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^{1}H, ^{13}C AND ^{195}Pt NMR STUDIES OF SOME PLATINUM—CYCLOPROPANE COMPOUNDS

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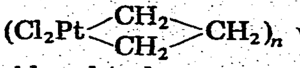
Summary

The ^{1}H, ^{13}C and ^{195}Pt NMR spectral parameters of some platinum—cyclopropane complexes are reported. The NMR parameters, particularly the ^{13}CH coupling constants, suggest the presence of a $\overline{\mathrm{PtCH_2CH_2CH_2}}$ ring in these compounds. However, there is probably some interaction between platinum and the β-carbon atom across the 4-membered ring.

Introduction

Reaction of cyclopropane with either hexachloroplatinic(IV) acid [1] or with Zeise's dimer [2—4] $[\mathrm{PtCl_2(C_2H_4)}]_2$, gives a compound $\mathrm{PtCl_2(C_3H_6)}$, (I), whose structure has been the subject of some controversy. Originally it was proposed that (I) was a platinum(II)—cyclopropane complex but later the structure  $(\mathrm{Cl_2Pt}{<}^{\mathrm{CH_2}}_{\mathrm{CH_2}}{>}\mathrm{CH_2})_n$ was proposed in which the cyclopropane ring was considered to have opened to give a trimethylene—platinum(IV) complex [5], containing a metallocyclobutane ring. This revised formulation was based on the low solubility of (I) suggesting a polymeric platinum(IV) complex and on IR and NMR studies of (I) and its bis(pyridine) adduct, $\mathrm{PtCl_2(C_3H_6)(C_5H_5N)_2}$, (II). Thus, for example, the ^{1}H—^{195}Pt NMR coupling constant $^2J(\mathrm{PtCH_2})$ for (II) was found to be comparable with similar values for methylplatinum compounds and suggested the ring-opened formulation. Further support came from the mass spectrum of (I) which indicated a tetrameric structure $[\mathrm{PtCl_2(C_3H_6)}]_4$ analogous to that for $(\mathrm{Me_3PtI})_4$ [6]. Finally, X-ray studies [7,8] showed that (II) has the molecular structure shown in Fig. 1.

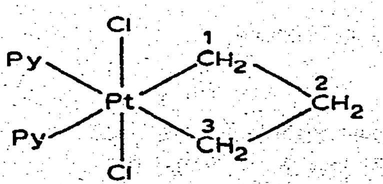


Fig. 1.

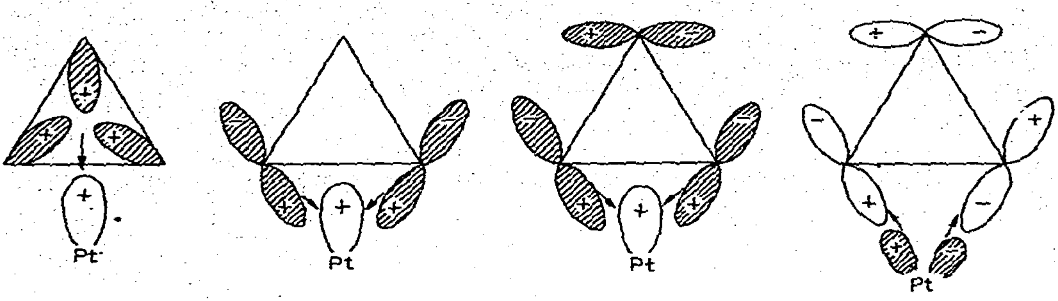


Fig. 2.

The distance C_1C_3 is 2.55 Å which was considered too long for there to be any significant interaction between these atoms.

On the other hand, theoretical studies suggest that some residual interaction between C_1C_3 might be present even though the internuclear distance is large [9, 10], and from a detailed interpretation of the ^1H NMR spectra of analogues of (II) with substituted cyclopropanes, a bonding model intermediate between the cyclopropane-complex and trimethylene-complex formulations was proposed [3]. This was based on overlap of filled Walsh orbitals of cyclopropane with a vacant σ-orbital on platinum, with back-bonding from filled π-orbitals on platinum to a vacant orbital of cyclopropane, as indicated in Fig. 2.

This bonding model can accommodate all structures between the cyclopropane-complex and trimethylene-complex formulations depending on the relative importance of the σ- and π-bonding effects, and is therefore very similar to the currently accepted model for metal—alkene complexes [11]. The model is also attractive in interpreting some of the chemical reactions of (I) and (II), such as the ready formation of cyclopropane on treatment with ligands having a high *trans*-influence [3].

