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DIMETHYLPLATINUM(IV) COMPOUNDS

III*. ACETYLACETONATE COMPLEXES

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Summary

A number of acetylacetonate complexes of dimethylplatinum(IV) have been prepared and structures proposed for them on the basis of infrared and ^{1}H NMR spectra.

Introduction

Studies on acetylacetonate complexes of trimethylplatinum(IV) have shown that the acetylacetonate ligand can coordinate in a variety of ways. The ligand may function as (*i*) a *tridentate* via the oxygen atoms to one Pt atom and via the central (γ) carbon atom to a second Pt atom as in $[Pt(CH_3)_3Acac]_2$ [1,2]; (*ii*) a *bidentate* through the oxygen atoms as in the compounds $[Pt(CH_3)_3Acac]_2En$ [3] and $Pt(CH_3)_3AcacR$ (R = a neutral unidentate ligand) [4,5]; or (*iii*) a *unidentate* via the γ-carbon atom as in $Pt(CH_3)_3BipyAcac$ [6,7] and $Pt(CH_3)_3PhenAcac$ [4,5]. No acetylacetonate complexes of dimethylplatinum(IV) have as yet been reported, although a greater variety than that found in the trimethylplatinum(IV) system should be possible. In this paper, the preparations of several acetylacetonate complexes of dimethylplatinum(IV) are described, and structures for them are proposed on the basis of ^{1}H NMR and infrared spectra.

Results and discussion

The preparations and reactions of the acetylacetonate complexes of dimethylplatinum(IV) reported in the present work are shown in Scheme 1.

$[Pt(CH_3)_2Br_2]_n$ [8] was found to react in benzene with thallium(I) acetylacetonate to give a yellow solid analysing for $Pt(CH_3)_2AcacBr$ which, from molecular weight measurements, is probably dimeric. As shown in

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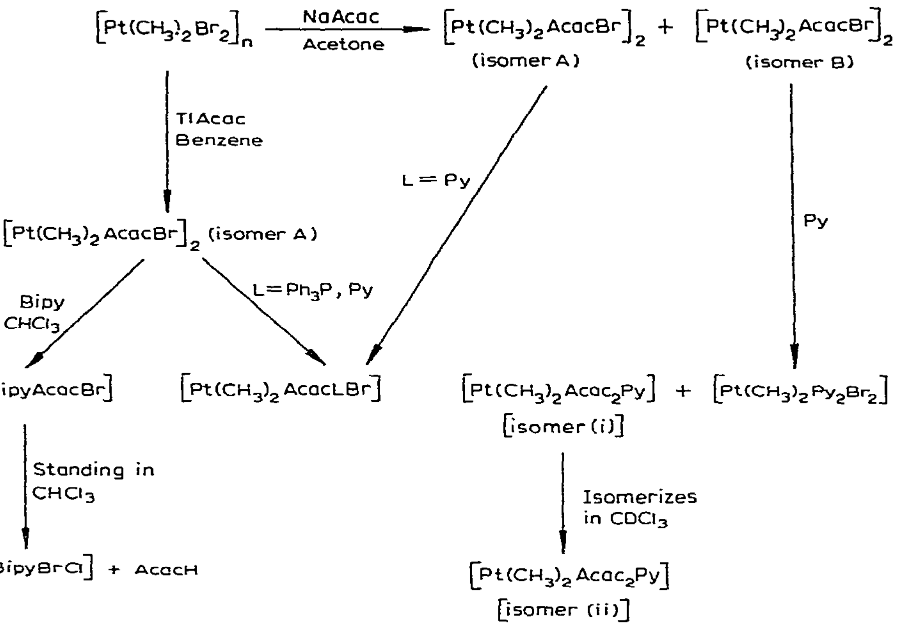
* For Part II see ref. [14].

