

¹⁹⁵Pt NMR OF ORGANOPLATINUM COMPOUNDS

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Summary

The ¹⁹⁵Pt chemical shifts of several organoplatinum compounds in solution have been determined. The $\delta(^{195}\text{Pt})$ values of the phosphine-Pt^{II} and -Pt⁰ compounds lie in separate ranges, and allow the metal-diene systems to be characterized either as metallacyclopentene or as η^2 -bonded diene. Although the two isomers of bis(η^3 -allyl)Pt (VIII) formally should be regarded as Pt^{II} compounds their ¹⁹⁵Pt shifts clearly lie in the region for Pt⁰ compounds. The large separation between the ¹⁹⁵Pt signals and the difference in ¹⁹⁵Pt-*T*₁ values for the two isomers of VIII are in accord with their having different geometries around the metal.

Introduction

As for many other metal nuclei [1,2], a relationship exists between the oxidation state of Pt and the ¹⁹⁵Pt chemical shift $\delta(^{195}\text{Pt})$ [3]. Recently, we have analysed the relaxation behaviour and the chemical shift range of zero-valent platinum-phosphorous compounds PtL_{*n*} [4]. We have now extended our studies to organoplatinum compounds to see, in part, whether typical coordination problems, such as the manner of complexation of a diene to a platinum atom or the nature of the bonding in bis(η^3 -allyl)Pt could be solved by use of ¹⁹⁵Pt NMR spectroscopy.

Results and discussion



The ¹⁹⁵Pt NMR data of the Pt⁰ compounds I–III [5–7] are listed in Table 1, and those for IV–VIII [6–8], in which Pt is formally in the oxidation state (II), in Table 2. The structures of I–VIII have been derived from their ¹H and ¹³C NMR spectra. It can be assumed that bis(cycloocta-1,5-diene)Pt (I) [5] has a quasi-tetrahedral

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TABLE 1




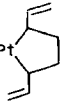
¹⁹⁵Pt NMR DATA AT 9.4 Tesla FOR ORGANOPLATINUM(0) COMPOUNDS IN THF-*d*₈^a

Compound	<i>T</i> (K)	$\delta(^{195}\text{Pt})$ (ppm)	<i>J</i> (Hz)	<i>T</i> ₁ (s) (9.4 Tesla)
Pt(COD) ₂ (I)	248	-4636		0.151
(PPh ₃) ₂ Pt-  (II)	240	-5102	¹ <i>J</i> (Pt,P) 3393	0.25
dRpePt- 				
R = <i>t</i> -Bu (IIIa)	213	-5239	¹ <i>J</i> (Pt,P) 3248 ¹ <i>J</i> (Pt,P') 3227 ³ <i>J</i> (P,P') 69	0.17
R = cyclohexyl (IIIb)	213	-5230	$\Sigma J(\text{Pt,P})$ 6335	

^a At 7.0 Tesla *T*₁ of I at 248 K is 0.197 s. At *T* 224 K and 9.4 Tesla *T*₁ of I is 0.059 s whereas 0.133 s at 7.0 Tesla. At 7.0 Tesla and 240 K *T*₁ of II is 0.39 s. ^b dRpe = R₂PCH₂CH₂PR₂.

TABLE 2

¹⁹⁵Pt NMR DATA FOR ORGANOPLATINUM(II) COMPOUNDS AT 9.4 T^a

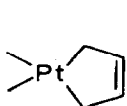
Compound	<i>T</i> (K)	$\delta(^{195}\text{Pt})$ (ppm)	¹ <i>J</i> (Pt,P) (Hz)	<i>T</i> ₁ (s) (9.4 Tesla)
LPt() ₂				
L = dmpe (IVa) ^b	263	-4669	1900	0.50
dcpe (IVb) ^b	263	-4737	1940	0.21
dppe (IVc) ^b	263	-4750	1919	0.16
dipePt-  (V) ^b	243	-4654	1805	0.45
(PMe ₃) ₂ Pt-  (VI) ^c	310	-4609	1783	0.83
dmpePt- 				
<i>cis</i> (VIIa) ^c	243	-4637	1842	
<i>trans</i> (VIIb) ^c	243	-4638	1832	
Pt(allyl) ₂ (VIIIa) ^b	278	-6192	-	0.40
(VIIIb) ^b		-5963	-	0.33

^a L = dRpe = R₂PCH₂CH₂PR₂ (R = m: methyl, R = c: cyclohexyl, R = p: phenyl, R = i: isopropyl). At 7.0 Tesla and *T* 278 K for VIII it was obtained *T*₁ (VIIIa) 0.55 s and *T*₁ (VIIIb) 0.47 s. ^b Solvent THF-*d*₈. ^c Solvent toluene-*d*₈.

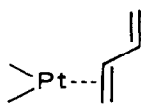
environment analogous to that of bis(cycloocta-1,5-diene)Ni [9]. At low temperatures, the olefinic double bonds of II and III lie in the trigonal coordination plane. Complex VI might be expected to exist as *cis* and *trans* isomers, but analysis of its ^1H NMR spectrum confirms that only the isomer with the three-membered rings in *trans* configuration is present ($^3J(\text{H}_\beta, \text{H}_\beta')$ 2.0 Hz). In VII both isomers exist in solution. Their ^{195}Pt signal separation is small, in contrast to that of the two isomers of VIII. Apparently, the value for $\delta(^{195}\text{Pt})$ is not very dependent upon whether the organic residues are fused to a strained ring (V–VII) or not (IV). For the 16-electron complex VIII two isomers are present in solution. For bis(2-methyl- η^3 -allyl)Pt a *trans* arrangement of the allyl groups has been found in the crystal [10]. The large ^{195}Pt signal separation indicates that the minor isomer has a different geometry, e.g. *cis*-(η^3 -allyl) $_2$ Pt.

