu_{asym}(NO_2)$), 1338 and 1328 cm^{-1} ($\nu_{sym}(NO_2)$), 829 cm^{-1} ($\delta(NO_2)$) and 550 cm^{-1} ($\rho_\omega(NO_2)$).

Addition of aqueous solutions of NaI and NaSCN to aqueous solutions containing $[Pt(CH_3)_2Br_4]^{2-}$ causes precipitation of the solids $[Pt(CH_3)_2I_2]_n$ and $[Pt(CH_3)_2(SCN)_2]_n$ respectively. The latter compound is insoluble in non-coordinating solvents so that no NMR spectrum could be obtained. Its infrared spectrum is of little assistance in determining its structure. In the C≡N stretching region a single broad intense peak appears at 2164 cm^{-1}, which may indicate the presence of bridging thiocyanate groups[16,17]. The lower frequency modes of the thiocyanate groups which are usually more diagnostic of the mode of bonding are extremely weak in this compound. A very broad, medium intensity band appears at 743 cm^{-1} and broad weak bands at 475 and 431 cm^{-1}. These peaks further suggest the presence of bridging thiocyanate groups but do not allow any particular structure to be assigned to this compound.

The compound $[Pt(CH_3)_2(SCN)_2]_n$ reacts with lutidine to give $[Pt(CH_3)_2Lut_2(SCN)_2]$, and the NMR spectrum of the product appears in Table 2. The infrared spectrum indicates that the thiocyanate groups are probably *S*-bonded. The C≡N stretching frequency appears at 2125 cm^{-1}, and lies in the range found for *S*-bonded thiocyanate groups[17], while peaks at 468, 431 and 419 cm^{-1} lie in the region usually assigned to δ(SCN) for *S*-bonded thiocyanate[16,17]. No peaks assignable to ν(C–S) are observed, but this mode may lie beneath one of the lutidine vibrations in this region. It is of interest to note that the corresponding trimethylplatinum(IV) compound, $[Pt(CH_3)_3Lut_2NCS]$ appeared to contain only *N*-bonded thiocyanate both in the solid state and in solution[15]. Also, the compound $[Pt(CH_3)_2Lut_2(SCN)_2]$ is stable at room temperature, while $[Pt(CH_3)_3Lut_2NCS]$ was found to lose one mole of lutidine readily to form the dimer $[Pt(CH_3)_3LutNCS]_2$[15].

Although $[Pt(CH_3)_2Br_2]_n$ is unaffected by aqueous $NaNO_3$, it reacts with aqueous $AgNO_3$. With a mole ratio of $AgNO_3$ to $[Pt(CH_3)_2Br_2]_n$ of 2/1, reaction for 30 min gives a solution containing predominantly only one species as evidenced by a single major triplet in the NMR (τ 8.00, *J* 75.7 Hz). Continued heating produces a further small peak at τ 7.97 (*J* 75.5 Hz). The initial species apparently contains one Br atom per Pt since addition of sodium chloride solution followed by pyridine precipitates $[Pt(CH_3)_2Py_2BrCl]$. The ^1H NMR spectrum of the latter compound was noted earlier. By reaction with $HClO_4$, it is converted to $[Pt(CH_3)_2BrCl]_n$, which is insoluble in non-coordinating solvents and an NMR spectrum could not be obtained. Its infrared spectral data are listed in Table 1. If the compound has a tetrameric structure similar to those postulated for $[Pt(CH_3)_2X_2]_n$, either the Br or Cl atom may bridge the Pt atoms. Comparison of bands below 400 cm^{-1} in this compound with those found for $[Pt(CH_3)_2Br_2]_n$ and $[Pt(CH_3)_2Cl_2]_n$ (Table 1) supports the presence of triply-bridged Br atoms and terminal Cl atoms. Peaks at 320 and 188 cm^{-1} correspond with those at 332 and 197 cm^{-1} in $[Pt(CH_3)_2Cl_2]_n$ which were assigned to ν(Pt–Cl) and δ(Pt–Cl) respectively for terminal Cl, while peaks at 212, 203 and 130 cm^{-1} are comparable with bands at 222, 202 and 128 cm^{-1} in $[Pt(CH_3)_2Br_2]_n$, assigned to ν(Pt–Br) and δ(Pt–Br) for a bridging Br atom. In general, bands above 400 cm^{-1} are intermediate between those found for $[Pt(CH_3)_2Br_2]_n$ and $[Pt(CH_3)_2Cl_2]_n$ (Table 1).