SCHEME 1



Scheme 1, reaction of the compound $[Pt(CH_3)_2AcacBr]_2$ (isomer A) with triphenylphosphine or pyridine gave the compounds $Pt(CH_3)_2AcacLBr$ ($L = Ph_3P$ or Py), which (neglecting isomers with *trans*-CH_3 groups) may exist as three geometric isomers*, as shown in Fig. 1. The ^1H NMR spectra of the compounds (Table 1) indicate the presence of only a single geometric isomer for each compound, even when the reaction is performed in an NMR tube and the spectrum recorded immediately. The compound $Pt(CH_3)_2Acac(Ph_3P)Br$ may be unequivocally assigned as isomer (a) of Fig. 1. Two non-equivalent methyl platinum triplets (^{195}Pt, $I = ½$, 34% abundance) with coupling constants of 72.5 and 60.8 Hz are observed and these may be assigned to the protons of CH_3 groups *trans* to an oxygen of an acetylacetonate group and *trans* to phosphorus respectively, since these values agree well with those found in $Pt(CH_3)_3Acac(Ph_3P)$ (74.2 and 60.4 Hz respectively) [5]. Each of the triplets is further split by coupling between the CH_3 protons and ^{31}P ($I = ½$, 100% abundance) and, as noted in a number of trimethylplatinum(IV) complexes containing triphenylphosphine [5], the value of $^3J(^{31}P—Pt—CH_3)$ is larger for the *trans*-CH_3 protons (8.9 Hz) than for the *cis*-CH_3 protons (7.8 Hz).

As expected for isomer (a) of Fig. 1, the methyl groups of the acetylacetonate ligand are non-equivalent. A significant feature of the NMR spectrum is that the protons of one of these methyl groups show a coupling with ^{195}Pt of 4.6 Hz. Although coupling of this type has been observed in acetylacetonatoplatinum(II) complexes [9], it has not been observed for acetylace-

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* (a) and (b) of Fig. 1 would exist as optical isomers. No attempt was made in the present study to investigate the question of optical activity.

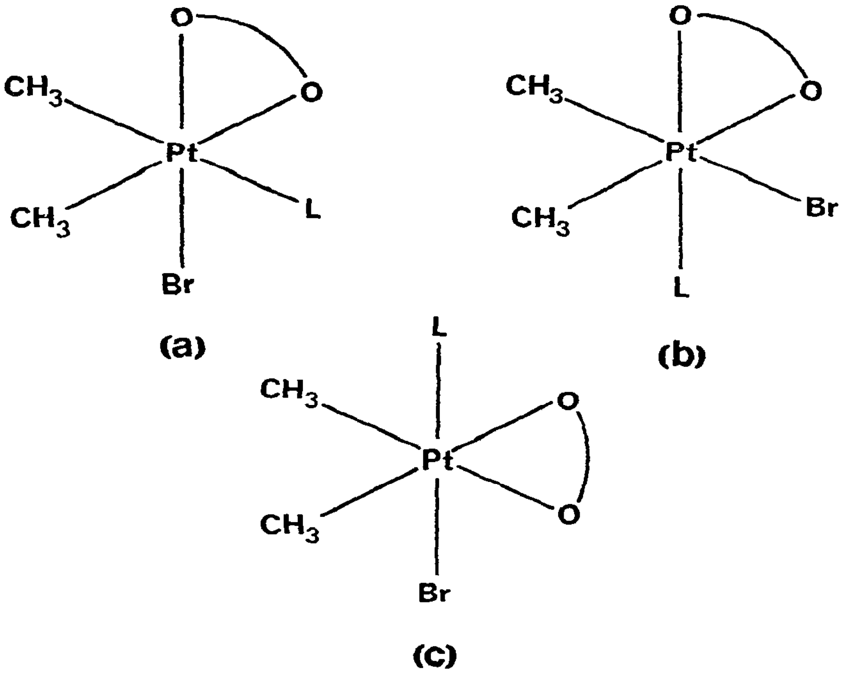

Fig. 1. Geometric isomers for $Pt(CH_3)_2AcacLBr$ (assuming *cis*-dimethyl configuration only).

tonate complexes of trimethylplatinum(IV) [1,5]. Such a variation in coupling in methylplatinum(IV) compounds may be explained in terms of the ligands in the *trans* positions. The greater the *trans* influence of a ligand, the weaker the bond in the *trans* position, and consequently the smaller the coupling through that bond [10,11]. Since the *trans* influence of a methyl group is much greater than that of a Br atom [12], any coupling through a bond *trans* to CH_3 would be smaller than the same coupling through a bond *trans* to Br. Thus in the compound $Pt(CH_3)_2Acac(Ph_3P)Br$ coupling between the acetylacetonate methyl protons and ^{195}Pt via the Pt—O bond *trans* to CH_3 is too small to be observed, while coupling between the protons of the other acetylacetonate methyl group and ^{195}Pt via the Pt—O bond *trans* to Br is observable (4.6 Hz). The central (γ) proton of the acetylacetonate group also couples with ^{195}Pt, and the magnitude of this coupling (4.2 Hz) is again somewhat higher than the value of $\approx$ 2 Hz found in the compounds $Pt(CH_3)_3AcacR$ [1,5]. The ^1H NMR spectrum of $Pt(CH_3)_2AcacPyBr$ is interpretable in terms of a similar structure (Table 1).

