Trimethylamine Complexes of Platinum(II) and Palladium(II) and their Vibrational and Proton Nuclear Magnetic Resonance Spectra

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Preparations of the complexes *trans*-$MX_2(NMe_3)_2$ and $Pr^n_4NMX_3NMe_3$ (MX = PdCl, PtCl, or PtBr) are reported. Their ^1H n.m.r., i.r., Raman, and electronic spectra are recorded and discussed. Complexes with MX = PdBr, PdI, or PtI could not be obtained and there was no indication of the parallel formation of $Pr^n_4NPtCl_3OMe_2$.

We have carried out extensive spectroscopic studies on trimethylphosphine and trimethylarsine complexes of platinum(II) and palladium(II).[1,2] As the role of π bonding is of particular interest in such compounds,[3] we wished to obtain results for the related trimethylamine complexes where π bonding is not possible. Despite the extremely large volume of work on tertiary phosphine and arsine complexes of these metals which has been published, reports of complexes with monodentate tertiary amines are extremely rare (there are several examples of complexes with polydentate ligands containing a tertiary amine group). The palladium compounds *trans*-$PdCl_2(NEt_3)(PMe_2Ph)$ [4] and $PdCl_2L_2$ (L = $Me_2NC_2H_4C_6H_5$ or $Me_2NC_3H_6C_6H_5$) [5] are known although the latter is described as difficult to handle. Chatt and Wilkins [6] state that 'even *trans*-$(NMe_3)_2PtCl_2$, where steric effects are negligible, is unknown'. We have been unable to find any reports of unsuccessful attempts to prepare such compounds, but our preliminary experiments to prepare trimethylamine platinum complexes by the methods used for dimethylamine as long ago as 1906,[7] showed that reaction, if any, was very slow and accompanied by the precipitation of platinum. Whilst it was possible that trimethylamine complexes might be unstable in terms of dissociation, the problem could be the inability of trimethylamine to replace chloride ions [*cf.* the use of $AgNO_3PMe_3$ to produce $Pt(PMe_3)_4(NO_3)_2$].[8] Such difficulty could be solved by using a chloro-bridged species where the neutral ligand could be co-ordinated without the necessity to completely dissociate a chloride ion. In fact, $Pt_2X_4(PMe_3)_2$ partially dissolved in dichloromethane reacts with an excess of trimethylamine (as a 10% solution in acetone) to give *trans*-PtX_2-NMe_3PMe_3 [9] when X = Cl or Br but not when X = I. The appropriate substrate to produce the anion PtX_3-NMe_3^- is the bridged anion $Pt_2X_6^{2-}$. $(Pr^n_4N)_2Pt_2Cl_6$ is soluble in *NN*-dimethylformamide and we find that this solution readily reacts with trimethylamine in acetone to produce the stable salt, $Pr^n_4NPtCl_3NMe_3$. Similar reactions occur with $(Pr^n_4N)_2Pd_2Cl_6$ and $(Pr^n_4N)_2Pt_2Br_6$ but not with the corresponding platinum iodide, palladium bromide, or palladium iodide salts. To prepare $PtCl_2(NMe_3)_2$, the chloro-bridged substrate would be platinous chloride. This is somewhat soluble in *NN*-dimethylformamide and under this solvent reacts with trimethylamine to yield the yellow *trans*-$PtCl_2(NMe_3)_2$. However, recovery of the product from this solvent is difficult and we find that a much more convenient method is to stir platinous chloride with an acetone solution of trimethylamine. Similarly, *trans*-bis(trimethylamine) complexes of $PtBr_2$ and $PdCl_2$ can be prepared in the same way but $PdBr_2$ does not seem to react to any significant extent.

Spectroscopic Results.—We have recorded the i.r. and Raman spectra of the complexes prepared and our observations below 600 cm^{-1} are listed in Table 1 (anions) and Table 2 (*trans* neutral species), together with the frequencies for the NC_3 stretching modes where these were observed. For the palladium compounds and $Pr^n_4NPtBr_3NMe_3$, Raman spectra could only be obtained on solutions as the solid was either too deeply coloured for study or decomposed in the laser beam.

