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PREPARATION OF DIMETHYLPLATINUM(IV) AND MONOMETHYLPLATINUM(IV) COMPOUNDS FROM MONOMETHYLPLATINUM(II) COMPOUNDS

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Summary

Using $PtCH_3(NBD)I$ (NBD = norbornadiene) as starting material, compounds of the type $PtCH_3L_2I$ (L_2 = 1,5-cyclooctadiene and *N,N,N',N'*-tetramethylethylenediamine, L = 3,5-lutidine and benzylamine) have been prepared and characterized by ^1H NMR and elemental analysis. The compounds with L = lutidine, L_2 = *N,N,N',N'*-tetramethylethylenediamine undergo oxidative addition with both CH_3I and I_2 to yield dimethylplatinum(IV) and monomethylplatinum(IV) compounds respectively.

Introduction

The chemistry of both the dimethylplatinum(IV) and monomethylplatinum(IV) systems has until the last few years been limited almost completely to those compounds containing tertiary phosphine and arsine ligands [1—4]. However, the compounds $[Pt(CH_3)_2X_2]_n$ have recently been prepared by several independent routes [5—7] and these have proved to be useful starting materials for the preparation of a variety of dimethylplatinum(IV) compounds [6, 8, 9]. For example, reaction of $[Pt(CH_3)_2X_2]_n$ with a variety of N-donor ligands yielded the complexes $[Pt(CH_3)_2L_2X_2]$, where L_2 is one bidentate or two unidentate ligands, and without exception these complexes had stereochemistry (a) of Fig. 1 [8].The compound $[PtCH_3I_3]_n$ has been reported [7, 10] and was found to decompose on reaction with pyridine [7]. In the present paper dimethylplatinum(IV) compounds of the type $[Pt(CH_3)_2L_2X_2]$ which have structures (b) and (c) of Fig. 1 have been prepared by addition of CH_3I to monomethylplatinum(II) compounds, and the first monomethylplatinum(IV) compounds containing N-donor ligands are also reported.

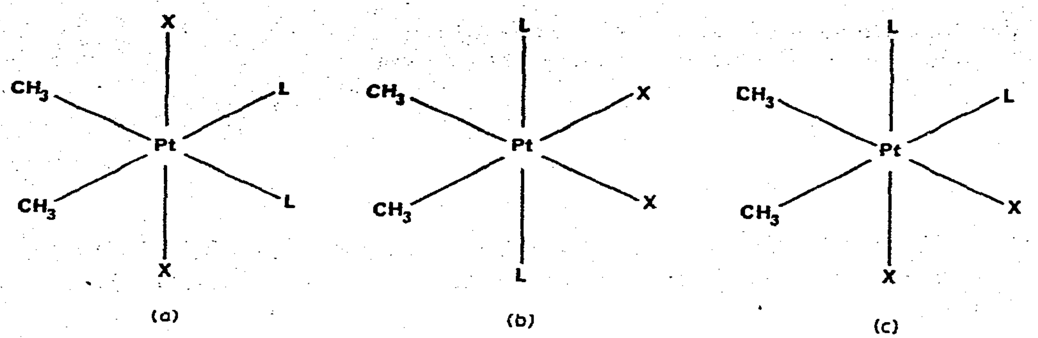
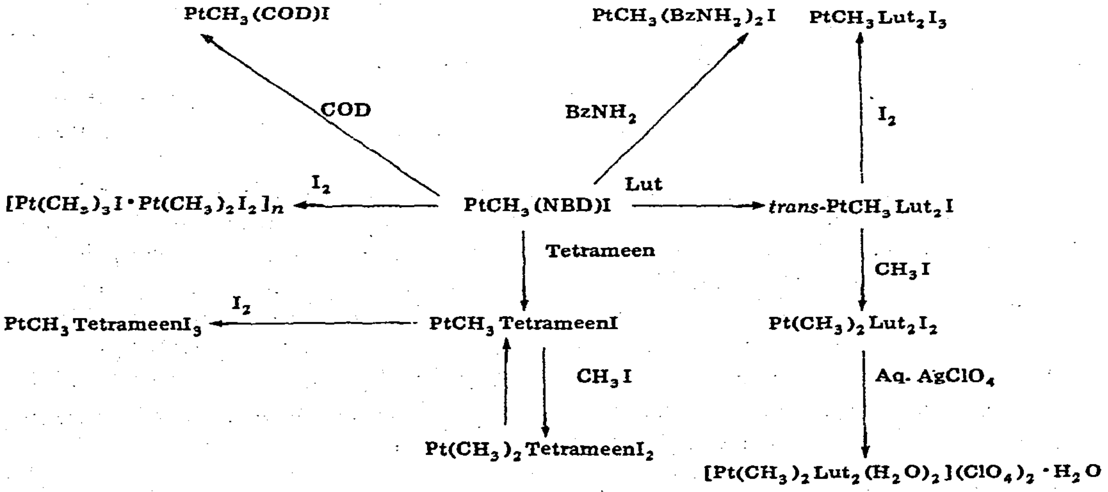