Providing no rapid isomerization has occurred during the reaction of $[Pt(CH_3)_2AcacBr]_2$ with Ph_3P or Py, the formation of the single isomer (a) (Fig. 1) of the compounds $Pt(CH_3)_2AcacLBr$ limits the number of geometrical isomers possible for $[Pt(CH_3)_2AcacBr]_2$. The parent compound was not sufficiently soluble in organic solvents to give an interpretable ^1H NMR spectrum, but the infrared spectrum of the solid exhibits strong bands at 1593 and 1575 cm^{-1} in the C=O stretching region, and these values are consistent with the

TABLE 1

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

Compound	No. of CH_3–Pt peaks	Ratio	*trans* atom	$\tau(CH_3–Pt)$	$^2J(^{195}Pt–CH_3)$	$\tau(H_\gamma)$	$^2J(^{195}Pt–C–H_\gamma)$	$\tau[CH_3(Acac)]$	$^4J[^{195}Pt–CH_3\text{-}(Acac)]^3$	$^3J(^{31}P–Pt–CH_3)$
$Pt(CH_3)_2Acac(Ph_3P)Br$	2	1	O	8.22	72.5	4.97	4.2	8.17		7.8
		1	P	8.31	60.8			8.44	4.6	8.9
$Pt(CH_3)_2AcacPyBr$	2	1	O	8.17	72.3	4.77	5.0	7.99		
		1	N	8.33	70.5			8.04	5.4	
$Pt(CH_3)_2BipyAcacBr$	1		N	7.85	68.9	5.12	3.5	8.05		
								8.21	3.5	
$[Pt(CH_3)_2AcacBr]_2$ (isomer B)	4	1	O	7.72	78.5	4.65	4.0	7.68		
		1	O	7.77	78.5	5.06	99.0	7.72		
		1	Br	8.33	75.4			8.02	3.0	
		1	O	8.55	66.8			8.06		
$Pt(CH_3)_2Acac_2Py$ [isomer (i)]	2	1	O	8.68	69.2	4.86	3.0	8.02		
		1	N	8.79	69.0	5.45	112.0	8.04		
								8.16		
$Pt(CH_3)_2Acac_2Py$ [isomer (ii)]	1		O	8.74	69.8	4.95	2.5	7.87		
						5.72	102.0	8.11		

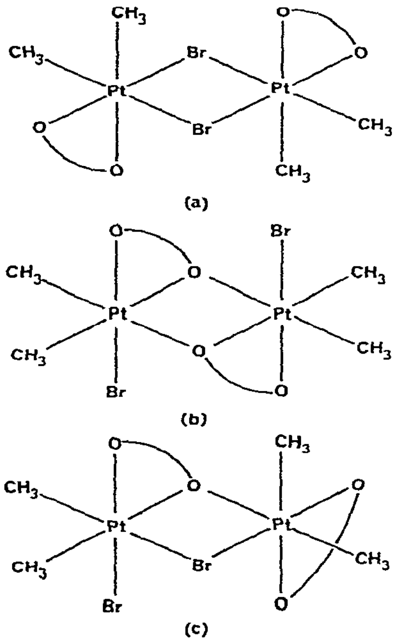

Fig. 2. Examples of the various types of bridging possible for $[Pt(CH_3)_2AcacBr]_2$ (isomer A).

presence of oxygen-bonded acetylacetonate groups [13]. Assuming there is one acetylacetonate group coordinated to each Pt atom in the dimer, there are three types of bridging possible, and examples of these are shown in Fig. 2. A total of 38 geometrical isomers may be formulated, but a number of these would give rise to a mixture of two isomeric species on reaction with Ph_3P or pyridine rather than the single isomer observed. There are, however, 2 isomers of bridging type (a) of Fig. 2, 6 isomers of bridging type (b), and 4 isomers of bridging type (c) which would give rise to the required isomer of $Pt(CH_3)_2AcacLBr$. The most likely mode of bridging is that of (a) (Fig. 2) since the starting material for the preparation of $[Pt(CH_3)_2AcacBr]_2$ (isomer A), viz., $[Pt(CH_3)_2Br_2]_n$, probably contains bridging Br atoms [14], and since acetylacetonate groups tend to bond via the γ-carbon atom rather than bridge via oxygen atoms in the trimethylplatinum(IV) system [1,5]. The far infrared region, which should contain modes characteristic of the bridging atoms, was complex, with seven bands of varying intensities ranging from 300 - 120 cm^{-1}. No definite assignment could be made.