Complexes analogous to (I) and (II) are believed to be intermediates in the transition-metal catalysed rearrangement of strained carbocyclic compounds [12—14], so that the nature of bonding in (I) and (II), which can be considered as model compounds for such intermediates, is of considerable interest. In order to investigate further the nature of bonding in these compounds we have examined the ^{13}C NMR spectra of a number of complexes $PtX_2(C_3H_6)L_2$, where $X =$ Cl or Br, and $L =$ pyridine, 4-methylpyridine, and ½ ethylenediamine. We also present some ^1H NMR data for these compounds, and ^{13}C NMR data for some alkyl platinum and platinum—alkene complexes for comparison purposes. ^{195}Pt chemical shifts have also been measured for some of the complexes.

Results and discussion

The NMR data are given in Table 1 and are discussed below.

(a). ^1H NMR spectra

The ^1H NMR spectra of some of the complexes (II) have been reported previously [3,5,6,8]. We find that the hydrogen—platinum coupling constant $^2J(PtCH_2)$ for $PtX_2(C_3H_6)L_2$, (II) falls in the range 78-88 Hz, being greater when

L = pyridine or 4-methylpyridine than when L = ethylenediamine and greater when X = Br than when X = Cl. The effect of the *trans*-ligand indicates a slightly greater *trans*-influence for ethylenediamine than for pyridine [15], and is paralleled as expected in the corresponding values of $^1J(^{195}Pt^{13}C)$. The magnitude of the influence of the *cis*-ligands (Br or Cl) on the coupling constant $^2J(PtCH_2)$ is surprising, especially since $^1J(^{195}Pt^{13}C)$ is greater when X = Cl than when X = Br (that is the effect is reversed). The hydrogen—platinum coupling constants $^2J(PtCH_2)$ are similar in magnitude to those found for alkylplatinum compounds (see Table 1); this similarity was originally taken as evidence for the trimethylene formulation of the compounds [5] but is probably fortuitous since the ^{13}C NMR parameters for (II) are quite different from those for typical alkylplatinum compounds (see below). In (II) the hydrogen—platinum coupling constant $^3J(PtCCH_2)$ is too small to be detected, whereas appreciable coupling from platinum to the β-hydrogen atoms is observed in ethylplatinum compounds, but this difference could be a consequence of the different conformation necessarily adopted in (II).

The observed ^1H NMR spectra of (II) vary markedly with the nature of X and L, largely due to changes in chemical shift of the α- and β-hydrogen atoms. Thus when X = Cl and L = pyridine, the α- and β-hydrogen atoms have the same chemical shift and appear as a singlet (with triplet satellites due to coupling of ^{195}Pt with the α-hydrogen atoms), but in most other cases the α- and β-hydrogen atoms have somewhat different chemical shifts and complex second-order splitting patterns result. The chemical shifts for both α- and β-hydrogen atoms fall in the range δ 2.07—2.84 ppm from TMS, considerably deshielded compared to cyclopropane (0.22 ppm) and cyclobutane (1.96 ppm), perhaps indicating that platinum acts as an electron acceptor from the C_3H_6 group as suggested by McQuillan and Powell [3].

(b). ^{13}C chemical shifts

The chemical shifts for the β-carbon atoms of the trimethylene ring in (II) fall in the narrow range δ 29.6—31.5 ppm from TMS, which are comparable with similar values for other heterocyclic $X(CH_2)_n$ derivatives (X = S, O, etc) [16]. However, the α-carbon atoms are strongly shielded (δ —21.4 to +3.8 ppm), which is unexpected if platinum is acting as an electron acceptor (see above). It is tempting to interpret this shielding in terms of back-bonding of electrons from filled orbitals on platinum to vacant antibonding orbitals of the C_3H_6 moiety, but, in view of the present controversy concerning ^{13}C chemical shifts in organotransition metal compounds [17,18], this conclusion may not be correct.

(c). $^{195}Pt^{13}C$ coupling constants

The coupling constants $^1J(^{195}Pt^{13}C)$ for (II) lie in the range 317—338 Hz. This is considerably lower than values of $^1J(^{195}Pt^{13}C)$ found in platinum(II) alkyls (594—833 Hz) [17—19] or for the platinum(IV) alkyl, $PtI_2(C_2H_5)_2(4\text{-}CH_3\text{-}C_5H_4N)_2$, for which $^1J(^{195}Pt^{13}C)$ is 507 Hz, but considerably higher than corresponding values for platinum(II) olefin complexes (see Table 1).