Fig. 1. Possible isomers for complexes of the type $Pt(CH_3)_2L_2X_2$ containing *cis* methyl groups.

Results and discussion

Kistner et al. [11] described the preparation of $PtCH_3(NBD)I$ (NBD = norbornadiene) and its reaction with pyridine to produce $PtCH_3Py_2I$, but apart from reporting the infrared spectrum of $PtCH_3(NBD)I$ the compounds were not further studied. We have found that a variety of ligands, including 1,5-cyclooctadiene (COD), *N,N,N',N'*-tetramethylethylenediamine (Tetrameen) and 3,5-lutidine (Lut), readily displace norbornadiene from $PtCH_3(NBD)I$ to form the compounds $PtCH_3L_2I$, where L_2 is one bidentate or two unidentate ligands (Scheme 1). These compounds are all soluble in organic solvents and the ^1H NMR spectra in $CDCl_3$ are recorded in Table 1. Reference to Table 1 shows that the ^1H NMR spectra are consistent with the compounds postulated above. The compounds $PtCH_3(NBD)I$ and $PtCH_3(COD)I$ both exhibit two distinct olefinic proton resonances each with a different coupling constant $^2J(^{195}Pt{-}CH)$, as would be predicted on the basis of the results of *trans* influence studies [12] which indicate that the coupling *trans* to CH_3 should be smaller than that *trans* to I. Thus the resonance with $J \sim 35$ Hz is assigned in each case to the olefinic



Scheme 1.

protons *trans* to CH_3 and that with $J \sim 76$ Hz to those *trans* to I. A similar non-equivalence of the N-methyl protons appears in the spectrum of $PtCH_3$TetrameenI, and the coupling constants for N-methyl protons *trans* to CH_3 and I are 16.3 Hz and 52.8 Hz respectively. As shown in Table 1 the methyl-platinum protons are also sensitive to the nature of the *trans* ligand, ranging from 77.4 to 85.3 Hz in these compounds.

For the compound $PtCH_3Lut_2I$, two isomers are possible viz. those with *cis* and *trans* lutidine groups. The ^1H NMR spectrum exhibits only a single lutidine α-proton resonance, $^3J(^{195}Pt—C—H_\alpha)$ 50.0 Hz, consistent with the presence of *trans* lutidine groups.

Preliminary experiments indicate that primary amines also react with $PtCH_3$(NBD)I, and with benzylamine the compound $PtCH_3(BzNH_2)_2I$ may be obtained in low yield. It may be noted that the reaction between $Pt(NBD)Cl_2$ and amines involved nucleophilic attack at one double bond of the diene rather than substitution at the platinum atom [13].

The compound $PtCH_3$(NBD)I reacts very slowly with CH_3I to form orange crystals of $[Pt(CH_3)_3I\cdot Pt(CH_3)_2I_2]_n$, identified from its infrared spectrum [8], rather than the expected product, $[Pt(CH_3)_2I_2]_n$. In contrast, both *trans*-$[PtCH_3Lut_2I]$ and $PtCH_3$TetrameenI react rapidly with CH_3I to form $Pt(CH_3)_2Lut_2I_2$ and $Pt(CH_3)_2$TetrameenI_2, respectively (Scheme 1).

$[Pt(CH_3)_2Lut_2I_2]$ is sparingly soluble in organic solvents and its NMR spectrum could not be obtained. The compound reacts with aqueous $AgClO_4$ and the NMR spectrum of the water-soluble product exhibits a single methyl-platinum triplet with $^2J(^{195}Pt—CH_3)$ 74.6 Hz, which suggests that the CH_3 groups are *trans* to O-donor (H_2O) ligands [12]. The α-protons of the lutidine molecules are represented by a single triplet with $^3J(^{195}Pt—N—C—H_\alpha)$ 35.4 Hz, indicating that these are in positions *trans* to each other rather than *trans* to CH_3 where a value of ~ 13 Hz would be expected [8]. The species in solution is thus $[Pt(CH_3)_2Lut_2(H_2O)_2]^{2+}$ with CH_3 *trans* to H_2O. By evaporation of the solution a white solid of formula $[Pt(CH_3)_2Lut_2(H_2O)_2](ClO_4)_2\cdot H_2O$ may be isolated. Assuming no rearrangement has occurred during the reaction, the compound $Pt(CH_3)_2Lut_2I_2$ must have structure (b) of Fig. 1.