The compound $[Pt(CH_3)_2AcacBr]_2$ (isomer A) reacted with 2,2'-bipyridine in $CHCl_3$ (Scheme 1) and the ^1H NMR spectrum (Table 1) of the product is consistent with the compound having the structure shown in Fig. 3. A single methyl-platinum triplet is observed with $^2J(^{195}Pt—CH_3)$ 68.9 Hz, indicative of methyl groups *trans* to 2,2'-bipyridine [12]; The central proton of the acetylacetonate group couples with ^{195}Pt with a magnitude of 3.5 Hz, ruling out the presence of a γ-carbon bonded acetylacetonate group. The methyl groups of the Acac ligand are non-equivalent and the protons of one of these

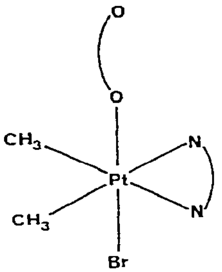

Fig. 3. Structure proposed for $Pt(CH_3)_2BipyAcacBr$.

groups exhibit a small coupling with ^{195}Pt of 3.5 Hz. These observations support the presence of a unidentate *O*-bonded acetylacetonate group in this compound. Such a mode of coordination of acetylacetone is unusual, but has been postulated in a silicon(IV) complex [15].

The compound is unstable in $CHCl_3$ solution, since a number of new peaks appear in the NMR spectrum on allowing the solution to stand. These peaks are readily identified as being due to the keto and enol forms of free acetylacetone. Furthermore, a solid analysing for $Pt(CH_3)_2BipyBrCl$ precipitated slowly from the solution. Apparently traces of HCl present in the $CHCl_3$ are sufficient to cause decomposition of the compound. Attempts to isolate pure $Pt(CH_3)_2BipyAcacBr$ were unsuccessful, as the product was always contaminated by decomposition product, but an impure sample did exhibit a strong band at 1620 cm^{-1} in the infrared, consistent with the presence of a free carbonyl group in the acetylacetonate ligand.

The formation of a unidentate *O*-bonded acetylacetonate group in this system and a unidentate γ-carbon bonded Acac group in the trimethylplatinum(IV) compound $Pt(CH_3)_3BipyAcac$ [6,7] may be rationalized in terms of the differences in the influences of the *trans* ligands in the two systems. The compound $Pt(CH_3)_3BipyAcac$ has been prepared by reaction of both $[Pt(CH_3)_3Acac]_2$ and $Pt(CH_3)_3AcacPy$ with 2,2'-bipyridine [4]. Although the former reaction may simply involve breaking of the Pt—O bonds in $[Pt(CH_3)_3Acac]_2$ with retention of the Pt—γ-carbon bond, the latter reaction requires at some stage a rearrangement from a Pt—O bond to a Pt—γ-carbon bond. Such a rearrangement to a more stable mode of bonding of the acetylacetonate ligand is probably due to the weakening of the Pt—O bond by the *trans*-CH_3 group. In the compound $Pt(CH_3)_2BipyAcacBr$ the ligand *trans* to the Pt—O bond is Br, which has a much weaker *trans* influence than CH_3 [12], and presumably does not weaken the Pt—O bond sufficiently to allow rearrangement of the *O*-bonded Acac ligand to the γ-carbon bonded form.

From the reaction between $[Pt(CH_3)_2Br_2]_n$ and sodium acetylacetonate in acetone two major products were isolated. One of these products was identified by its infrared spectrum and its reaction with pyridine to give $Pt(CH_3)_2AcacPyBr$ as the same compound (isomer A) as that prepared from the thallium(I) acetylacetonate reaction (Scheme 1).