We may use the comparison of the results for $PtCl_2$-

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[1] D. A. Duddell, J. G. Evans, P. L. Goggin, R. J. Goodfellow, A. J. Rest, and J. G. Smith, *J. Chem. Soc.* (*A*), 1969, 2134.

[2] D. A. Duddell, P. L. Goggin, R. J. Goodfellow, M. G. Norton, and J. G. Smith, *J. Chem. Soc.* (*A*), 1970, 545.

[3] L. M. Venanzi, *Chem. in Britain*, 1968, 162.

[4] S. O. Grim and R. L. Kelter, *Inorg. Chim. Acta*, 1970, **4**, 56.

[5] A. C. Cope and E. C. Friedrich, *J. Amer. Chem. Soc.*, 1968, **90**, 909.

[6] J. Chatt and R. G. Wilkins, *J. Chem. Soc.*, 1952, 4300.

[7] S. M. Jorgensen, *Z. anorg. Chem.*, 1906, **48**, 374.

[8] J. G. Evans, P. L. Goggin, R. J. Goodfellow, and J. G. Smith, *J. Chem. Soc.* (*A*), 1968, 464.

[9] P. S. Maddren, B.Sc. Thesis, Bristol, 1970.

TABLE 1

Infrared and Raman spectra (below 600 cm^{-1} and NC_3 symmetric stretching) of complexes $Pr^n{}_4NMX_3NMe_3$ (MX = PtCl, PtBr, or PdCl)

	$Pr^n{}_4NPtCl_3NMe_3$				$Pr^n{}_4NPtBr_3NMe_3$			$Pr^n{}_4NPdCl_3NMe_3$		
	I.R. mull	I.R. soln	R solid	R soln ^{b}	I.R. mull	I.R. soln	R soln ^{b}	I.R. mull	R soln ^{b}	R soln ^{e}
N–C_3 sym str	831s		831m		824s			825vs		
M–N str	549s		549wm	552m,p	545ms	548ms ^{b}	548w,p	536ms	536m,p	*d*
NC_3 sym def	251w,bd	248w ^{a}	250m	249wm,p	245m	248w ^{b}	247w,p	232w	232w,p	229w,p
MX_2 sym str	337sh		336s	328vs,p	193w		192,sp	305s	*d*	285s,p
MX_2 asym str	329vs	330vs ^{b}			221s	222s ^{a}		337vs		
MX str	314m,sh	309m,sh ^{b}	315s	310ms,p			218s,p	325sh	318w,p	322m,p
NC_3 rock	273m,bd	268sh ^{b}			270w,bd			285w,sh		
CH_3 torsion								255w		
MX_3N def	177m	181ms ^{a}	176s	180m,dp	158ms	150w ^{a}	148w,p	184sh	176m,dp	170m,dp
	167w,sh				125w	142w ^{a}		175m		
	139m	144m ^{a}	140vw,bd		116w		115w,dp	146m		
					110sh	*ca.* 100sh ^{a}				
Lattice vibrations	50s,bd				63ms					
					52ms					
Cation and others	518w				517w	513w ^{b}				
			437w,bd	442vvw,p	511w	318w,bd ^{b}	305vw,p	435vw	434vw,vbd,p	
				374vvw,p	344w,bd	230sh ^{a}				
Limit of study	(40)	(90)	(100)	(80)	(40)	(90)	(90)	(40)	(90)	(110)

^{a} In $CHCl_3$. ^{b} In CH_2Cl_2. ^{e} In $(CH_3)_2CO$. ^{d} Obscured by solvent.

