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^{1}H NMR SPECTRA OF SOME β-DICARBONYL COMPLEXES OF TRIMETHYLPLATINUM(IV)

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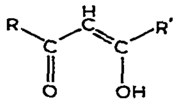
SUMMARY

Variable-temperature NMR spectra of a number of dimeric β-dicarbonyl complexes of trimethylplatinum(IV), where β-dicarbonyl = malondialdehyde, acetoacetaldehyde, acetylacetone and diisobutyrylmethane, have been recorded in deuterochloroform. Results indicate that above room temperature, rapid dissociation of the bond between platinum and the γ-carbon atom of the β-dicarbonyl ligand occurs.

X-ray structures of several β-dicarbonyl complexes of trimethylplatinum(IV)[1-4] show the molecules to be dimeric with each β-dicarbonyl chelate coordinating through both oxygen atoms to one platinum atom, and through the central (γ) carbon atom to the second platinum atom.

We have prepared some analytically pure trimethylplatinum(IV) complexes with the ligands malondialdehyde (Malal), acetoacetaldehyde (Acal), acetylacetone



(I) $R = R' = H$
(II) $R = H$, $R' = CH_3$
(III) $R = R' = CH_3$
(IV) $R = R' = i\text{-}C_3H_7$

Fig. 1.

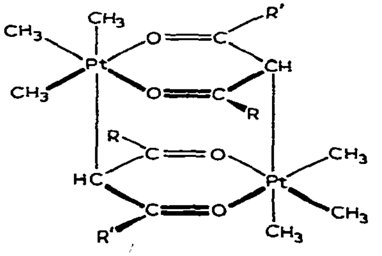


Fig. 2.

TABLE 1

^{1}H NMR SPECTRA OF SOME β-DICARBONYL COMPLEXES OF TRIMETHYLPLATINUM(IV) IN $CDCl_3$ SOLUTION[a]

Compound	Temp. (°C)	No. of $PtCH_3$ peaks	Ratio	$J(Pt–CH_3)$	$J[Pt–H(\gamma)]$[b]	$J[Pt–H(t)]$[b]	$J[H(\gamma)–H(t)]$[b]	$\tau(PtCH_3)$[c]	$\tau[CH_3(lig)]$[c]	$\tau[H(\gamma)]$[c]	$\tau[H(t)]$[c]
$[Pt(CH_3)_3Malal]_2$	33	1		75.7		23.8	3.5	8.78		5.16	1.55
	−30.5	2	2	75.5	42.5	23.8	3.5	8.77		5.14	1.53
			1	75.5				8.85			
$[Pt(CH_3)_3Acal]_2$	34	1		75.2		25.5	3.5	8.88	7.98	5.32	1.75
	−38	3	1	74.5	42.0	25.5	3.5	8.83	7.96	5.29	1.73
			1	75.3				8.87			
			1	74.5				8.93			
$[Pt(CH_3)_3Acac]_2$	32.5	1		74.8				8.99	8.02	5.37	
	−21.5	2	2	75.1	42.0			8.97	8.00	5.35	
			1	73.3				9.06			
$[Pt(CH_3)_3Dibm]_2$	59	1		74.5				9.08	8.95[d]	5.53	
	−30.5	2	2	75.8	41.0			9.02	8.96	5.61	
			1	71.0				9.32			

[a] Recorded on a Varian A-60 NMR spectrometer (sweep width 500 Hz). [b] H(γ), H(t) refer to the protons on the γ and terminal C atoms respectively. [c] Solution referenced with tert-BuOH; τ values obtained using τ(tert-BuOH) = 8.72 ppm. Values in each case refer to centres of absorption. [d] $J[(CH_3)_2–CH] = 6.8$ Hz.

(Acac), and di-isobutyrylmethane (Dibm) [Fig. 1, compounds (I)–(IV) respectively]. Complexes with ligands (III) and (IV) are known to be dimeric in benzene[5,6], and we have found that the complexes with ligands (I) and (II) are dimeric also. It is assumed that the structure of these molecules in solution is of the type described above and shown in Fig. 2. An NMR study of the complexes in $CDCl_3$ solution has been made at temperatures ranging from −38° to 59°. The spectra support a dimer formulation and reveal evidence for a rapid dissociation involving the platinum–γ-carbon bonds. Details of the spectra are included in Table 1.

The spectra of the compounds may be divided into three regions:

(1) The platinum-methyl region at approximately τ 9 ppm,
(2) The central (γ) proton region at approximately 5.5 ppm,
(3) The protons on the terminal carbon atoms of the ligand for $[Pt(CH_3)_3Malal]_2$ and $[Pt(CH_3)_3Acal]_2$, at approximately 1.5 ppm.