The other major product of the reaction (isomer B) was a yellow solid which also analysed for $Pt(CH_3)_2AcacBr$ and was found to be dimeric in chlo-

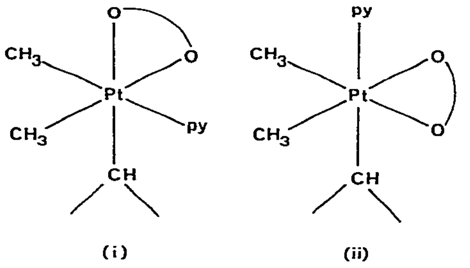

Fig. 4. Structures for isomers of $Pt(CH_3)_2Acac_2Py$.

roform solution. A $CDCl_3$ solution of $[Pt(CH_3)_2AcacBr]_2$ (isomer B) reacts with pyridine, and the ^1H NMR spectrum of the resultant solution indicates that two compounds are formed in equal proportions (Scheme 1). One of these products is readily identified from the chemical shift and coupling constant values of its methyl-platinum protons as the same isomer of $Pt(CH_3)_2Py_2Br_2$ (with CH_3 *trans* to pyridine) as that reported previously [14] by reaction of $[Pt(CH_3)_2Br_2]_n$ with pyridine. The other product is unstable in solution and converts to a third species which may be isolated from the reaction mixture as a colourless solid analysing for $Pt(CH_3)_2Acac_2Py$. The ^1H NMR spectrum of this compound (isomer ii) is recorded in Table 1, and on the basis of this the compound is postulated to have structure (ii) of Fig. 4. A single methyl-platinum triplet is observed with a coupling constant of 69.8 Hz, which may be assigned to methyl groups *trans* to the oxygen atoms of a bidentate acetylacetonate group. Only two acetylacetonate methyl resonances are present so that the CH_3 groups within each of the two acetylacetonate ligands are equivalent. Two γ-proton resonances are present, one exhibiting a coupling with ^{195}Pt of 2.5 Hz (*O*-bonded Acac), the other a coupling of 102.0 Hz (γ-carbon bonded Acac).

The ^1H NMR spectrum of the mixture from the reaction of $[Pt(CH_3)_2AcacBr]_2$ (isomer B) with pyridine indicates that the second product formed initially [isomer (i)] probably has structure (i) of Fig. 4 so that isomerization apparently occurs in solution. As shown in Table 1, there are two non-equivalent methyl platinum triplets with coupling constants of 69.0 and 69.2 Hz assignable to methyl groups *trans* to pyridine and an oxygen of a bidentate acetylacetonate group. Two γ-proton resonances are again observed, one of which shows a coupling with ^{195}Pt of 3.0 Hz (*O*-bonded Acac) and the other a coupling of 112.0 Hz (γ-carbon bonded Acac). Only three of the four possible acetylacetonate methyl resonances are observed in the spectrum of the mixture, the fourth probably lying beneath a resonance of $Pt(CH_3)_2Py_2Br_2$.

The above isomerization presumably is able to occur because of the labilizing effect of the carbon-bonded groups on the three *trans* ligands, which must allow rearrangement to occur by slow exchange of one of these *trans* ligands, probably the pyridine. The compound $Pt(CH_3)_2AcacPyBr$ [Fig. 1, isomer (a), L = pyridine] where only two *trans* bonds are weakened by carbon-bonded groups, showed no evidence for any such rearrangement to the more symmetrical isomer (c) of Fig. 1.

The infrared spectrum of $Pt(CH_3)_2Acac_2Py$ [isomer (ii) of Fig. 4] is con-

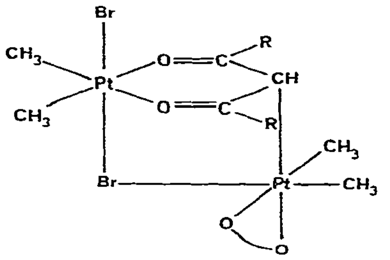

Fig. 5. Structure tentatively assigned to $[Pt(CH_3)_2AcacBr]_2$ (isomer B) ($R = CH_3$).

sistent with the presence of both unidentate and bidentate acetylacetonate groups. Bands observed at 1682 and 1661 cm^{-1} are characteristic of C=O stretching vibrations of a unidentate γ-carbon bonded acetylacetonate group, while a band at 1580 cm^{-1} may be assigned to ν(C=O) of an *O*-bonded bidentate acetylacetonate group [13].

The initial products of the reaction between $[Pt(CH_3)_2AcacBr]_2$ (isomer B) and pyridine indicate that in the parent compound the two Br atoms in the dimer are both associated with one Pt atom, and the two acetylacetonate groups with the other Pt atom. On the basis of the ^1H NMR and infrared spectra of $[Pt(CH_3)_2AcacBr]_2$ (isomer B) discussed below, the structure tentatively assigned to this compound is that shown in Fig. 5.