TABLE 2

Infrared and Raman spectra (below 600 cm^{-1} and NC_3 stretching frequencies) of *trans*-$MX_2(NMe_3)_2$ (MX = PtCl, PtBr, or PdCl)

	$PtCl_2(NMe_3)_2$				$PtBr_2(NMe_3)_2$				$PdCl_2(NMe_3)_2$		
	I.R. mull	I.R. soln	R solid	R soln	I.R. mull	I.R. soln ^{c}	R solid	R soln ^{e}	I.R. mull	I.R. soln ^{e}	R soln ^{c}
NC_3 asym str	979sh				968s				982s		
	971s				962s				974s		
			976w								
			970w								
NC_3 sym str A_g			834m				829m				
B_u	821s				816s				819vs		
M–N_2 sym A_g			563ms	559s,p ^{b}			564m	562mp			542m,p
NC_3 sym def A_g			243s	244ms,p ^{b}			248s	245ms,p			218wm,p
M–N_2 asym str B_u or NC_3 sym def B_u	560s	556s ^{c}			556ms	560vs			548s	544s	
M–X_2 sym A_g			318s	317s,p ^{d}			190s	189vs,p			288s,p
M–X_2 asym str B_u	342vs	342vs ^{c}			216vs	216vs			351vs	351vs	
M–N_2 asym str,	310m,bd	310wm,bd ^{c}			313m,bd	307m,bd			300wm,bd	300w	
NC_3 sym def,	274m	270m ^{e}			304vvw						
NC_3 rock or	256m	256sh ^{c}			278vvw				261sh		
CH_3 torsion	242vvw	242vvw ^{e}			254m	249m			249ms	252ms	
							312w,bd				
In-plane deformation A_g			185vs	171m,dp ^{b}			155s	152m,dp			175wm,dp
Skeletal deformations $2A_u$ + $2B_u$	197ms	197wm ^{a}			161vs	159vs			204wm	200m	
	165s	163m ^{a}			145m	144ms			168ms	163ms	
	146w	132w ^{a}			126w,sh				148w	137w	
					86wm						
Lattice	90m	*ca.* 90vvw			60wm				89w		
Other bands	500w		340vvw, sh	344vw, sh,p ^{d}	576vvw, sh	331w,bd				219vw	
	447w	440w,bd ^{e}		444w,p ^{d}	500vw	189vw		210vw			
					446vw						
Limit of study	(40)	(90)	(40)	(80)	(40)	(90)	(100)	(120)	(40)	(90)	(140)

^{a} In $CHCl_3$. ^{b} In CH_2Cl_2. ^{c} In C_6H_6. ^{d} In CH_2Br_2.

$(NMe_3)_2$ and $PtBr_2(NMe_3)_2$ to find the MX_2 stretching frequencies of the neutral complexes. Firstly, the non-coincidence of these bands between i.r. and Raman spectra shows that all three are *trans* (point group C_{2h}). The MCl_2 (asym) frequencies are within the narrow range found for this vibration [10] but the symmetric counterpart is some 10 cm^{-1} below the values found in phosphine and arsine complexes. The symmetric $PtBr_2$ stretch for $PtBr_2(NMe_3)_2$ is *ca.* 16 cm^{-1} below those in comparable compounds whilst the asymmetric band is at 216 cm^{-1}. This is considerably below the usual range of 249 ± 9 cm^{-1} (ref. 10) and 11 cm^{-1} below the value for the diamine complex where hydrogen bonding may be responsible for the low frequency. Thus, although this assignment seems abnormal, there is no obvious alternative interpretation of the spectra. The M–Cl stretching modes of the chloro-anions may be assigned by comparison with the bromo-anion and previous examples,[11] the lower frequency polarised Raman band being MCl (*trans* to N) stretching. The MX_2 symmetric stretch is usually more polarised than the MX (*trans* to L) vibration in MX_3L. For $PtBr_3NMe_3^-$, the Raman band at 218 cm^{-1} is more polarised than that at 192 cm^{-1} but as ν_{MX_2} (sym) is usually similar in frequency in MX_3L and *trans*-MX_2L_2 [2] and because, to judge from the chloro-anions, MBr (*trans* to N) should be considerably higher than when *trans* to phosphorus (*ca.* 190 cm^{-1}) it seems better to assign these bands contrary to the polarisation results. Since ν_{MBr_2} (asym) is always strong in the i.r. region, this must contribute to the band at 221 cm^{-1} as well as the MBr stretch.