The compounds $[Pt(CH_3)_3X\cdot Pt(CH_3)_2X_2]_n$ *(X = I and Br)*

The preparations of the compounds were reported previously[8]. These compounds apparently have a definite stoichiometry since the products obtained from different preparative routes yield identical infrared spectra. The orange and brown forms of $[Pt(CH_3)_3I \cdot Pt(CH_3)_2I_2]_n$ noted previously[8] also have identical infrared spectra and both produce equimolar amounts of $[Pt(CH_3)_3Py_2I]$ and $[Pt(CH_3)_2Py_2I_2]$ on dissolution in pyridine, as confirmed by NMR. The compounds $[Pt(CH_3)_3X \cdot Pt(CH_3)_2X_2]_n$ may be made up of tetrameric units containing two trimethylplatinum(IV) moieties and two dimethylplatinum(IV) moieties per unit, so that $n = 2$. The infrared data for these compounds are shown in Table 1. They contain features attributable to both moieties, but are not simple superimpositions of the spectra of $[Pt(CH_3)_3X]_4$ and $[Pt(CH_3)_2X_2]_n$.

Reaction of a chloroform solution containing equimolar quantities of $[Pt(CH_3)_3Py_2I]$ and $[Pt(CH_3)_2Py_2Br_2]$ with HCl gave a precipitate whose infrared spectrum was different from that of either $[Pt(CH_3)_3I]_4$ or $[Pt(CH_3)_2Br_2]_n$. When this solid was treated with pyridine and the NMR spectrum of the product recorded, peaks due to both $[Pt(CH_3)_3Py_2I]$ and $[Pt(CH_3)_2Py_2Br_2]$ were observed, so that the initial product probably contained the species $[Pt(CH_3)_3I \cdot Pt(CH_3)_2Br_2]_n$. However the NMR spectrum also indicated the presence of the species $[Pt(CH_3)_3Py_2Br]$ and $[Pt(CH_3)_2Py_2I_2]$ in 2/1 mole ratio, so that some exchange of halogen atoms must have occurred during the reaction.

EXPERIMENTAL

Preparation of $[Pt(CH_3)_2X_2]_n$ ($X = I$, *Br and Cl*)

The preparation of these compounds has been described previously[8]. The compounds are slightly soluble in solvents such as dioxane, ethyleneglycol and ethanol, but such solutions probably result from coordination of the solvent. $[Pt(CH_3)_2Br_2]_n$ can be recovered unchanged by careful crystallization from ethanol, but prolonged heating in ethanol, and also in solvents such as dioxane, ethyleneglycol or dimethylsulfoxide leads to decomposition to metallic platinum.

Preparation of $[Pt(CH_3)_2(CH_3NH_2)_2Br_2]$

$[Pt(CH_3)_2Br_2]_n$ (0.2 g) was suspended in chloroform (5 ml) and a 40% solution of methylamine in ethanol (5 ml). The mixture was heated for 30 min during which time the $[Pt(CH_3)_2Br_2]_n$ dissolved to give a yellow solution. On concentration of the solution and cooling, yellow plates of the product were obtained. Yield 80% (Found: C, 11.0; H, 3.6; Br, 35.9; N, 6.2; Pt, 43.4. $C_4H_{16}Br_2N_2Pt$ calcd.: C, 10.7; H, 3.6; Br, 35.7; N, 6.3; Pt, 43.6%).