$Pt(CH_3)_2$TetrameenI_2 is unstable both in the solid state and in solution, losing CH_3I to reform $PtCH_3$TetrameenI. The ^1H NMR spectrum (Table 1) of a freshly prepared sample is consistent with the compound having structure (c) of Fig. 1. There are two non-equivalent methyl-platinum triplets with coupling constants of 68.8 Hz and 70.4 Hz which are tentatively assigned to CH_3 groups *trans* to I and lutidine respectively. Four non-equivalent N-methyl resonances are observed with different coupling constants which result from different *trans* groups and different spatial arrangements of the CH_3 groups. The peaks at τ 6.51 and 7.28 with coupling constants 11.5 and 14.8 Hz may be assigned to the protons on the N-methyl groups *trans* to CH_3 while those at τ 6.70 and 7.59 with coupling constants of 32.0 and 37.4 Hz are assigned to the N-methyl protons *trans* to I.

Both $PtCH_3Lut_2I$ and $PtCH_3$TetrameenI readily add iodine to produce the monomethylplatinum(IV) compounds $PtCH_3Lut_2I_3$ and $PtCH_3$TetrameenI_3 respectively (Scheme 1), The former is a dark brown solid and the latter is dark green. Both are sparingly soluble in organic solvents and NMR spectra were not

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TABLE 1

^{1}H NMR SPECTRA OF MONOMETHYLPLATINUM(II) AND DIMETHYLPLATINUM(IV) COMPOUNDS IN $CDCl_3$ SOLUTION

Compound	$J(^{195}Pt-CH_3)$	Donor atom *trans*-CH_3	$\tau(CH_3-Pt)$	$J(Pt-H(lig))$ [a]	Donor atom *trans*-H(lig)	$\tau(Pt-H(lig))$
$PtCH_3(NBD)I$	85.3	[b]	9.03	33.8	C	4.25
				78.5	I	5.10
$PtCH_3(COD)I$	72.9	[b]	8.88	37.4	C	4.40
				75.0	I	5.30
$PtCH_3$ TetrameenI	77.4	N	9.28	16.3	C	7.11
				52.8	I	7.12
$PtCH_3Lut_2I$	86.3	I	9.14	50.0	N	1.41
$Pt(CH_3)_2TetrameenI_2$	70.4	N	7.85	11.5	C	6.51
	68.8	I	8.21	32.0	I	6.70
				14.8	C	7.28
				37.4	I	7.59
$[Pt(CH_3)_2Lut_2(H_2O)_2]^{2+}$ [c]	74.6	O	—	35.4	N	—

[a] Values refer to coupling between ^{195}Pt and olefinic protons, $N-CH_3$ protons and H_α protons (Lut). [b] Olefinic bond *trans*-methyl.
[c] Measured in H_2O solution, not referenced.