The A_g in-plane deformation of the *trans*-complexes is the only skeletal deformation that can be definitely assigned as for these complexes it is the only Raman active one. On account of the lighter neutral ligand, these frequencies are higher than for the trimethylphosphine analogues but like them, are not observed to be polarised. The Raman spectra of the anionic complexes show a band at a similar frequency which is probably also a ' scissors ' type of in-plane deformation but we do not understand why this band is slightly polarised for $PtBr_3NMe_3^-$. Since all the i.r. bands below 200 cm^{-1} show substantial halogen sensitivity, we consider that these must arise from skeletal deformations rather than ligand vibrations such as rocking modes.

The vibrations of trimethylamine relevant to this work are the two NC_3 stretches, the two NC_3 deformations and the methyl torsion, which have been assigned as 825 (sym) and 1043 cm^{-1} (asym), 366 (sym) and 423 cm^{-1} (asym), and 269 cm^{-1} respectively for the gaseous free ligand and are not significantly different for the solid state.[12] The symmetric NC_3 stretch of the complexes is almost at the same frequency as in the free ligand. Because of confusion with the bands of the cation, we cannot identify the asymmetric NC_3 stretch in the spectra of the anionic complexes but they are easily identified for the neutral compounds in the region of 970 cm^{-1} as previously found for trimethylamine complexes of boron halides [13] and of Br_2, I_2, and IBr.[14] Other workers have assigned the NC_3 asymmetric deformation in complexes at a similar frequency to that of the free ligand [13-15] and we have done the same for PMe_3 and $AsMe_3$ complexes.[2] Some i.r. spectra show weak bands near 440 cm^{-1} which could, perhaps, be this vibration; since ghosts of the 647·1 nm exciting line are sometimes observed at 436 and 395 cm^{-1} on our Raman spectrometer, we have not included weak features at these frequencies in the tables. Two other motions which one would expect to find in the region 600 to 200 cm^{-1} are the M–N stretch and NC_3 symmetric deformation (for the *trans*-complexes, one of each should occur non-coincidently in the Raman and i.r. spectra). The obvious choices for these are bands near 540 and 240 cm^{-1} (for the *trans*-complexes the Raman and i.r. bands are close in frequency but not quite as much so as the ' coincident ' bands of the anions).[11] For any M–N stretching vibration, there will always be an NC_3 deformation of the same symmetry which makes description difficult if not meaningless. Amster and Taylor [13] have assigned this latter vibration to frequencies in the range 337—316 cm^{-1} for boron trihalide complexes of trimethylamine and found it to be insensitive to the boron isotopic mass in contrast to the BN stretching frequencies around 700 cm^{-1}. Gayles [14] has assigned such vibrations at 365, 340, and 320 cm^{-1} for the I_2, IBr, and Br_2 complexes respectively, so that here the deformation frequency is higher than that of the N–M stretch. Beattie and Ozin [15] found two, frequencies 540 cm^{-1}, 275 cm^{-1}, and 573 cm^{-1}, 310 cm^{-1} for $GaCl_3NMe_3$ and $AlCl_3NMe_3$ respectively but, on the basis of the potential-energy contributions derived from a somewhat simplified force-field calculation, suggested that the modes were so greatly mixed that individual description was unjustified. In our complexes, assignment of the NC_3 deformation to one of the two available sets of frequencies would make it *ca.* 170 cm^{-1} greater or *ca.* 120 cm^{-1} less than in the free ligand. Either seems to be an excessive shift so that it seems more reasonable to adopt Beattie and Ozin's explanation and not identify the NC_3 deformations and MN stretches separately. We note, however, that Durig and his coworkers [16] assigned the asymmetric PdN_2 stretching vibrations in *trans*-$PdCl_2(NMeH_2)_2$ at 502 cm^{-1}, 6 cm^{-1} higher than in *trans*-$PdCl_2(NH_3)_2$, and we see no reason to criticise this assignment. Ligand rocking vibrations have been assigned by Beattie and Ozin between 250 and 200 cm^{-1} in the complexes with IIIB elements but we have found such features to be weak, generally, in the Raman effect. Methyl torsional vibrations might also