Preparation of $[Pt(CH_3)_2(CH_3NH_2)_4]Br_2$

$[Pt(CH_3)_2Br_2]_n$ (0.2 g) was suspended in 33% aqueous methylamine solution (10 ml) and the mixture heated. The solid dissolved to give a yellow solution initially, but on continued heating an almost colourless solution resulted. Careful evaporation to dryness gave colourless crystals of the product. The compound, however, was apparently unstable and analytical figures were not good. As noted in the discussion, the NMR spectrum of the compound in D_2O was consistent with the presence of the ion $[Pt(CH_3)_2(CH_3NH_2)_4]^{2+}$.

Preparation of $[Pt(CH_3)_2L_2Br_2]$ ($L =$ *ethylamine, benzylamine, aniline, o-chloroaniline*)

A solution of $[Pt(CH_3)_2Br_2]_n$ (0.05 g) in conc. aqueous NaBr (50 ml) was treated with the appropriate amine. The product precipitated immediately and was extracted into chloroform. The chloroform solution was dried with anhydrous Na_2SO_4, concentrated to a small volume, and the product precipitated by addition of n-hexane. Yield 85–95%. The *o*-chloroaniline complex was unstable in the solid state, but an NMR spectrum of the compound in $CDCl_3$ solution was obtained in the presence of excess ligand. For L = ethylamine, Found: C, 15.3; H, 4.4; Br, 34.2; N, 5.8; Pt, 41.2. $C_6H_{20}Br_2N_2Pt$ calcd.: C, 15.2; H, 4.2; Br, 33.6; N, 5.9; Pt, 41.1%. For L = benzylamine, Found: C, 32.1; H, 4.1; Br, 26.2; N, 4.6; Pt, 32.0. $C_{16}H_{24}Br_2N_2Pt$ calcd.: C, 32.1; H, 4.0; Br, 26.7; N, 4.7; Pt, 32.5%. For L = aniline, Found: C, 29.1; H, 3.7; Br, 27.6; N, 5.1; Pt, 34.0. $C_{14}H_{20}Br_2N_2Pt$ calcd.: C, 29.4; H, 3.5; Br, 28.0; N, 4.9; Pt, 34.1%.

Preparation of $[Pt(CH_3)_2EnBr_2]$

$[Pt(CH_3)_2Br_2]_n$ (0.1 g) was suspended in chloroform (5 ml) and a 2 mole ratio of ethylenediamine added. The mixture was refluxed until the solid dissolved to give a yellow solution, which was concentrated to a small volume and the product precipitated with n-hexane. Yield 90% (Found: C, 10.8; H, 3.2; Br, 35.7; N, 6.4; Pt, 44.1. $C_4H_{14}Br_2N_2Pt$ calcd.: C, 10.8; H, 3.2; Br, 35.9; N, 6.3; Pt, 43.8%).

Preparation of $[Pt(CH_3)_2L_2Br_2]$ *(L_2 = N-methylethylenediamine, N,N'-dimethylethylenediamine, N,N-dimethylethylenediamine, N,N,N',N'-tetramethylethylenediamine)*

A solution of $[Pt(CH_3)_2Br_2]_n$ (0.05 g) in conc. aqueous NaBr (50 ml) was treated with the appropriate diamine. The product, which precipitated immediately, was extracted into chloroform. The chloroform extract was dried with anhydrous Na_2SO_4, concentrated to a small volume, and the product precipitated as yellow crystals by addition of n-hexane. Yield 80–95%. For L_2 = *N*-Meen, Found: C, 13.3; H, 3.7; Br, 35.2; N, 6.2; Pt, 42.2. $C_5H_{16}Br_2N_2Pt$ calcd.: C, 13.1; H, 3.5; Br, 34.8; N, 6.1; Pt, 42.5%. For L_2 = *N,N'*-Dimeen, Found: C, 15.5; H, 4.0; Br, 33.6; N, 5.6; Pt, 40.9. $C_6H_{18}Br_2N_2Pt$ calcd.: C, 15.2; H, 3.8; Br, 33.8; N, 5.9; Pt, 41.2%. For L = *N,N*-Dimeen, Found: C, 15.4; H, 3.9; Br, 33.8; N, 5.9; Pt, 41.4. $C_6H_{18}Br_2N_2Pt$ calcd.: C, 15.2; H, 3.8; Br, 33.8; N, 5.9; Pt, 41.2%. For L = *N,N,N',N'*-Tetrameen, Found: C, 19.8; H, 4.5; Br, 32.1; N, 5.8; Pt, 38.6. $C_8H_{22}Br_2N_2Pt$ calcd.: C, 19.2; H, 4.4; Br, 31.9; N, 5.6; Pt, 38.9%.