The NMR spectrum of $[Pt(CH_3)_2AcacBr]_2$ (isomer B) is shown in Fig. 6. There are four non-equivalent methyl-platinum triplets with coupling constants of 78.5, 78.5, 75.4 and 66.8 Hz (Table 1). Peaks 1 and 2 of Fig. 6 may be assigned to the methyl groups *trans* to the O atoms of the tridentate acetylacetonate group, since the chemical shifts are almost identical and the coupling constants are the same for these resonances. Peak 3 (*J* 75.4 Hz) is assigned to the methyl group *trans* to the bridging Br atom and peak 4 (*J* 66.8 Hz) to that *trans* to an oxygen of the bidentate acetylacetonate group. Although this latter value is somewhat lower than that observed for methyl *trans* to O in a number of trimethylplatinum(IV) complexes containing bidentate acetylacetonate groups [5] and is perhaps more consistent with a CH_3 group *trans* to *C*-bonded acetylacetone, the high value of 99.0 Hz observed for $^2J(^{195}Pt—C_\gamma—H_\gamma)$ in the compound (Table 1) suggests that the Pt—γ-carbon bond is *trans* to O rather than CH_3. Furthermore, the isomer of $Pt(CH_3)_2Acac_2Py$ first formed in the reaction of $[Pt(CH_3)_2AcacBr]_2$ with pyridine [isomer (i) of Fig. 4] has the Pt—γ-carbon bonded acetylacetonate ligand *trans* to O of bidentate acetylacetone.

As required by the model of Fig. 5, there are four non-equivalent acetylacetonate methyl resonances (Fig. 6). Two γ-proton resonances are observed, one exhibiting coupling with ^{195}Pt of 4.0 Hz (*O*-bonded Acac) the other a coupling of 99.0 Hz (tridentate Acac). The latter coupling is substantially lower than that found for coupling between the γ-proton of the unidentate acetylacetonate group and ^{195}Pt in isomer (i) of Fig. 4 (112.0 Hz). A similar effect was observed in the trimethylplatinum(IV) system, where coupling between ^{195}Pt and the γ-proton of the tridentate acetylacetonate group in $[Pt(CH_3)_3Acac]_2$ (42.0 Hz) [1,2] was smaller than that between ^{195}Pt and the γ-proton

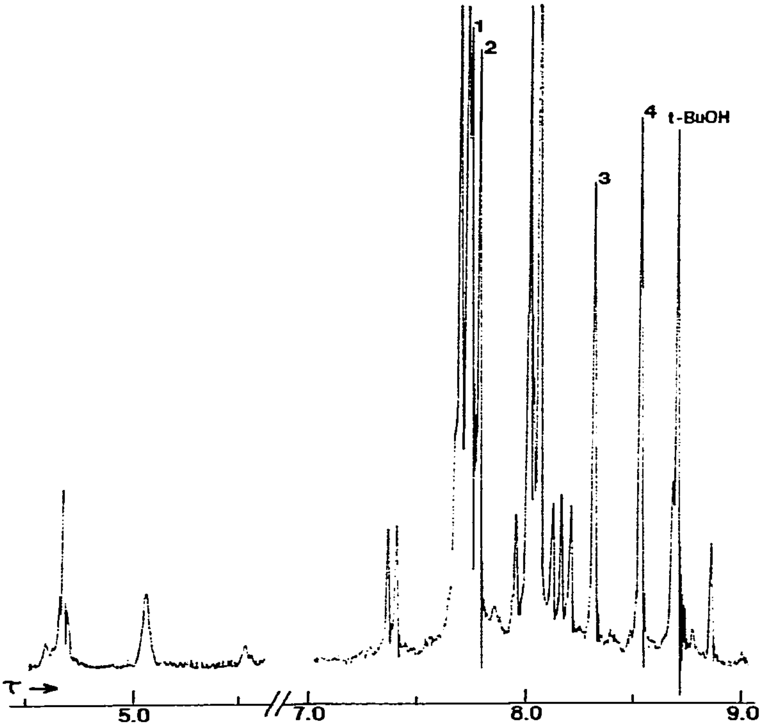

Fig. 6. ^{1}H NMR spectrum of [Pt(CH$_3$)$_2$AcacBr]$_2$ (isomer B).

of the unidentate acetylacetonate group in Pt(CH$_3$)$_3$BipyAcac [5] (51.5 Hz).