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[10] D. M. Adams, J. Chatt, J. Gerratt, and A. D. Westland, *J. Chem. Soc.*, 1964, 734.

[11] R. J. Goodfellow, P. L. Goggin, and D. A. Duddell, *J. Chem. Soc.* (*A*), 1968, 504.

[12] J. N. Gayles, *Spectrochim. Acta*, 1967, **23***A*, 1521.

[13] R. L. Amster and R. C. Taylor, *Spectrochim. Acta*, 1964, **20**, 1487.

[14] J. N. Gayles, *J. Chem. Phys.*, 1968, **49**, 1840.

[15] I. R. Beattie and G. A. Ozin, *J. Chem. Soc.* (*A*), 1968, 2373.

[16] J. R. Durig, R. Layton, D. W. Sink, and B. R. Mitchell, *Spectrochim. Acta*, 1965, **21**, 1367.

be observed in this region. The anionic complexes all show an i.r. band between 275 and 255 cm^{-1} that we have not otherwise assigned and for $PtBrNMe_3^-$ there is a weak feature at 318 cm^{-1} (a region which is obscured by skeletal modes in the chlorides) which presumably arises from such vibrations.

The parameters obtained from ^1H n.m.r. measurements on 0·1M-solutions of these complexes in dichloromethane are recorded in Table 3.

TABLE 3

^1H N.m.r. parameters of trimethylamine in platinum and palladium complexes

	τ	^3J(Pt–H)
$Pr^n{}_4NPdCl_3NMe_3$	7·48	
$Pr^n{}_4NPtCl_3NMe_3$	7·28	31·6
$Pr^n{}_4NPtBr_3NMe_3$	7·16	32·9
trans-$PdCl_2(NMe_3)_2$	7·42	
trans-$PtCl_2(NMe_3)_2$	7·34	28·6
trans-$PtBr_2(NMe_3)_2$	7·21	28·6

Visible and u.v. spectra have also been recorded for dichloromethane solutions. The observed maxima and their intensities are listed in Table 4 together with those of the ions $PtCl_3L^-$ (L = SMe_2, PMe_3, $AsMe_3$, and $SbMe_3$) for comparison. The spectra of the last three anions closely resemble each other and the five bands may perhaps, following the argument of Chatt, Gamlen, and Orgel,[17] be assigned as $^3A_{2g}$, ^3E_g, $^1A_{2g}{}^g$ ^1E_g, and charge transfer respectively, in order of increasing frequency. The spectrum of $KPtCl_3NH_3$ showed bands at 20·7 (2·8), 24·1 (19·8), 28·9 (118), and 33·3 (74) and including this with the data in the Table for other $PtCl_3L^-$, it is most reasonable to assume that we do not observe the counterpart of the lowest frequency band for $PtCl_3NMe_3^-$. The much lower intensity of the bands when a phosphine ligand is replaced by an amine has previously been found for $PtCl_2$(piperidine)L, (L = PR_3 and piperidine).[18]