If (II) are considered as platinum(IV)—trimethylene complexes, then the low values of $^1J(^{195}Pt^{13}C)$ must be due to effects of ring strain. Such an effect is likely since the carbon atoms in small-ring compounds tend to hybridise so as

TABLE 1

^1H, ^{13}C AND ^{195}Pt NMR DATA FOR ORGANOPLATINUM COMPOUNDS

Compound	$\delta(H_\alpha)$ (ppm)	$^2J(PtH_\alpha)$ (Hz)	$\delta(H_\beta)$ (ppm)	$^3J(H_\alpha H_\beta)$ (Hz)	$\delta(C_\alpha)$ (ppm)	$^1J(PtC_\alpha)$ (Hz)	$\delta(C_\beta)$ (ppm)	$^2J(PtC_\beta)$ (Hz)	$\delta(Pt)$[h] (ppm)
1. Pt(0) compounds									
$Pt(C_2H_4)(PPh_3)_2$	2.15	62[d]			39.6	194			
2. Pt(II) compounds									
$K[PtCl_3(C_3H_4)]$	4.75	34			67.1	195			
$Pt(CH_2CH_3)_2COD$	4.76[a]	38[a]	1.90[a]		98.9[a]	47[a]	29.5[a]	<5[a]	
	1.87[b]	92.2[b]	1.52[b]		19.2[b]	833[b]	15.7[b]	35[b]	
$Pt(CH_3)_2COD$	4.65[a]	40[a]	2.15[a]		98.8[a]	55[a]	29.9[a]	<8[a]	
	0.58[c]	83.4[c]			4.7[c]	773[c]			
3. Pt(IV) compounds									
$PtCl_2(CH_2)_3(C_5H_5N)_2$	2.6[e]	82	2.6[f]	7.5	−15.2	335	30.0	105	1342
$PtBr_2(CH_2)_3(C_5H_5N)_2$	2.80	88	2.44	8.0	−17.9	325	30.4	110	827
$PtCl_2(CH_2)_3(4\text{-}CH_3C_5H_4N)_2$	2.58	83	2.58	7.2	3.77	338	29.9	105	1313
$PtBr_2(CH_2)_3(4\text{-}CH_3C_5H_4N)_2$	2.84	88	2.61	7.5	−18.5	323	30.5	103	836
$PtCl_2(CH_2)_3(NH_2CH_2CH_2NH_2)$	2.17	78	2.40	7.0	−18.9	332	29.6	108	
$PtBr_2(CH_2)_3(NH_2CH_2CH_2NH_2)$	2.43	83	2.43	7.8	−21.4	317	30.4	105	
$PtCl_2(CH_2)_3(NH_3)_2$	2.07	82	2.40	7.0					
$PtBr_2(CH_2)_3(NH_3)_2$	2.44	81	2.54	8.0					
$PtI_2(CH_2CH_3)_2(4\text{-}CH_3C_5H_4N)_2$	4.21	87.0	1.25[g]		−2.4	507	31.5	<8	

[a] Data for cyclo-octadiene group. [b] Data for ethyl group, $^3J(PtH_\beta)$ 80.5 Hz. [c] Data for methyl group. [d] $^1J(^{13}CH)$ 146.5 Hz. [e] $^1J(^{13}CH)$ 148 Hz. [f] $^1J(^{13}CH)$ 135 Hz, $^3J(PtNCH)$ 17 Hz. [g] $^3J(PtH_\beta)$ 29.2 Hz. [h] Chemical shifts are given in ppm to low field from $(Me_3PtI)_4$ reference, which has a Ξ value of 21,422,412.29 Hz.

to concentrate *s* character in the C—H bonds, with the remaining bonds having low *s* character. Since the coupling constants between directly bound atoms is dependent on the degree of *s* character in the bonds, the effect will lead to high values of $^1J(^{13}CH)$ and low values of $^1J(^{195}Pt^{13}C)$ in (II), as is observed.

The coupling constants from platinum to the β-carbon of the trimethylene group in (II), $^2J(^{195}PtC^{13}C)$, are large (103—110 Hz) compared with similar values in ethylplatinum (0—38 Hz) or platinum—olefin complexes (usually too low to be observed). The difference is almost certainly a result of the much shorter distance (ca. 2.5-2.6 Å) between these atoms in the ring compound [7,8]. In fact some direct overlap of orbitals of these atoms is expected in terms of both the platinum(II)—cyclopropane formulation [3] and platinum(IV)—trimethylene structure (cf. cyclobutane [20]) for (II).