Preparation of $[Pt(CH_3)_2Py_2X_2]$ *(X = I, Br and Cl)*

These compounds were prepared as described previously[8].

Reaction of $[Pt(CH_3)_2Py_2Br_2]$ *with* $HClO_4$

As noted previously[8] reaction of $[Pt(CH_3)_2Py_2Br_2]$ in acetone with excess 30% $HClO_4$ slowly yields the compound $[Pt(CH_3)_2Br_2]_n$. If, however, a chloroform solution of $[Pt(CH_3)_2Py_2Br_2]$ is shaken with 30% $HClO_4$ in the cold, a yellow solid precipitates after several minutes. This compound, which is sparingly soluble in the usual organic solvents, analyses for $Pt(CH_3)_2PyBr_2$ and is presumably dimeric with bridging Br atoms, analogous to the compound $[Pt(CH_3)_3PyI]_2$[18]. (Found: C, 18.3; H, 2.5; Br, 34.8; N, 3.0; Pt, 42.2. $C_7H_{11}Br_2NPt$ calcd.: C, 18.1; H, 2.4; Br, 34.4; N, 3.0; Pt, 42.0%.

Preparation of $[Pt(CH_3)_2Lut_2X_2]$ *(X = I, Br and Cl)*

$[Pt(CH_3)_2Py_2X_2]$ (0.1 g) in chloroform was treated with excess 3,5-lutidine and the mixture refluxed for 1 hour. On concentration of the solution and addition of 95% ethanol, the product crystallized out and was filtered off, washed with ethanol, and air-dried. Yield 90–95%. As for the corresponding pyridine derivatives, $[Pt(CH_3)_2Lut_2I_2]$ is orange, $[Pt(CH_3)_2Lut_2Br_2]$ yellow, and $[Pt(CH_3)_2Lut_2Cl_2]$ pale yellow. For X=I, Found: C, 27.8; H, 3.4; I, 37.1; N, 4.4; Pt, 27.9. $C_{16}H_{24}I_2N_2Pt$ calcd.: C, 27.7; H, 3.5; I, 36.6; N, 4.0; Pt, 28.1%. For X=Br, Found: C, 32.1; H, 4.1; Br, 26.7; N, 4.3; Pt, 32.2. $C_{16}H_{24}N_2Br_2Pt$ calcd.: C, 32.1; H, 4.1; Br, 26.7; N, 4.7; Pt, 32.5%). For X=Cl, Found: C, 37.6; H, 4.8; Cl, 14.1; N, 5.3; Pt, 38.1. $C_{16}H_{24}N_2Cl_2Pt$ calcd.: C, 37.6; H, 4.7; Cl, 13.9; N, 5.5; Pt, 38.2%.

Preparation of $[Pt(CH_3)_2BiPyBr_2]$

$[Pt(CH_3)_2Py_2Br_2]$ (0.064 g) in chloroform (10 ml) was treated with 2,2′-Bipyridine (0.02 g) and the solution refluxed for 30 min. On concentration of the solution and cooling, yellow crystals of the product precipitated and these were filtered off, washed with cold chloroform, and air-dried. The yield was quantitative. The product is a yellow solid, sparingly soluble in common organic solvents. (Found: C, 26.9; H, 2.7; Br, 29.8; N, 5.4; Pt, 35.7. $C_{12}H_{14}Br_2N_2Pt$ calcd.: C, 26.6; H, 2.6; Br, 29.5; N, 5.2; Pt, 36.0%.

