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PREPARATION AND ^{1}H NMR STUDY OF COMPLEXES OF TRIMETHYLPLATINUM(IV) WITH SOME TRIDENTATE SCHIFF BASE LIGANDS CONTAINING N, O, AND S DONOR ATOMS

DUNCAN H. GOLDSWORTHY and KENNETH KITE
Department of Chemistry, University of Exeter, Exeter EX4 4QD (Great Britain)

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Summary

The Schiff base ligands I–V, made by condensing either 2-acetylpyridine (I), 8-quinolinecarboxaldehyde (II and III), or *o*-methylthiobenzaldehyde (IV and V) with either *N,N'*-dimethyl-1,3-diaminopropane (I, II, and IV), 2-aminomethylpyridine (III), or 2-(2-aminoethyl)-pyridine (V), give ionic $Pt^{IV}Me_3$ complexes containing tridentate NNN- or SNN-bonded ligands. With $PtMe_3Br$ ligand V gives a neutral complex XI in which it is coordinated only via the two N atoms. A monomeric $Pt^{IV}Me_3$ salicylaldiminate complex results on treating the dimeric trimethylplatinum(IV) salicylaldehyde complex with the bidentate amine $H_2N(CH_2)_3NMe_2$. The complexes have been fully characterised by ^{1}H NMR spectroscopy.

Introduction

In trimethylplatinum(IV) compounds the metal is almost invariably octahedrally coordinated, and the methyl groups have a *fac* orientation [1]. These two stereochemical demands require that complexes of the type $[PtMe_3(L–L)]$ where (L–L) is an anionic bidentate ligand, e.g. the Schiff bases derived from salicylaldehyde $[C_6H_4(OH)CH{=}NR]$, R = Et, ^{n}Pr, Ph [2] and R = Me, ^{i}Pr, Bz [3] are dimeric, presumably via oxygen bridges as in the salicylaldehyde complex [4]. If the R group is extended to include a third potential donor the unsymmetrical tridentate ligand would afford a mononuclear complex which would necessarily by asymmetric. Complexes of $Pt^{IV}Me_3$ in which a single ligand occupies all the *trans* sites are limited to nitrogen and oxygen donors, i.e. with pyrazolylborates $[(C_3H_3N_2)_nBH_{4-n}]^-$ (n = 3,4) [5], with tris(1-pyrazolyl)methane and tris(2-pyridyl)methane [6], and with imidodiacetate (IDA), its *N*-methyl analogue (MIDA), and nitrilotriacetate (NTA) [1]. ^{1}H NMR studies show that in D_2O solution the anions $[PtMe_3(IDA)]^-$, $[PtMe_3(MIDA)]^-$, and $[PtMe_3(HNTA)]^-$ all have ONO coordination with the tridentate ligand. We have used the Schiff base condensation reaction

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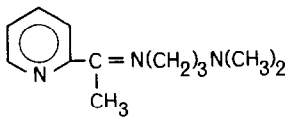
to make five neutral tridentate ligands (Fig. 1), initially with a view to resolving the optically active cationic complexes with the $PtMe_3^+$ ion since bidentate Schiff base ligands have been shown to be strong N-donors towards this ion [2,3]. The variation in ring size and substituents chosen were directed towards achieving maximum asymmetry in the chelates. In complexes of IV and V there is the additional possibility of inversion at the thioether sulphur atom which is such a striking feature of the complexes of the $Pt^{IV}Me_3$ halides with bidentate thioethers [7]. The same condensation reaction has also been used to give a salicylaldiminate complex by treating the dimeric trimethylplatinum salicylaldehyde complex with the bidentate amine $H_2N(CH_2)_3NMe_2$.

Results and discussion

The ligands I–V (Fig. 1) were made by condensing either 2-acetylpyridine (I), 8-quinolinecarboxaldehyde (II and III), or *o*-methylthiobenzaldehyde (IV and V) with either *N,N'*-dimethyl-1,3-diaminopropane (I, II, and IV), 2-aminomethylpyridine (III), or 2-(2-aminoethyl)-pyridine (V). The ionic $Pt^{IV}Me_3$ complexes VI–X (Table 1) were all made by treating $[(PtMe_3)_2SO_4 \cdot 4H_2O]$ in methanol with the ligand in the same solvent at room temperature, evaporating to dryness and treating an aqueous solution of the residue with $NaBPh_4$. The use of this counter ion invariably gave highly crystalline pale-yellow solids, which could be readily purified by crystallisation from acetone. The compounds were soluble in polar organic