TABLE 4

Visible and ultraviolet spectra [a]

trans-$PdCl_2(NMe_3)_2$			23·8 (230)	27·0 (270)	
trans-$PtCl_2(NMe_3)_2$		24·2 (26)	28·8 (59)	34·4 (175)	
trans-$PtBr_2(NMe_3)_2$		21·8 (41)	26·3 (110)	31·3 (190)	39·8 (2500)
$Pr^n{}_4NPdCl_3NMe_3$			22·8 (275)		30·0 (1600) 35·8 (7200)
$Pr^n{}_4NPtCl_3NMe_3$		22·5 (26)	27·5 (62)	31·5 (140)	39·2 (960)
$Pr^n{}_4NPtBr_3NMe_3$		20·7 (43)	25·6 (150)		31·6 (1600) 37·9 (3100)
$Pr^n{}_4NPtCl_3PMe_3$	23·1 (17)	27·5 (140)	31·1 (410)	35·7 (450)	41·4 (1650)
$Pr^n{}_4NPtCl_3AsMe_3$	21·9 (21)	25·6 (120)	29·2 (500)	34·2 (490)	40·4 (8600)
$Pr^n{}_4NPtCl_3SbMe_3$	21·2 (37)	24·4 (150)	28·2 (700)	33·1 (1250)	35·6 (12,000)
$Pr^n{}_4NPtCl_3SMe_2$		24·2 (57)	28·1 (190)	32·8 (310)	

[a] Positions of maxima in kK, intensities (l mol^{-1} cm^{-1}) in parentheses.

DISCUSSION

The relatively weak nature of the platinum–nitrogen co-ordinate bond is reflected in the donor atom–metal bond distances. Platinum–nitrogen distances,[19] like Pt–Cl [20,21] and Pt–Br,[20] are close to the sum of the covalent radii in contrast to platinum–phosphorus [20,21] and –arsenic [22] distances which are significantly shorter than the sum of covalent radii: platinum–sulphur [23] appears to be an intermediate case. This is in agreement with the spectrochemical order derived from the electronic spectra of the anions, $PtCl_3L^-$, and we note that NMe_3 comes considerably lower in this order than NH_3. The *trans*-influence of NMe_3 indicated by ν_{MCl} of the anions is similar to or slightly less than that of alkyl sulphides [11] and much less than for the phosphines and arsines. The ratio of $^3J_{PtH}$ in *trans*-$PtCl_2L_2$ to $^3J_{PtH}$ in $PtCl_3L^-$ for NMe_3 complexes is considerably greater (0·90$_5$) than for the PMe_3 (0·69) and $AsMe_3$ (0·79) complexes but only slightly more than that for the SMe_2 complexes (0·88) implying that the *trans*-influence of nitrogen is much less than phosphorus and nearer to that of the chloride ion. A similar deduction was made from the values of $^3J_{PtH}$ in the mixed ligand complexes *trans*-PtX_2LL'.[9] Thus bond length, electronic spectra, and *trans*-influence (from ν_{MCl} and from $^3J_{PtH}$) all show the same pattern for these donor atoms. If trimethylamine is a hard or ' Class A ' donor then one would expect it to form stronger bonds to the less soft (Class B) acceptor,[24,25] palladium(II) compared to platinum(II). However, all the frequencies identified with M–N stretching and NC_3 symmetric deformations are substantially lower for the palladium compounds than the counterparts for the platinum compounds despite the smaller mass of palladium. As M–P and M–As stretching frequencies behave in the same way, there is no indication here of a fundamentally different nature to trimethylamine as a ligand. Thus, whilst it is clear that

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[17] J. Chatt, G. A. Gamlen, and L. E. Orgel, *J. Chem. Soc.*, 1958, 486.

[18] J. Chatt, G. A. Gamlen, and L. E. Orgel, *J. Chem. Soc.*, 1959, 1047.

[19] ' International Tables for X-ray Crystallography, Vol. III,' Kynoch Press, Birmingham, England, 1962, p. 269.

[20] G. G. Messmer and E. L. Amma, *Inorg. Chem.*, 1966, **5**, 1775.

[21] G. G. Messmer, E. L. Amma, and J. A. Ibers, *Inorg. Chem.*, 1967, **6**, 725.

[22] S. F. Watkins, *J. Chem. Soc. (A)*, 1970, 168.