Reaction of $[Pt(CH_3)_2Br_2]_n$ with aqueous NaBr

$[Pt(CH_3)_2Br_2]_n$ dissolved slowly in hot aqueous solutions containing at least a two mole ratio of NaBr to give a yellow solution. On concentration of such solutions $[Pt(CH_3)_2Br_2]_n$ was recovered unchanged. However, addition of a solution of tetraphenylphosphonium chloride to the solution precipitated a yellow solid which analysed for $(Ph_4P)_2[Pt(CH_3)_2Br_4]$. (Found: C, 49.0; H, 4.1; Br, 25.9. $C_{50}H_{46}Br_2P_2Pt$ calcd.: C, 49.1; H, 3.8; Br, 26.1%). $[Pt(CH_3)_2Br_2]_n$ also dissolved in concentrated hydrobromic acid, giving a yellow solution which presumably contains the species $[Pt(CH_3)_2Br_4]^{2-}$.

Reaction of $[Pt(CH_3)_2Br_2]_n$ with aqueous NaCl

$[Pt(CH_3)_2Br_2]_n$ (0.1 g) was suspended in water (20 ml) containing a large excess of sodium chloride. After heating and stirring for 15 min a clear yellow solution was obtained. The heating was continued for about 4 h, by which time the solution was almost colourless. Addition of pyridine or 3,5-lutidine to this solution precipitated pale yellow solids confirmed to be $[Pt(CH_3)_2Py_2Cl_2]$ and $[Pt(CH_3)_2Lut_2Cl_2]$ by NMR spectra.

When a mole ratio of NaCl to $[Pt(CH_3)_2Br_2]_n$ of 5/1 was used, and pyridine added to the resultant solution, a mixture of $[Pt(CH_3)_2Py_2Br_2]$ and $[Pt(CH_3)_2Py_2BrCl]$ was obtained as confirmed by NMR.

Reaction of $[Pt(CH_3)_2Br_4]^{2-}$ with aqueous sodium iodide

$[Pt(CH_3)_2Br_2]_n$ (0.2 g) was suspended in water (200 ml) containing excess NaBr and the mixture heated until the solid dissolved. Addition of a solution containing excess sodium iodide to this solution produced an orange-red precipitate. Yield 80%. The infrared spectrum of the solid confirmed the compound was $[Pt(CH_3)_2I_2]_n$, and the solid dissolved in pyridine to give $[Pt(CH_3)_2Py_2I_2]$ as confirmed by NMR.

Reaction of $[Pt(CH_3)_2Br_2]_n$ *with aqueous sodium nitrite*

$[Pt(CH_3)_2Br_2]_n$ (0.1 g) was suspended in water (10 ml) containing an excess of $NaNO_2$. Heating and stirring for 2 h gave a colourless solution. Addition of 3,5-lutidine to the solution caused precipitation of a white solid which was filtered off, air-dried, and recrystallized from an ethanol–chloroform mixture. Yield 90%. The product analysed for $[Pt(CH_3)_2Lut_2(NO_2)_2]$. (Found: C, 35.7; H, 4.5; N, 10.2; Pt, 36.5. $C_{16}H_{24}N_4O_4Pt$ calcd.: C, 36.2; H, 4.5; N, 10.5; Pt, 36.7%).

Reaction of $[Pt(CH_3)_2Br_4]^{2-}$ *with aqueous potassium thiocyanate*

$[Pt(CH_3)_2Br_2]_n$ (0.2 g) was suspended in water (200 ml) containing excess NaBr and the mixture heated until the solid dissolved. Addition of a solution of potassium thiocyanate to this solution and continued heating caused precipitation of a pale yellow solid which was filtered off, washed with water and acetone, and air-dried. Yield 92%. The product, which was insoluble in common organic solvents, analysed for $Pt(CH_3)_2(SCN)_2$. (Found: C, 14.1; H, 1.9; N, 8.1; Pt, 57.0; $C_4H_6N_2PtS_2$ calcd.: C, 14.1; H, 1.8; N, 8.2; Pt, 57.2%).