TABLE 2

ANALYSES AND YIELDS OF THE PRODUCTS OBTAINED

Compound	Empirical formula	Yield (%)	Analysis (found (calcd.)) (%)				
			C	H	I	N	Pt
$Pt(NBD)I_2$	$C_8H_{11}I_2Pt$	85	15.7 (15.5)	1.5 (1.5)			35.8 (36.1)
$PtCH_3(NBD)I$	$C_8H_{11}IPt$	90	22.4 (22.4)	2.6 (2.6)	30.0 (29.6)		45.2 (45.5)
$PtCH_3(COD)I$	$C_9H_{15}IPt$	80—90	24.5 (24.3)	3.4 (3.4)	28.7 (28.5)		43.6 (43.8)
$PtCH_3$TetrameenI	$C_7H_{19}IN_2Pt$	80—90	18.4 (18.5)	4.1 (4.2)	28.4 (28.0)	6.2 (6.2)	43.2 (43.0)
$PtCH_3Lut_2I$	$C_{15}H_{21}IN_2Pt$	80—90	32.5 (32.7)	3.8 (3.8)		5.0 (5.1)	35.0 (35.4)
$PtCH_3(BzNH_2)_2I$	$C_{15}H_{21}IN_2Pt$	15	32.6 (32.7)	3.9 (3.8)	23.6 (23.0)	5.0 (5.1)	35.2 (35.4)
$Pt(CH_3)_2Lut_2I_2$	$C_{16}H_{24}I_2N_2Pt$	60	27.7 (27.7)	3.6 (3.5)	36.9 (36.6)	3.8 (4.0)	28.0 (28.1)
$[Pt(CH_3)_2Lut_2(H_2O)_2](ClO_4)_2 \cdot H_2O$	$C_{16}H_{30}Cl_2N_2O_{11}Pt$	90	27.9 (27.8)	4.2 (4.4)		3.9 (4.0)	
$Pt(CH_3)_2$TetrameenI$_2$	$C_8H_{22}I_2N_2Pt$	90	16.6 (16.1)	3.8 (3.7)	42.1 (42.6)	4.4 (4.7)	32.2 (32.8)
$PtCH_3Lut_2I_3$	$C_{15}H_{21}I_3N_2Pt$	90	22.6 (22.4)	2.8 (2.6)	46.9 (47.3)	3.3 (3.5)	23.9 (24.2)
$PtCH_3$TetrameenI$_3$	$C_7H_{19}I_3N_2Pt$	90	11.7 (11.9)	2.7 (2.7)	54.1 (53.9)	3.6 (4.0)	27.2 (27.6)

obtained. Both compounds tend to decompose on prolonged standing in solution, apparently with loss of the methyl group.

Experimental

Analytical data and yields see Table 2.

Preparation of $Pt(NBD)I_2$. The compound was prepared by the method of Alexander et al. [14] and recrystallized from chloroform.

Preparation of $PtCH_3(NBD)I$. The compound was prepared by the method of Kistner et al. [11] and recrystallized from chloroform—petr. ether.

Preparation of $PtCH_3L_2I$ (L_2 = *COD, Tetrameen*, L = *Lut*, $BzNH_2$). $PtCH_3$(NBD)I (0.2 g) was dissolved in chloroform (5 ml) and a slight excess of the appropriate ligand added. After refluxing for 30 min the solution was concentrated to a small volume and the product precipitated out with petr. ether.

Preparation of $Pt(CH_3)_2Lut_2I_2$. $PtCH_3Lut_2I$ (0.2 g) was dissolved in chloroform (5 ml) and CH_3I (5 ml) added. On heating the mixture a fawn solid precipitated out and was filtered off and washed with chloroform.

Preparation of $[Pt(CH_3)_2Lut_2(H_2O)_2](ClO_4)_2 \cdot H_2O$. $Pt(CH_3)_2Lut_2I_2$ (0.1 g) was suspended in acetone (5 ml) and water (5 ml), and 2.4 ml of 0.12 *M* $AgClO_4$ solution added. The mixture was boiled for 10 minutes and filtered to remove AgI and the resultant solution evaporated to dryness. The product was a white crystalline solid.

Preparation of $Pt(CH_3)_2TetrameenI_2$. $PtCH_3$TetrameenI (0.2 g) was dissolved in chloroform (5 ml) and CH_3I (5 ml) added. The mixture was boiled for 5 minutes, the yellow solution concentrated to a small volume and the product precipitated with petr. ether. The product is a bright yellow solid which slowly decomposes both in the solid state and in solution to regenerate $PtCH_3$TetrameenI.

Preparation of $PtCH_3Lut_2I_3$. $PtCH_3Lut_2I$ (0.1 g) was suspended in chloroform (5 ml) and a solution of iodine (0.046 g) in chloroform (5 ml) added. The solution immediately turned red-brown and a brown solid precipitated slowly. Addition of petr. ether completed the precipitation and the product was filtered off, washed with petr. ether and air-dried.

Preparation of $PtCH_3TetrameenI_3$. $PtCH_3$TetrameenI (0.1 g) was dissolved in chloroform (5 ml) and a solution of iodine (0.056 g) in chloroform (5 ml) added. The solution immediately turned a deep green and a dark green solid precipitated. The precipitation was completed by addition of petr. ether (20 ml) and the product filtered off and washed with petr. ether.

^1H NMR spectra were recorded on a JEOL MH 100 spectrometer using a sweep width of 540 Hz and TMS as internal reference. Spin—spin coupling constants are considered accurate to ± 0.5 Hz and τ values to ± 0.01 ppm.

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