(d). ^{13}CH *coupling constants*

The coupling constant $^1J(^{13}CH)$ for cycloalkanes varies markedly with ring size, being 161 Hz for cyclopropane, 134 Hz for cyclobutane and 128 Hz for cyclopentane [21]. Compound (II), X = Cl and L = C_5H_5N, has $^1J(^{13}CH)$ values of 148 Hz and 135 Hz for the α- and β-carbon atoms, respectively. The value for the β-carbon atom is almost identical with that for cyclobutane and for other $X(CH_2)_3$ derivatives, X = CH_2, O, S, NH [22], and is consistent with the platinum(IV)—trimethylene formulation, though it should be pointed out that the geometry of the ring is rather different from that of the parent cyclobutane (in particular the C—C—C angle is 100° or over) as a result of the long Pt—C bonds [8]. The value of $^1J(^{13}CH)$ for the α-carbon atoms is more difficult to interpret, since it will be influenced by the nature of the direct Pt—C bond [17,23]; it is considerably larger than $^1J(^{13}CH)$ for the methyl groups in $(Me_3PtI)_4$ (138 Hz), which is itself considerably higher than for methane (125 Hz).

(e). ^{195}Pt *chemical shifts*

The ^{195}Pt chemical shifts for (II) are strongly influenced by the nature of the halogen, resonances being at lower fields for the chlorides than for the bromides [24,25], all being down-field from trimethylplatinum iodide. However, no conclusions about the oxidation state of platinum in (II) can be drawn until more ^{195}Pt shifts for analogous alkylplatinum compounds are available.

Conclusions

We conclude that the bonding in the ground state of (II) is best represented by the platinum(IV)—trimethylene formulation. This conclusion is based mainly on interpretation of the ^{13}CH coupling constants for (II), but is consistent with the remainder of the NMR data. However, the ^{13}C NMR evidence does suggest that there is some direct interaction between platinum and the carbon atom across the 4-membered ring.*

Although it seems that the platinum(II)—cyclopropane model is not a good description of the ground state of (II), the model is nevertheless valuable in describing the probable transition state during formation of (I) from cyclopropane and Zeise's complex and during the elimination of cyclopropane from (I) and

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* A similar bonding scheme has recently been suggested [26].

(II). It is also possible that for other complexes the ground state could be described by this model. Such complexes would be expected to have low stability, but could be formed as intermediates in catalysis of skeletal rearrangements of strained ring compounds by for example silver(I) ions, when formation of trimethylene—silver(III) complexes seems unlikely on thermodynamic grounds.

Experimental

Starting materials

Compounds were prepared by published methods [1,5,6,8], and were characterised by elemental analysis, melting point, IR and NMR spectra. The compounds $PtX_2C_3H_6(NH_3)_2$ where X = Cl or Br are new and were prepared as follows.

$PtCl_2(C_3H_6)(NH_3)_2$ was prepared by condensing dry ammonia onto $[PtCl_2(C_3H_6)]_4$ at −80°, then shaking at −80° until the precipitate became white and allowing the excess ammonia to evaporate at −45°. The product was washed with water and dried under vacuum. It decomposed above 130° to give ammonium chloride and propene among the decomposition products. (Found: C, 10.62; H, 3.44; N, 8.21; Pt, 57.40. $C_3H_{12}Cl_2N_2Pt$ calcd.: C, 10.5; H, 3.5; N, 8.2; Pt, 57.03%.) IR (KBr disc): 3340 m, 3265 m ν(NH); 3180 w, 2990 m, 2985 m ν(CH); 1600 m, 1232 m, 1198 s, 1070 m, 930 w, 872 w cm^{-1}.

$PtBr_2(C_3H_6)(NH_3)_2$ was prepared from $[PtBr_2(C_3H_6)]_4$. It was difficult to purify, apparently containing excess ammonia. (Found: C, 8.31; H, 3.10; N, 7.92. $C_3H_{12}Br_2N_2Pt$ calcd.: C, 8.35; H, 2.80; N, 6.49%.) It decomposed on heating at 105—110°.

NMR spectra

^1H NMR spectra were recorded using a Varian HA 100 spectrometer at 100 MHz with TMS internal standard. ^{13}C NMR spectra were recorded using a Varian XL 100 spectrometer at 25.2 MHz in the Fourier transform mode using TMS internal standard. Unless the ^{13}CH coupling constants were required, proton noise decoupling was employed. ^{195}Pt NMR spectra were obtained by the double resonance method using a Varian XL 100 spectrometer. NMR spectra were recorded using $CDCl_3$ solvent, except for the ethylenediamine and ammonia complexes for which DMSO-d_6 was used.

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