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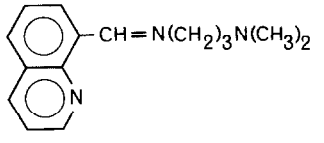

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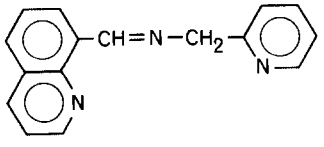

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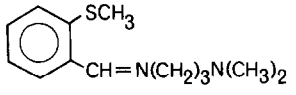

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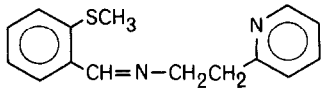

V

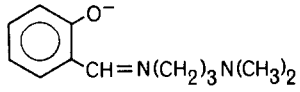

Fig. 1. Neutral tridentate Schiff base ligands I–V: the ionic salicylaldiminate ligand is also shown.

TABLE 1

ANALYTICAL, CONDUCTIVITY AND IR DATA FOR THE $Pt^{IV}Me_3$ COMPLEXES

Ligand	Complex	Analysis (Found (calc)(%))			M.p. [a] (°C)	Λ_M [b] (Ω^{-1} mol^{-1} cm^3)	ν(C=N) (cm^{-1})
		C	H	N			
I	$[PtMe_3(C_6H_4NC(Me):N(CH_2)_3NMe_2)]^+ BPh_4^-$ (VI) [c]	60.8 (61.3)	6.58 (6.48)	5.19 (5.29)	219–220(d)	125	1622
II	$[PtMe_3(C_9H_6NCH:N(CH_2)_3NMe_2)]^+ BPh_4^-$ (VII)	62.9 (63.0)	6.13 (6.04)	5.18 (5.25)	211–214(d)	118	1649
III	$[PtMe_3(C_9H_6NCH:NCH_2C_5H_4N]^+ BPh_4^-$ (VIII)	64.0 (64.0)	5.22 (5.25)	5.10 (5.21)	198–201(d)	118	1664
IV	$[PtMe_3(MeSC_6H_4CH:N(CH_2)_3NMe_2)]^+ BPh_4^-$ (IX)	60.1 (60.4)	6.21 (6.21)	3.46 (3.52)	198–200(d)	122	1631
V	$[PtMe_3(MeSC_6H_4CH:N(CH_2)_2C_5H_4N)]^+ BPh_4^-$ (X)	61.5 (61.8)	5.56 (5.68)	3.32 (3.43)	81– 84	101	1630
V	$[PtMe_3Br(MeSC_6H_4CH:N(CH_2)_2C_5H_4N)]$ (XI)	37.0 (37.4)	4.25 (4.54)	4.66 (4.85)	141–145	–	1630
	$[PtMe_3(OC_6H_4CH:N(CH_2)_3NMe_2)]$ (XII)	40.2 (40.4)	6.07 (5.88)	6.15 (6.29)	204–205	–	1627

[a] (d) indicates melts with decomposition. [b] In acetone solution. [c] Crystallises with 0.5 mol of acetone.

solvents like nitrobenzene and acetone, and all possess well-defined melting points. Conductivity measurements show that the BPh_4^- salts are 1:1 electrolytes in acetone solution (ca. 10^{-4} *M*) [8], indicating tridentate coordination of the Schiff base.

Attempts to resolve the cations proved unsuccessful. Treatment of aqueous solutions containing the sulphate with methanolic solutions of barium *d*-bis(3-trifluoroacetylcamphorate) and of silver *d*-tartrate, and a methanolic solution of the sulphate with ammonium *d*-3-bromocamphor-8-sulphonate did give precipitates of barium, silver and ammonium sulphate respectively, but only glasses or oils could be isolated from the filtrates.

A second complex of ligand V was made by refluxing stoichiometric amounts of $[PtMe_3Br]_4$ and V in benzene. Evaporation to dryness gave a yellow oil, from which cold methanol extracted X, and left a neutral yellow solid XI which gave no precipitate with $NaBPh_4$ in warm methanol (in which XI is soluble, and from which it could be recrystallised). The neutral salicylaldiminate XII is similar in appearance to compounds VI–XI, but is soluble in both polar and non-polar organic solvents (in contrast to the reported insolubility of the Schiff base complex having R = H [3]).

Not surprisingly the IR spectra of the BPh_4^- salts are extremely complex, but it is possible to pick out a strong C=N stretching mode from the Schiff bases [9] in the range 1620–1660 cm^{-1} (Table 1). Complex VI shows a strong band at 1710 cm^{-1} attributable to acetone of crystallisation.