Comparison between the values of $^2J(^{195}\text{Pt—C}_\gamma\text{—H}_\gamma)$ in the compounds [Pt(CH$_3$)$_2$AcacBr]$_2$ (99.0 Hz) and [Pt(CH$_3$)$_3$Acac]$_2$ (42.0 Hz) [1,2] indicates that the Pt—γ-carbon bond of the tridentate acetylacetonate group in the dimethylplatinum(IV) compound is significantly stronger than that in the trimethylplatinum(IV) compound even after allowance is made for the fact that the *trans* atom is oxygen in [Pt(CH$_3$)$_2$AcacBr]$_2$ and carbon in [Pt(CH$_3$)$_3$-Acac]$_2$. On the other hand, the protons of the CH$_3$ group *trans* to the O atoms of the tridentate acetylacetonate in [Pt(CH$_3$)$_2$AcacBr]$_2$ have coupling constants higher than those in [Pt(CH$_3$)$_3$Acac]$_2$ (78.5 Hz, cf. 75.1 Hz [2]) which suggests that the Pt—O bonds may be weaker in the dimethylplatinum(IV) compound. Hence in this compound it is the Pt—O bonds rather than the Pt—γ-carbon bond of the tridentate acetylacetonate ligand which are postulated to break on reaction of [Pt(CH$_3$)$_2$AcacBr]$_2$ (isomer B) with pyridine.

The infrared spectrum of the compound exhibits peaks at 1658 and 1582 cm^{-1} in the C=O stretching region. The peak above 1600 cm^{-1} is characteristic of a γ-carbon bonded acetylacetonate group, and that below 1600 cm^{-1} of a bidentate oxygen-bonded acetylacetonate group.

Experimental

Reaction of $[Pt(CH_3)_2Br_2]_n$ with thallium(I) acetylacetonate

$[Pt(CH_3)_2Br_2]_n$ (0.9 g) was suspended in benzene (10 ml), TlAcac (1.4 g) was added and the mixture refluxed for five hours. The mixture was filtered to remove precipitated TlBr, the filtrate evaporated to dryness and the residue treated with boiling water to remove any remaining thallium salts. The residue was recrystallized from chloroform to give a yellow solid which analysed for $Pt(CH_3)_2AcacBr$ (isomer A). Yield 43%. (Found: C, 20.7; H, 3.2; Br, 19.3; Pt, 48.4. $C_7H_{13}BrO_2Pt$ calcd.: C, 20.8; H, 3.2; Br, 19.8; Pt, 48.3%.) The product was only sparingly soluble in chloroform, and a molecular weight determination was inconclusive, but the compound is probably dimeric. Mol. wt.: 680; dimer calcd.: 808.

Preparation of $Pt(CH_3)_2Acac(Ph_3P)Br$

$[Pt(CH_3)_2AcacBr]_2$ (isomer A) (0.03 g) was suspended in chloroform (5 ml) and a solution of triphenylphosphine (0.02 g) in chloroform (2 ml) added. Heating for several minutes gave a yellow solution which was concentrated and treated with n-hexane to precipitate the product as pale yellow crystals. Yield 80% (Found: C, 46.1; H, 4.3; Br, 11.6. $C_{25}H_{28}BrO_2PPt$ calcd.: C, 45.4; H, 4.2; Br, 12.0%)

Preparation of $Pt(CH_3)_2AcacPyBr$

$[Pt(CH_3)_2AcacBr]_2$ (isomer A) (0.05 g) was suspended in chloroform (5 ml) and excess pyridine was added. On heating the mixture the solid dissolved readily to give a yellow solution. On concentration of the solution to a small volume and addition of n-hexane, yellow crystals of the product precipitated. Yield 90%. (Found: C, 29.3; H, 3.6; Br, 16.3; N, 3.3; Pt, 40.0. $C_{12}H_{18}BrNO_2Pt$ calcd.: C, 29.8; H, 3.7; Br, 16.5; N, 2.9; Pt, 40.4%.)

Reaction of $[Pt(CH_3)_2AcacBr]_2$ (isomer A) with 2,2'-bipyridine

$[Pt(CH_3)_2AcacBr]_2$ (isomer A) (0.10 g) and 2,2'-bipyridine (0.39 g) were treated with chloroform (1 ml) in an NMR tube. On heating for several minutes the solid dissolved to give a yellow solution. The NMR spectrum of such solutions indicated the presence of the species $Pt(CH_3)_2BipyAcacBr$, but attempts to isolate this in pure form by evaporation of the solution were unsuccessful. On allowing such solutions to stand, yellow crystals of a compound analysing for $Pt(CH_3)_2BipyBrCl$ were obtained. (Found: C, 29.6; H, 3.0; N, 5.5. $C_{12}H_{14}BrClN_2Pt$ calcd.: C, 29.0; H, 2.8; N, 5.6%.)