The relaxation of the ^{195}Pt nucleus in phosphorous-platinum compounds has been shown to be governed by the Chemical Shift Anisotropy (CSA) and the Spin-Rotation [4]. This also holds for II, for which at 9.4 T 75% of the relaxation is due to CSA. Because of the absence of Pt–H NOE enhancements, we assume that the remaining relaxation is caused by the Spin-Rotation mechanism. For determining the influence of the CSA, T_1 measurements were carried out at different magnetic fields. They showed that at 9.4 T the CSA contributes to the relaxation of I to ~40% at 248 K and to ~60% at 224 K. Since the NOE enhancement is zero, it can be concluded that in addition to CSA the Spin-Rotation contributes to the relaxation in I, since this mechanism yields higher relaxation rates with increasing temperature. For VIII similar results were obtained: the CSA contributes to the relaxation by 50% for both isomers at 278 K. The T_1 values for the isomers VIIIa and VIIIb are different (cf. Table 2) which is in accord with the assumed different geometries for VIIIa and VIIIb, as indicated by their large signal separation.

The ^{195}Pt chemical shifts for I–VII confirm that there is a correlation between the formal oxidation state of the metal and $\delta(^{195}\text{Pt})$. The $\delta(^{195}\text{Pt})$ shifts of the π -compounds, e.g. III lie approximately 500 ppm to higher field than those of the bis- σ -compounds, IV–VII. Thus by $\delta(^{195}\text{Pt})$ the complexation of a diene as η^2 -ligand (B), e.g. in III, or as metallacyclopentene (A), e.g. in V, can be distinguished. Since a qualitatively similar behaviour can be expected for other types of ligands this trend



(A)

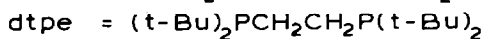
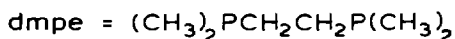
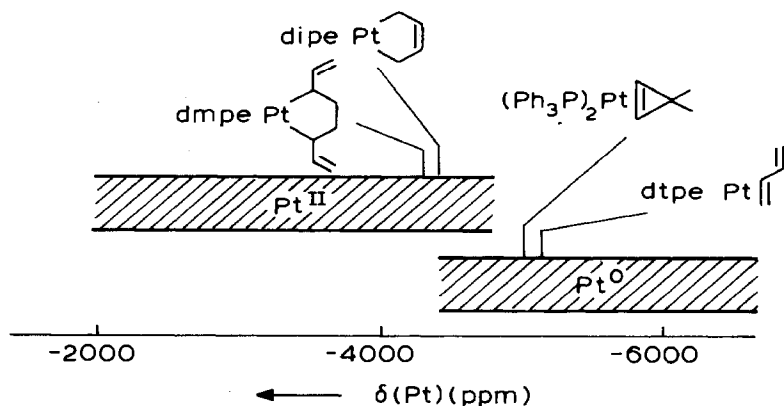


(B)

could be of use, particularly for those complexes for which no spin–spin couplings of ^{195}Pt with hetero atoms of the ligand are observable. In principle, this information could also be obtained from the $^1J(\text{Pt}, ^{13}\text{C})$ coupling constants [11]. However, the ^{13}C nucleus has an intrinsic sensitivity which is significantly lower than that of the ^{195}Pt nucleus, particularly at high magnetic fields.

The $^1J(\text{Pt}, \text{P})$ coupling constants in IV–VII differ markedly from those of the Pt^0 complexes II and III. The smaller values for the Pt^{II} compounds are usually rationalized in terms of the Fermi contact term [12] which relates J to the electron density at the coupled nuclei. Thus this coupling can also be used to distinguish Pt^{II}

from Pt⁰ complexes.



Since the influence of CSA is in the same order both for I, VIIIa and VIIIb, we attribute the extremely high shielding of the ¹⁹⁵Pt nucleus in bis(η^3 -allyl)Pt to electronic effects. From the NMR-point of view the Pt nucleus in VIIIa and VIIIb can be regarded to have a d^{10} electron configuration rather than a d^8 -configuration. Probably in VIII the donor and acceptor contributions to the bonding lead to a partial charge at Pt closer to zero rather than to that of Pt^{II}. We have observed similar but not as strong pronouncedly effects for the chemical shifts of the metal in tris(η^3 -allyl)Co compounds [13] as well as in bis(cyclopentadienyl)magnesium [14].

Experimental

The NMR measurements were carried out with Bruker WH 400 and WM 300 NMR spectrometers, equipped with the standard 10 mm multinuclear probehead. At 9.4 and 7.0 T the ¹⁹⁵Pt 90° pulse was 25 and 19 μs , respectively. The ¹⁹⁵Pt shifts are given as δ values relative to $[(\text{PtCl}_6)]^{2-}$ in D₂O as external standard. Shifts due to different solvents were corrected from their ²H-resonance frequencies. The limit of error for $\delta(^{195}\text{Pt})$ is ± 1 ppm and for $^1J(\text{Pt},\text{P}) \pm 5$ Hz. All measurements were performed under temperature control, the calibration of the temperatures was performed using the shift differences of the protons in methanol. The ¹⁹⁵Pt relaxation time measurements were performed using the inversion recovery technique including composite pulses [15]. The T_1 values stem from regression analysis. For the preparation of I cf. ref. 5, for II and VI cf. ref. 6, for III–V and VII cf. ref. 7 and for the preparation of VIII cf. ref. 8.

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