NMR spectra

^1H NMR data for complexes VI–XII at room temperature are recorded in Table 2, and with the exception of XI are consistent with the presence of a mononuclear cationic or neutral species with the Schiff base bonded to the metal as a tridentate ligand. In each compound the platinum methyl groups are unrelated by any symmetry element and three equally intense Pt-Me signals are seen. One resonance, the central one in all but VIII, may be consistently assigned in all seven compounds to a methyl group *trans* to the imino N atom (sp^2-hybridised) on the basis of the low $^2J(^{195}Pt-^1H)$ values (62.3–67.9 Hz) as found in the salicylaldiminates for which a range of 65.7–68.2 Hz was reported [3]. This lower value of ^2J, indicating a strong bond *trans* to Pt-Me, is to be expected as the lone pair on the nitrogen atom is now in an orbital with higher *s*-character. The other two Pt-Me signals cannot be so certainly assigned, but none has a ^2J value outside the usual range for the *trans* ligands specified [10].

For VI, VII, IX, and XII which have a donor NMe_2 group, two N-Me signals with different $^3J(NCH_3)$ coupling constants are observed. This is understandable as the methyl groups are in dissimiliar chemical environments, but the marked difference in ^3J values (5.4–8.5 and 11.0–16.8 Hz) probably results from ring strain (see below) and the interaction of the NMe groups with the Pt-Me groups. A similar but less striking difference is seen in the $^3J(PtNCH_3)$ values in a series of complexes $[PtMe_3X \cdot L]$, where X = halide and L = $Me_2N(CH_2)_3NH_2$ and $Me_2N(CH_2)_3NMe_2$ [11].

In IX and X a single S-Me resonance is seen at room temperature showing clear coupling to ^{195}Pt. Since there are two possible conformations for the S-Me group (corresponding to the two N-Me environments above), inversion at the S atom must

TABLE 2

PROTON NMR DATA[a] FOR THE $Pt^{IV}Me_3$ COMPLEXES

Complex [b]	Pt-Me signals			Ligand X-Me signals			Imino-NH signals	
	δ	^2J	*trans* atom [c]	δ	^3J	X	δ	^3J
VI	0.28	69.8	N	2.01	7.3	N	[d]	[d]
	0.92	64.9	N*	2.40	15.4	N		
	0.97	67.4	N					
VII	0.29	68.6	N	2.50	6.8	N	8.64	32.2
	0.76	62.3	N*	2.62	16.1	N		
	1.02	68.9	N					
VIII	*0.23*	*70.3*	*N*	[e]	[e]		*8.41*	*31.0* [f]
	0.91	72.3	N					
	0.96	64.0	N*					
IX	0.42	68.1	N or S	2.43	16.8	N	8.30	34.2
	0.72	65.9	N*	2.69	12.9	S		
	1.03	67.4	S or N	2.89	8.5	N		
X	0.47	69.3	N or S	2.39	11.0	S	8.43	34.9
	1.02	65.2	N*					
	1.06	69.8	S or N					
XI	0.94	73.7	Br	2.52	–	S	[g]	[g]
	1.26	67.9	N*					
	1.30	69.3	N					
XII	0.61	72.0	N or O	2.40	5.4	N	7.82	28.3
	0.73	64.7	N*	2.46	13.7	N		
	0.82	72.3	O or N					

[a] Solvents $C_6D_5NO_2$ for VI–X; CD_2Cl_2 for XI; $CDCl_3$ for XII. δ in ppm; J in Hz. [b] Numbering as in Table 1. [c] Imino nitrogen atom asterisked. [d] $\delta(NCCH_3)$ 2.64 ppm; ^4J(Pt–H) 3.42 Hz. [e] N-CH_2 signals an AB quartet, J(HH) 15.5, ^3J(Pt–H) 20.4 Hz. [f] Approximate value; resonance partly obscured. [g] Obscured by the other resonances.

either be very rapid at room temperature, giving an averaged signal, or be prevented by the conformation of the chelate rings, the S-Me group being locked in one position. Molecular models show that the latter explanation is far more likely, though the spectrum of X was unchanged at 80°C.

The second complex with ligand V derived from $[PtMe_3Br]_4$ (XI) is a neutral species, and since the analysis is consistent with the presence of one bromine atom the ligand is presumably bidentate. This is confirmed by the ^1H NMR spectrum in CD_2Cl_2. Of the three Pt-Me signals, the central resonance is clearly assignable to methyl *trans* to N(sp^2) (^2J 67.9 Hz). The parameters for the high field signal are typical in both δ and ^2J values for methyls *trans* to terminal bromide, e.g. in adducts of $PtMe_3Br$ with bidentate nitrogen donors [12,13], where the signal from the Me group *trans* to Br is invariably at highest field, and ^2J is in the range 70.8–75.7 Hz. The assignment of the third signal to Me *trans* to the pyridine N atom follows from the fact that the S-Me proton signal does not show the coupling to ^{195}Pt observed in X, even at −60°C (which rules out ligand dissociation), while the pyridine α-protons do show a small coupling to the metal.