Reaction of $[Pt(CH_3)_2Br_2]_n$ with sodium acetylacetonate

$[Pt(CH_3)_2Br_2]_n$ (3.0 g) and sodium acetylacetonate (1.0 g) were suspended in acetone (30 ml) and the mixture refluxed. After about 60 min the solution was bright yellow and a colourless precipitate, presumably NaBr, had formed. The solution was evaporated to dryness, which caused some decomposition to metallic platinum, and the residue then extracted with boiling chloroform. On evaporation of the chloroform extract, a yellow solid was obtained and infrared and NMR spectra indicated that the solid was a mixture of products.

Treatment of the solid with a minimum of cold chloroform left as residue a yellow solid which after recrystallization from $CHCl_3$ was found to be identical to that obtained from the thallium(I) acetylacetonate experiment (isomer A) by infrared spectra and elemental analysis. Yield 25%. (Found: C, 20.9; H, 3.3; Br, 19.8. $C_7H_{13}BrO_2Pt$ calcd.: C, 20.8; H, 3.2; Br. 19.8%.)

From the chloroform extract a bright yellow solid, also analysing for $Pt(CH_3)_2AcacBr$ (isomer B), was obtained by concentration and precipitation with pet. ether. Yield 22% (Found: C, 20.9; H, 3.3; Br, 19.8; Pt, 48.2. C_7H_{13}-BrO_2Pt calcd.: C, 20.8; H, 3.2.; Br, 19.8; Pt, 48.3%.) The compound was readily soluble in organic solvents such as chloroform, benzene and acetone. It was found to be dimeric in chloroform: Mol.wt.: 817. dimer calcd.: 808.

For some of the reactions between $[Pt(CH_3)_2Br_2]_n$ and sodium acetylacetonate a small quantity of orange-yellow solid, only sparingly soluble in hot chloroform, was obtained. Infrared spectra of the solid indicated that it contained coordinated acetylacetone, but it was obtained in insufficient quantity to allow it to be characterized completely.

Reaction of $[Pt(CH_3)_2AcacBr]_2$ (isomer B) with pyridine

$[Pt(CH_3)_2AcacBr]_2$ (0.1 g) was dissolved in $CDCl_3$ (0.5 ml) and excess pyridine added. Slow evaporation of the solution gave a mixture of yellow and colourless crystals. The two compounds were readily separated by fractional crystallization from chloroform or acetone solutions. The yellow solid, which was less soluble in organic solvents, was identified from infrared and NMR spectra as $Pt(CH_3)_2Py_2Br_2$. The colourless species analysed for $Pt(CH_3)_2$-$Acac_2Py$. (Found: C, 40.2; H, 4.9; N, 2.9; Pt, 38.6. $C_{17}H_{25}NO_4Pt$ calcd.: C, 40.6; H, 5.0; N, 2.9; Pt, 38.8%.)

^1H NMR spectra of the initial solution and the white compound isolated indicated that an isomer of $Pt(CH_3)_2Acac_2Py$ [isomer (i)] was initially formed in the reaction, but attempts to isolate this isomer were unsuccessful, rapid evaporation of such solutions leading only to intractable oils from which white crystals of isomer (ii) were obtained on standing.

General

Nuclear magnetic resonance spectra were recorded at 100 MHz on a JEOL MH100 spectrometer using a sweep width of 540 Hz and t-BuOH as internal reference. Spin-spin coupling constants are considered accurate to ± 0.5 Hz, and τ values to ± 0.01ppm.

Infrared spectra were recorded from 4000 to 400 cm^{-1} on a Perkin—Elmer Model 457 spectrometer as Nujol and hexachlorobutadiene mulls between KBr plates. Frequencies are considerd accurate to ± 2 cm^{-1}. The far infrared spectrum (40 - 400 cm^{-1}) of $[Pt(CH_3)_2AcacBr]_2$ was run as a Nujol mull on a Beckmann-RIIC FS-720 fourier spectrometer.

Molecular weights were measured in $CHCl_3$ at 37° using a Hewlett-Packard model 302 vapour pressure osmometer.

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