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A ^{1}H NMR INVESTIGATION OF THE ISOMERISM OF A DIMERIC TERTIARY ARSINE CHELATE COMPOUND CONTAINING PLATINUM(II)—CARBON σ-BONDS.

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Summary

The Pt^{II} complex of the chelate ligand *ortho*-vinylphenyldiphenylarsine (VPA) is susceptible to nucleophilic attack at the coordinated olefin to give four geometrical isomers of a dimeric product containing Pt—C σ-bonds. The NMR spectra of the monomers obtained by cleavage of the chlorine-bridged dimer with acetylacetonate or hexafluoroacetylacetonate show that methoxide attack occurs exclusively at the β-carbon atom to give a five membered chelate ring in which the α-carbon and arsenic atoms are the donors.

Introduction

The Pt^{II} chelate complexes of olefinic tertiary Group V ligands are known to be attacked at the coordinated olefin by nucleophiles [1-3]. The products have been shown to contain a sigma bond between the Pt^{II} and one of the olefinic carbons, the other being bonded to the nucleophile. The size of the chelate ring so formed depends on which of the olefinic carbons is attacked by the nucleophile.

Cope, Kliegman and Friedrich [4] found that treatment of the complex of *N*,*N*-dimethylallylamine with methoxide gave a type B (n = 4) chelate. Their investigation entailed reductive degradation of the complex with sodium borohydride followed by separation and identification of the released ligand. Similarly Kasahara, Tanaka and Izumi [2] found that methoxide attack on the complex of 2-vinylpyridine gave a type B (n = 4) product. We have found, as have other authors [3], that when the Group V donor is P or As this reduction procedure yields intractable products. The degradation of the complex is possi-

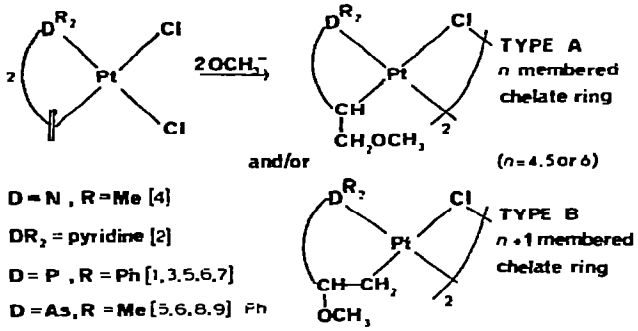


Fig. 1.

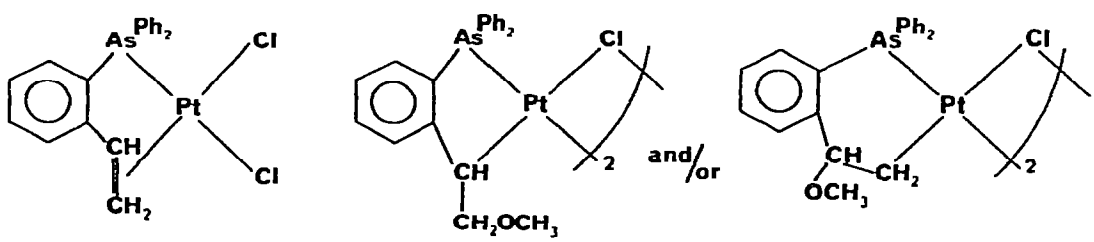
bly inhibited by the formation of moderately stable complexes of phosphorus and arsenic with Pt^0.

It was suggested by Haszeldine, Lunt and Parish [3] that the complex of 4-pentenyldiphenylphosphine formed a mixture of types A and B (n = 6) products on methoxide attack, because of the two methoxy resonances observed in the NMR spectrum. We discuss below an alternative explanation of this observation in terms of geometrical isomerism of a dimer containing one type of chelate ring.

Hewertson and Taylor [1] recorded the NMR spectrum of the product formed by treating the complex of 3-butenyldiphenylphosphine (n = 5) with methoxide but found it too complicated to determine the size of the chelate ring. They apparently did not consider a type A structure for the analogous product from the allyldiphenylphosphine complex (n = 4).

Results and Discussion

The π-bonded olefin chelate complex of VPA (I) is analogous to the previously reported compounds (Fig. 1) and reacts in a similar manner with sodium methoxide in methanol/chloroform. The NMR spectrum of the product II (Fig. 2) shows four singlets between δ3.0 and 3.3 ppm that we assign to the methoxy protons. Spin—spin coupling of protons of this type is unknown and indeed separation of the peaks is dependent on field strength and temperature. The four signals must therefore represent four unique methoxy environments.



(I) (II)

Three types of isomerism may be envisaged for II. 1. Five or six membered chelate rings (type A or B (n = 5)). 2. Arsine groups *cis* or *trans* across the dimer. 3. Methoxy groups *cis* or *trans* relative to the coordination plane of the dimer.