Reaction of $[Pt(CH_3)_2(SCN)_2]_n$ *with 3,5-lutidine*

$[Pt(CH_3)_2(SCN)_2]_n$ (0.065 g) was dissolved in lutidine (1 ml), the solution evaporated to dryness, and the residue extracted with chloroform. The product was recrystallized from ethanol–chloroform. The pale yellow crystals analysed for $[Pt(CH_3)_2Lut_2(SCN)_2]$. (Found: C, 39.0; H, 4.5; N, 9.8; Pt, 35.0. $C_{18}H_{24}N_4PtS_2$ calcd.: C, 38.9; H, 4.4; N, 10.1; Pt, 35.1%).

Reaction of $[Pt(CH_3)_2Br_2]_n$ *with silver nitrate*

$[Pt(CH_3)_2Br_2]_n$ (0.3 g) was suspended in aqueous silver nitrate (0.26 g in 10 ml). The mixture was heated for several hours at near-boiling, then cooled and the residue of AgBr filtered off. Aqueous NaCl was added to the filtrate precipitating excess silver ions, and after filtration pyridine was added to the filtrate. The pale yellow solid which precipitated was filtered off and air dried. The compound, which analysed for $[Pt(CH_3)_2Py_2BrCl]$, was recrystallized from ethanol–chloroform. Yield 50%. (Found: C, 29.0; H, 3.3; N, 6.1; Pt, 38.8. $C_{12}H_{16}BrClN_2Pt$ calcd.: C, 28.9; H, 3.2; N, 5.6; Pt, 39.1%).

Heating a solution of $[Pt(CH_3)_2Py_2BrCl]$ in acetone with excess 30% $HClO_4$ for 30 min gave a yellow precipitate analysing for $Pt(CH_3)_2BrCl$. (Found: C, 7.1; H, 1.7; Pt, 57.2. $C_2H_6BrClPt$ calcd.: C, 7.1; H, 1.8; Pt, 57.3%).

Preparation of $[Pt(CH_3)_3X \cdot Pt(CH_3)_2X_2]_n$ *(X = I and Br)*

These were prepared as described previously[8]. The compound with X = I was also prepared by dissolving $[Pt(CH_3)_3Py_2I]$ (0.2 g) and $[Pt(CH_3)_2Py_2I_2]$ (0.24 g) in chloroform (10 ml) and shaking this solution with 2 *M* HCl (10 ml) until an orange-red solid precipitated. This was filtered off, washed with water and acetone, and air-dried. Yield 93%. The infrared spectrum of the product was identical to that of an authentic sample of $[Pt(CH_3)_3I \cdot Pt(CH_3)_2I_2]_n$, and dissolution of the product in pyridine gave equimolar amounts of $[Pt(CH_3)_3Py_2I]$ and $[Pt(CH_3)_2Py_2I_2]$ as confirmed by NMR.

^1H NMR spectra were recorded in $CDCl_3$ or D_2O solutions on a Varian A 60 Spectrometer with a sweep width of 540 Hz and using TMS and DSS* as reference.

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* TMS = tetramethylsilane, DSS = sodium salt of 3-(trimethylsilyl)propanesulphonic acid.

Chemical shifts are considered accurate to ±0.01 ppm and coupling constants to ±0.5 Hz.

Infrared spectra between 4000 and 400 cm^{-1} were recorded on a Perkin–Elmer 457 Spectrometer using Nujol and hexachlorobutadiene mulls between KBr plates. Frequencies are considered accurate to ± 2 cm^{-1}. Spectra below 400 cm^{-1} were recorded on an Hitachi FIS-3 (low range) infrared spectrometer as Nujol mulls on polythene plates.

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