[23] D. L. Sales, J. Stokes, and P. Woodward, *J. Chem. Soc. (A)*, 1968, 1852.

[24] S. Ahrland and J. Chatt, *Quart. Rev.*, 1958, **12**, 265.

[25] R. G. Pearson, *J. Amer. Chem. Soc.*, 1963, **85**, 3533.

NMe_3 is a much weaker ligand than PMe_3 or $AsMe_3$, it is not obvious that this is due to differences in the orbitals available for bonding with the metal except perhaps for comparison of symmetric and asymmetric MN_2 frequencies. As the trimethylamine complexes most resemble those of dimethyl sulphide where we have suggested that non-bonding interactions are responsible for the weakness of the M–S bond,[26,27] a similar explanation may be relevant here. Although co-ordinated trimethylamine does not have the extra lone pair that dimethyl sulphide has, there could be significant interaction between the filled, non-bonding platinum *d*-orbitals and the N–C bonds in view of the shortness of the Pt–N bond. Also, from molecular models we estimate that one hydrogen atom of the trimethylamine group must always be between 2·0 and 2·7 Å from the *cis*-chloride in $PtCl_3$-NMe_3 whilst the sum of Van der Waal's radii is 3·0 Å. The corresponding ranges for trimethylphosphine and trimethylarsine are 2·3—2·9 Å and 2·4—3·0 Å respectively. Hence, on either count, there should be considerably more steric repulsion associated with the Pt–NMe_3 bond than with the Pt–PMe_3 and Pt–$AsMe_3$ bonds. We hope to obtain further information on the relative natures of NMe_3, PMe_3, and SMe_2 as ligands from a study of their platinum(IV) complexes.

TABLE 5

Analytical data for the complexes

			Analysis %							
			C		H		N		X	
	Colour	M.p.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
$Pr^{n}_{4}NPdCl_{3}NMe_{3}$	Orange-brown	106—109 *	39·35	39·3	8·1	8·15	6·25	6·1	22·95	23·2
$Pr^{n}_{4}NPtCl_{3}NMe_{3}$	Yellow-orange	140—143	33·0	32·95	6·85	6·8	5·05	5·1	19·25	19·45
$Pr^{n}_{4}NPtBr_{3}NMe_{3}$	Deep orange	129—130 *	26·55	26·5	5·5	5·5	4·25	4·1	35·1	35·2
trans-$PdCl_2(NMe_3)_2$	Yellow-brown	115 *	24·4	24·4	6·25	6·15	9·5	9·5	23·85	24·0
trans-$PtCl_2(NMe_3)_2$	Golden yellow	207—208 *	18·95	18·75	4·7	4·7	7·15	7·3	18·45	18·45
trans-$PtBr_2(NMe_3)_2$	Orange	144—146 *	15·3	15·2	3·9	3·8	5·95	5·9		

* With decomp.

In view of the success of the present approach to the preparation of trimethylamine complexes, we explored the reaction between a solution of $Pr_4NPt_2Cl_6$ in dimethylformamide and gaseous dimethyl ether. There was no evidence of the reaction to form $Pr_4NPtCl_3OMe_2$ and the starting material slowly precipitated from the ether saturated solution. We take this to indicate that dimethyl ether is a less effective donor than even bridged chloride.

EXPERIMENTAL

Infrared and ^1H n.m.r. measurements were made as previously reported.[1,2]

Raman spectra of solutions and, where possible, powdered solids, were recorded with a Coderg PHO Raman Spectrometer using 647·1 nm excitation from a Coherent Radiation Laboratories 52 MG krypton–argon ion laser. A grating premonochromator was used to eliminate plasma lines when making measurements on solids. The spectrometer was calibrated against argon and neon spectral lines. Raman frequencies are accurate to ± 2 cm^{-1}.

Visible and ultraviolet spectra were recorded with a Unicam SP 800 spectrophotometer for dichloromethane solutions in 1·0 cm silica cells.