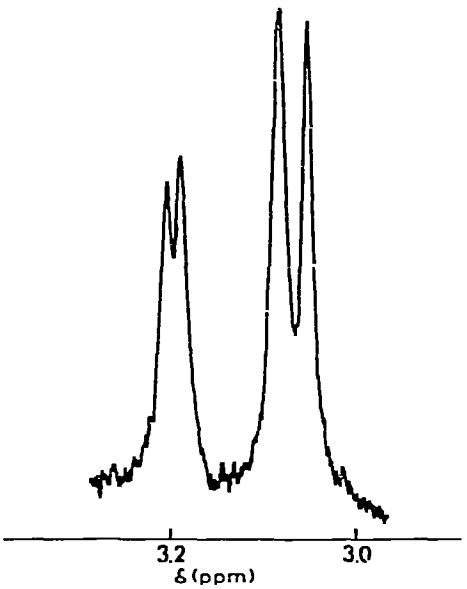


Fig. 2. 60 MHz spectrum of the methoxy protons of $(PtClVPA.OCH_3)_2$. Chemical shifts relative to TMS.

To establish the nature of the observed isomerism, the dimer II was reacted with thallium(I) acetylacetonate to give a highly soluble monomer $Pt(VPA.OCH_3)$-(acac) (IIIa) for which only type 1 isomerism is possible. Only one sharp resonance is observed (δ3.18 ppm) for the methoxy protons of this complex indicating the presence of a single ring size isomer*. Because the chemical shifts of the remaining protons are almost identical to those of II we can assume that the size of the chelate ring was not altered by the bridge splitting reaction.

The four methoxy signals from II must therefore arise from isomers of types 2 and 3. These peaks, shown in Fig. 2, are in the form of a pair of doublets. Within each doublet the resonances are of equal intensity but the upfield doublet is more intense (ca. 1.6/1) than the one at lower field. It is likely that the major splitting is due to a pair of isomers one of which is preferentially formed, and that the minor splitting is due to another pair of isomers in which there is no such preference. Isomerism of types 2 and 3 respectively are consistent with this reasoning.

The size of the chelate ring in II was determined by comparison of the NMR spectrum of IIIa with its hexafluoroacetylacetonate analogue IIIb (Fig. 3). In the spectra of both compounds the chemical shift of the methoxy singlet and the envelope of the methylene protons remain unchanged, but in IIIb the methine quartet is deshielded relative to IIIa by 0.24 ppm. This influence of the *trans* ligand on the methine resonance suggests that it is the methine carbon that is σ-bonded to the platinum, and that the chelate ring is of type A (n = 5).

The 100 MHz spectrum of IIIa shows a very broad peak 56.5 Hz downfield from the methine quartet, but the equivalent position upfield is obscured by the

* This conclusion is supported by the presence of only four methoxy resonances in the spectrum of II. If both type 1 isomers were present there could be up to sixteen unique methoxy environments.

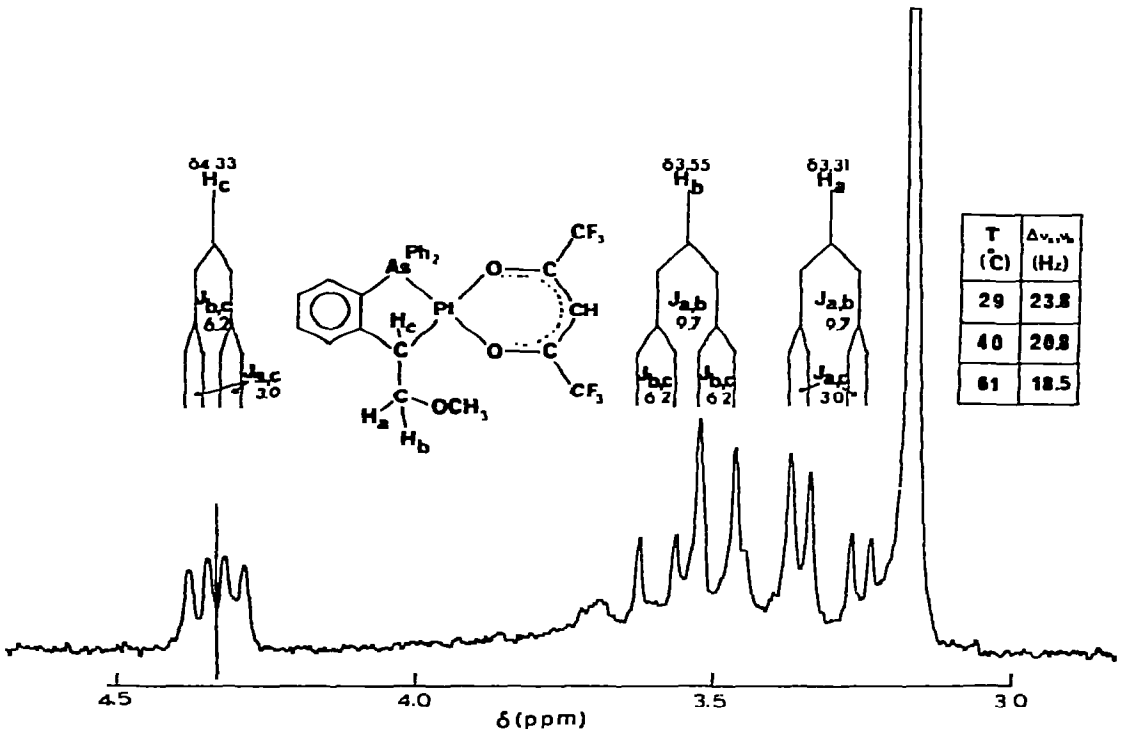


Fig. 3. 100 MHz spectrum of Pt(VPA.OCH_3)(hfac). The table shows the progressive collapse of the methylene octet upon increasing the sample temperature.