It is surprising to find that ^2J for methyls *trans* to N(sp^2) in X and XI are 65.2 and 67.9 Hz respectively, when the stronger Pt–N bond might have been expected with the bidentate ligand, especially as molecular models indicate that in this form ring strain is smaller. One possible explanation for this reversal is the different *cis* influences of the Br and SMe groups. If the *cis* influence parallels the *trans* influence (S > Br), the apparently stronger Pt–N bond in X may be a reflection of a weaker *trans* Pt–Me bond caused by the *cis* ligands. However, the relationship between *cis* and *trans* influences is not well understood [12,13], and other factors may well be involved.

Clear Pt–H coupling is also apparent in the imino NCH signal in VII–X and XII, ^3J being 28.3–34.9 Hz, proving the coordination of the imine group. The sp^2-hybridised donor N atom again accounts for this value being higher than ^3J(Pt–NCH_3) in I, II, IX, X, and XII where only sp^3 hybrids join the coupled atoms. In VI where the imino group has a methyl substituent, the N-Me signal shows ^4J(Pt–H) coupling (3.4 Hz). The presence of 0.5 mol of acetone of crystallisation in VI is detectable by integration of the sharp, uncoupled signal at 2.13 ppm.

Examination of the spectrum of VIII reveals an interesting Karplus-type dependence in the ^3J(PtNCH_2) values of the methylene proton signals [14]. The expected AB quartet is seen, with J(HH) 15.5 Hz, but only one of the protons is coupled to ^{195}Pt (J 20.4 Hz). Molecular models show that in the CH_2 group one proton lies in a plane at almost 90° to the Pt–N–C plane ($J \sim 0$ Hz) while the other is approximately in the Pt–N–C plane ($J > 0$ Hz). This can only be the case if there is no flexibility in this ring, and it illustrates the high degree of rigidity in these systems. A similar argument may account for the very different ^3J values for the NMe_2 methyl groups referred to above.

Experimental

2-Acetylpyridine, *N,N'*-dimethyl-1,3-diaminopropane, salicylaldehyde, 2-aminomethylpyridine, and 2-(2-aminoethyl)-pyridine were obtained commercially. $[PtMe_3Br]_4$, $[PtMe_3I]_4$, and $[(PtMe_3)_2SO_4 \cdot 4H_2O]$ were prepared by literature methods [15,16]. 8-Quinolinecarboxaldehyde, made by heating 8-methylquinoline [17] with SeO_2, was a white solid m.p. 92–94°C (lit. 95–96°C [18]). *O*-Methylthiobenzaldehyde (b.p. 92–94°C/0.5 mmHg; lit. 149°C/19 mmHg [19]) was made from *o*-methylthiobenzoic acid by the literature method [20,21]. The Schiff base ligands were made by the method of Sacconi and Speroni [22] as required, ^{1}H NMR spectra showing that the condensations went to completion.

Preparation of $[PtMe_3(C_5H_4NC(Me):N(CH_2)_3NMe_2)]^+ BPh_4^-$ *(VI)*

To a solution of $(PtMe_3)_2SO_4 \cdot 4H_2O$ (100 mg, 0.16 mmol) in methanol (10 cm^3) was added a solution of I (164 mg, 0.31 mmol) in methanol (5 cm^3) and the mixture was stirred for 30 min. A pale yellow colour developed, and after removal of solvent an aqueous solution of the product was treated with $NaBPh_4$ (110 mg, 0.32 mmol) to yield a yellow precipitate. The solid was recrystallised from acetone as pale yellow crystalline blocks containing 0.5 mol of acetone of solvation (157 mg, 66%).

Preparation of $[PtMe_3(C_9H_6NCH:N(CH_2)_3NMe_2)]^+ BPh_4$ *(VII)*

A pale yellow solution of II made from 8-quinolinecarboxaldehyde (61 mg, 0.38 mmol) and *N,N'*-dimethyl-1,3-diaminopropane (40 mg, 0.38 mmol) in methanol (12

cm^3) was added to $(PtMe_3)_2SO_4 \cdot 4H_2O$ (126 mg, 0.19 mmol) in methanol (10 cm^3) and the mixture was stirred for 1 h. The solution was filtered then was concentrated and treated with a solution of $NaBPh_4$ (130 mg, 0.38 mmol) in water (5 cm^3). A pale yellow precipitate was immediately formed. Recrystallisation from acetone gave pale yellow crystalline flakes (179 mg, 59%).