Preparation of the Complexes.—*trans*-$PtCl_2(NMe_3)_2$. Platinum(II) chloride (1·1 g) was stirred with a 10% solution of trimethylamine in acetone (20 ml) for 30 min at room temperature (20 °C). After this time the solution was yellow and there was a copious deposit of yellow solid with no obvious sign of platinous chloride remaining. Recrystallisation from hot acetone gave the pure product (0·8 g, 50%) as golden plates. The acetone solutions tended to darken when heated in air but the natural colour was restored with animal charcoal. The preparation of *trans*-$PtBr_2(NMe_3)_2$ and *trans*-$PdCl_2(NMe_3)_2$ followed the same procedure but on a similar scale (by weight) the reaction times were 8 and 4 h respectively for complete reaction. Their acetone solutions decompose more readily than that of $PtCl_2(NMe_3)_2$ and the yields of pure product were 45 and 60% respectively.

$Pr^{n}_{4}NPtCl_{3}NMe_{3}$. $(Pr^{n}_{4}N)_2Pt_2Cl_6$ (1 g) was shaken with *NN*-dimethylformamide (10 ml) (in which it does not all dissolve) and a 10% solution of trimethylamine in acetone (15 ml) was added. After 30 min at room temperature all the solid had dissolved and the colour of the solution changed from brown to yellow-orange. Ether (200 ml) was added to precipitate the product which was then dissolved in acetone, and dried ($MgSO_4$). The pure product (0·7 g) crystallised as long yellow-orange needles on the slow addition of ether. The preparations of $Pr^{n}_{4}NPtBr_{3}NMe_{3}$ and $Pr^{n}_{4}NPdCl_{3}NMe_{3}$ followed the same procedure although the yields of the pure products were lower and there was a tendency for the acetone solutions to decompose.

The starting materials for these reactions were prepared by slightly different routes. Addition of an aqueous solution of $Pr^{n}_{4}NCl$ to an aqueous solution of Na_2PdCl_4 immediately produces a quantitative precipitation of $(Pr^{n}_{4}N)_2Pd_2Cl_6$. For the corresponding platinum compound, the monomer–dimer equilibrium is slow to establish and the compound must be prepared from a solution dilute enough to avoid precipitation of $(Pr^{n}_{4}N)_2PtCl_4$. A reliable method communicated to us by Barr[28] employs K_2PtCl_4 (5 g) in water

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[26] P. L. Goggin, R. J. Goodfellow, D. L. Sales, J. Stokes, and P. Woodward, *Chem. Comm.*, 1968, 31.

[27] P. L. Goggin, R. J. Goodfellow, and F. J. S. Reed, *J. Chem. Soc.* (*A*), 1971, 2031.

[28] R. Barr, Department of Chemistry, The Polytechnic of North London, personal communication.

(100 ml) and $Pr^n{}_4NCl$ (8 g) in water (100 ml). No precipitation occurs on mixing the solutions but after warming above 80° for 6 h, an 80% yield of the precipitated $(Pr^n{}_4N)_2Pt_2Cl_6$ can be collected. Attempts to prepare the bromo-analogue by a similar route, using K_2PtCl_4 with KBr to produce K_2PtBr_4 *in situ*, always resulted in some chloride contamination of the product. Pure $(Pr^n{}_4N)_2Pt_2Br_6$ was prepared by stirring platinous bromide (3·5 g) with a solution of $Pr^n{}_4NBr$ (2·6 g) in *NN*-dimethylformamide (100 ml) for 6 h. The crude product was precipitated with ether (1 l) and then stirred with hot water (80°) for 2 h to remove the excess of $Pr^n{}_4NBr$ and equilibrate any $(Pr^n{}_4N)_2PtBr_4$ to $(Pr^nN)_2Pt_2Br_6$. After drying the residue, it was continuously extracted with hot acetone. The first hour's extract was rejected after which a yield of 4·5 g (75%) was recovered from the acetone.

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