(1). At the operating temperature of the instrument (32–34°), $[Pt(CH_3)_3Malal]_2$, $[Pt(CH_3)_3Acal]_2$ and $[Pt(CH_3)_3Acac]_2$ show a "triplet" signal composed of a doublet resonance due to the molecules containing ^{195}Pt ($I=\frac{1}{2}$; 34% abundance), flanking the main resonance due to molecules containing other Pt nuclei. A similar pattern is observed for $[Pt(CH_3)_3Dibm]_2$ on heating to 59°. Since both chemical shifts and coupling constants of methyl groups bonded to platinum have been shown to be sensitive to the nature of the atom or group in the *trans* position[7–9], two "triplets" in the intensity ratio of 2/1, each having a different coupling constant would be expected for $[Pt(CH_3)_3Malal]_2$, $[Pt(CH_3)_3Acac]_2$. and $[Pt(CH_3)_3Dibm]_2$, and three "triplets" (with different coupling constants) in the intensity ratio of 1/1/1 for $[Pt(CH_3)_3Acal]_2$, due to the unsymmetrical ligand*. On cooling the solutions to the temperatures given in Table 1 the anticipated patterns in the correct intensity ratio are observed, the average of the coupling constants in each case agreeing well with the single coupling constant at the higher temperatures. The coalescence of these methyl resonances at higher temperatures suggests that some process producing equivalence of the methyl groups must be occurring, but the persistence of satellites means that this process does not involve dissociation of the methyl groups themselves.

(2). At the higher temperatures noted in Table 1, the γ-proton absorption region consists of a broad peak for all four compounds, with no evidence for the satellites due to coupling with ^{195}Pt which would be expected if the chelate is acting as a tridentate. This could be explained by rapid exchange of the γ-proton or by rapid dissociation of the platinum–γ-carbon bond. On cooling to lower temperatures (see Table 1), the peak in each case gradually sharpens and satellites appear ($J \approx 40$ Hz). As expected, a single main resonance is observed for $[Pt(CH_3)_3Acac]_2$ and $[Pt(CH_3)_3Dibm]_2$, while $[Pt(CH_3)_3Acal]_2$ and $[Pt(CH_3)_3Malal]_2$ show a doublet and triplet respectively, due to coupling with the terminal protons. The peaks however do not become sufficiently sharp for any coupling of this proton to the other platinum atom via the oxygen atoms to be observed.

(3). This region gives unequivocal evidence for a mechanism involving breaking of the Pt–γ-carbon bond for $[Pt(CH_3)_3Malal]_2$ and $[Pt(CH_3)_3Acal]_2$. At 33°, the terminal protons of both compounds give a central doublet due to coupling with

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* Two isomers are possible for $[Pt(CH_3)_3Acal]_2$ depending on the positions of $R=H$ and $R'=CH_3$ in Fig. 2. No evidence for more than one isomer was observed.

the γ-proton ($J = 3.5$ Hz) together with satellites ($J \approx 24$ Hz) presumably due to coupling with ^{195}Pt via the oxygen atoms. This part of the spectrum remains unchanged on cooling.

It follows from the above observations that the γ-proton is not exchanging rapidly in $[Pt(CH_3)_3Malal]_2$ and $[Pt(CH_3)_3Acal]_2$ (since proton–proton coupling with the terminal protons is observed over the whole temperature range), and therefore that the Pt–γ-carbon bond must be breaking. Also, since coupling between ^{195}Pt and the terminal protons is observed over the whole temperature range, the Pt–O bonds must remain intact, or at least have a lifetime longer than $1/(2\pi \cdot J)$. These results would suggest that a plausible mechanism for producing the equivalence of methyl peaks involves rapid dissociation of one of the Pt–γ-carbon bonds to form a five-coordinate intermediate at one of the platinum atoms.

Although Kite, Smith, and Wilkins[8] proposed, on the basis of their spectra of $[Pt(CH_3)_3Acac]_2$ and $[Pt(CH_3)_3Dibm]_2$, a mechanism involving rapid dissociation of one of the Pt–O bonds, the Pt–γ-carbon bond remaining intact, the similarity in the behaviour of both the platinum-methyl and γ-proton absorptions to those of $[Pt(CH_3)_3Malal]_2$ and $[Pt(CH_3)_3Acal]_2$ suggests that in the former cases also, a mechanism involving dissociation of Pt–γ-carbon bonds applies.

The rate of dissociation of the platinum–γ-carbon bond in complexes of this type is under investigation.

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