resonance of the methylene protons. This broad signal was shown to be a ^{195}Pt side band (s = 1/2, 34% natural abundance) by its collapse upon irradiation of the ^{195}Pt nucleus at 21.415 MHz. Confirmation of the assignment followed observance in the 60 MHz spectrum of a similar signal 56 Hz downfield from the methine quartet.

A value of 113 Hz for this ^{195}Pt—^{1}H coupling constant (120 Hz for IIIb) is large and typical for a methine group σ-bonded to platinum in a cyclic system [11,12]. The absence of platinum side bands around the methylene octet suggests that coupling to these protons by ^{195}Pt is less than ca. 20 Hz. The broad nature of the sideband may be due to a rapid relaxation of the ^{195}Pt arising from the interaction with the large quadrupole (0.29 barn) of the ^{75}As [13].

The methine carbon of a chelate ring of either type A or B is an asymmetric centre and therefore the methylene protons are intrinsically non-equivalent. Only in a ring of type A however would there be a temperature dependance of the chemical shifts of the methylene protons. To confirm the presence of a five membered ring in IIIb, spectra were recorded at probe temperatures between 30° and 64° (Fig. 3). At the higher temperature the difference between the chemical shifts of the methylene protons decreased by 25%, thus confirming a chelate ring structure of type A for these compounds and the halogen bridged dimers.

Experimental

The ligand VPA was prepared by Bennett's procedure [12].

$PtCl_2$ VPA (I)

A solution of VPA (1.25 g, 3.76 mmol) in chloroform (15 ml) was added slowly to a stirred suspension of $PtCl_2$ (1.00 g, 3.76 mmol) in chloroform (30 ml), refluxed for 1 h then filtered. The resultant golden yellow solution was concentrated under reduced pressure to 15 ml and after the addition of an equal quantity of ethanol was maintained at −5° overnight to yield yellow crystals which were recrystallized from dichloromethane/methanol (1.91 g, 85%) m.p. 260° dec. (Found: C, 39.95; H, 3.02; Cl, 12.3 $C_{20}H_{17}AsCl_2Pt$ calcd.: C, 40.15; H, 2.86; Cl, 11.9%.)

$(PtCl VPA.OCH_3)_2$ (II)

A solution of sodium (0.023 g, 1 mmol) in methanol (2 ml) and chloroform (8 ml) was added slowly to a stirred solution of I (0.598 g, 1 mmol) in chloroform (30 ml) at room temperature. After stirring for 1/4 h the solution was filtered, methanol (30 ml) added, and evaporated under reduced pressure to 15 ml. The precipitated white powder was filtered, washed with MeOH and dried under vacuum (0.582 g, 98%) m.p. 189-191°. (Found: C, 41.79; H, 3.74; Cl, 7.5. $C_{42}H_{40}As_2O_2Pt_2$ calcd.: C, 42.47; H, 3.39; Cl, 6.0%.)

$Pt(VPA.OCH_3)(acac)$ (IIIa) and $Pt(VPA.OCH_3)(hfac)$ (IIIb)

A solution of the appropriate thallium(I) β-diketonate (0.84 mmol) in chloroform (10 ml) was added slowly to a solution of II (0.50 g, 0.42 mmol) in chloroform (30 ml) at room temperature. After stirring for 1/4 h the solution was filtered then evaporated to dryness under reduced pressure. The residue was dissolved in methanol (5 ml) and the solution kept at −5° for 24 h to yield the product which was recrystallized from a small amount of hot methanol. IIIa: 65%, m.p. 157-159°. (Found: C, 47.40; H, 4.33. $C_{20}H_{27}AsO_3Pt$ calcd.: C, 47.49; H, 4.14%.) IIIb: 50%, m.p. 127-128°. (Found: C, 40.97; H, 2.84; As, 10.02; F, 15.08; Pt, 25.75. $C_{26}H_{21}AsF_6O_3Pt$ calcd.: C, 38.88; H, 2.85; As, 10.10; F, 15.37; Pt, 26.31%.)

Measurements

^1H NMR spectra were recorded on Varian HA100 and EM360 instruments. Microanalyses were performed by the Australian Microanalytical Service, C.S.I.R.O., Melbourne or by Alfred Bernhardt, Mikroanalytisches Laboratorium, Elbach, West Germany.

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