Preparation of $[PtMe_3(C_9H_6NCH:NCH_2C_5H_4N)]^+ BPh_4^-$ *(VIII)*

A solution of 8-quinolinecarboxaldehyde (157 mg, 1 mmol) and 2-aminomethylpyridine (108 mg, 1 mmol) in methanol (10 cm^3) was refluxed for 15 min. The pale yellow solution of III was added to $(PtMe_3)_2SO_4 \cdot 4H_2O$ (324 mg, 0.5 mmol) in methanol (10 cm^3) and the mixture stirred for 30 min. Work up as described for VII above, followed by recrystallisation from acetone/methanol gave pale yellow crystalline plates (712 mg, 90%).

Preparation of $[PtMe_3(MeSC_6H_4CH:N(CH_2)_3NMe_2)]^+ BPh_4^-$ *(IX)*

$(PtMe_3)_2SO_4 \cdot 4H_2O$ (111 mg, 0.17 mmol) and IV (81 mg, 0.34 mmol) were stirred together in methanol (12 cm^3) for 1 h. The procedure for VII was followed, and recrystallisation from acetone gave large pale yellow crystalline blocks (211 mg, 78%).

Preparation of $[PtMe_3(MeSC_6H_4CH:N(CH_2)_2C_5H_4N)]^+ BPh_4^-$ *(X)*

A solution of $(PtMe_3)_2SO_4 \cdot 4H_2O$ (100 mg, 0.15 mmol) in methanol (8 cm^3) was added to a solution of V (79 mg, 0.3 mmol) in methanol (8 cm^3) and the mixture was set aside for 2 h. Procedure as for VII and recrystallisation from acetone/aqueous ethanol gave fine pale yellow crystals (210 mg,77%).

Preparation of $[PtMe_3Br(MeSC_6H_4CH:N(CH_2)_2C_5H_4N)]$ *(XI)*

A solution containing $PtMe_3Br$ (236 mg, 0.74 mmol) and V (189 mg, 0.74 mmol) in benzene (30 cm^3) was refluxed for 3.5 h. The deep yellow solution was evaporated to dryness and the residual yellow oil was treated with cold methanol to give a yellow solid. Recrystallisation from hot methanol gave yellow nodular crystals (179 mg, 42%).

Preparation of thallium(I) salicylaldehydate (Tlsalic)

Tl_2CO_3 (9.0 g, 0.019 mol) was stirred under gentle reflux with salicylaldehyde (4.9 g, 0.04 mol) in ethanol (50 cm^3) for 11 h. The deep yellow-green solution was filtered hot from unreacted carbonate, concentrated and cooled. Bright yellow needles of Tlsalic were obtained (1.24 g, 10%). (Found: C, 26.2; H, 1.54. $C_7H_5O_2Tl$ calcd.: C, 25.8; H, 1.54%).

Preparation of $[PtMe_3(sal)]_2$

Though this compound has been reported in the literature [23] its preparation has not been described. It was made from the thallous salt as follows.

A mixture of $[PtMe_3I]$ (443 mg, 1.12 mmol) and Tlsalic (400 mg, 1.23 mmol) in benzene (50 cm^3) was refluxed with stirring for 8 h. Precipitated thallous iodide was filtered off and the yellow filtrate evaporated to dryness to leave a yellow oily solid. Recrystallisation from toluene/light petroleum gave yellow crystals (154 mg, 36%). (Found: C, 33.1; H, 4.00. $C_{10}H_{14}O_2Pt$ calcd.: C, 33.2; H, 3.90%).

Preparation of [$PtMe_3(OC_6H_4CH:N(CH_2)_3NMe_2)$] (XII)

A mixture of $[PtMe_3(salic)]_2$ (135 mg, 0.19 mmol) and *N,N'*-dimethyl-1,3-diaminopropane (46 mg, 0.45 mmol) in benzene (15 cm^3) was heated under reflux for 3 h. The golden yellow solution was evaporated to dryness, and the yellow oily residue recrystallised from light petroleum as yellow crystalline blocks (135 mg, 81%).

IR spectra were run as KBr discs on a Perkin–Elmer 357 spectrometer. ^1H NMR spectra were recorded using a 100 MHz JEOL MH100 spectrometer for room temperature data, and a JEOL PS/PFT 100 spectrometer for variable temperature studies. Melting points were taken on a Mettler hot stage microscope, and are uncorrected.

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