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Preliminary communication

EVIDENCE FOR RESTRICTED ROTATION OF THE Pt—P BOND OF $[\eta^3\text{-}C_3H_5Pt[P(C_6H_{11})_3]_2]^+PF_6^-$

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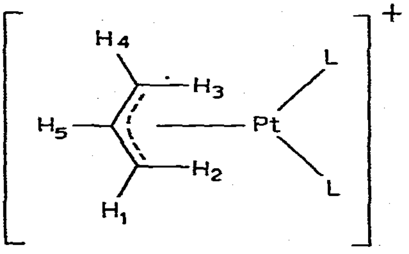
Summary

The low-temperature proton NMR spectrum of $[\eta^3\text{-}C_3H_5Pt(PCy_3)_2]^+$ PF_6^- (Cy = cyclohexyl) shows that the two *syn* protons of the allyl group are non-equivalent; this is attributed to the restricted rotation of the Pt—P bonds

Cationic η^3-allyl platinum(II) complexes of the general formula $[\eta^3\text{-allyl } PtL_2]^+$ X^- (I) have been shown by NMR spectroscopy to have either "static" or "dynamic" π-allyl structures in solution depending on the nature of the anion X [1-3]. The complex I has a "static" structure when X^- is BF_4^-, PF_6^-, ClO_4^- or NO_3^- and exhibits an AM_2X_2 (AB_2C_2) pattern for the allylic protons. In the "static" allyl complexes no *syn—anti* proton exchange is observed.



(I)

When X^- is Cl^- or Br^-, I has a "dynamic" structure in solution and the allylic protons give rise to an AX_4 spin system. A "static" structure is obtained in these cases at low temperatures. The *syn—anti* exchange of protons H(1) and

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H(2) (and H(3) and H(4)) is believed to occur via a σ-allyl intermediate [1]. The dependence of the structure of I on the anion has been attributed to the ability of chloride or bromide to more effectively stabilize the σ-allyl intermediate than BF_4^-, PF_6^-, ClO_4^-, or NO_3^- [3].

During our investigations of the reactions of olefins and acetylenes with [*trans*-PtH(CH_3OH)(PCy_3)$_2$]$^+$ PF_6^- (II), we found that the reaction of allene and II afforded the η^3-allyl complex [η^3-$C_3H_5Pt(PCy_3)_2$]$^+$ PF_6^- (III). While III was found to have a "static" η^3-allyl structure in solution at room temperature by NMR spectroscopy, non-equivalence of the *syn* protons H(1) and H(4) was observed at low temperatures (Fig. 1).

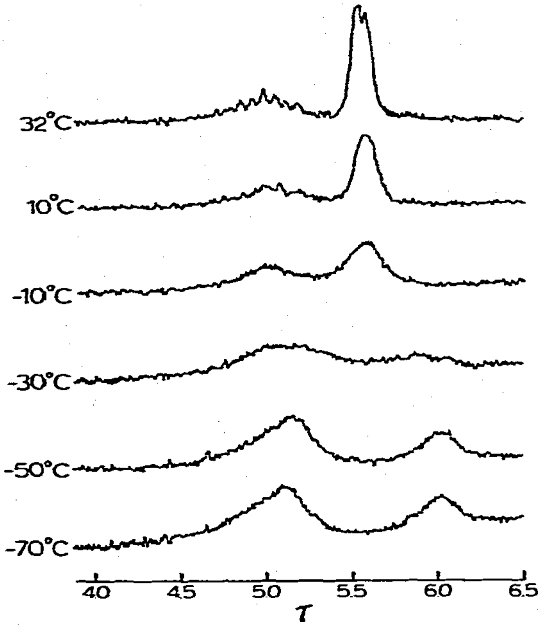
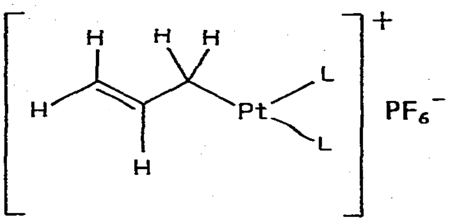


Fig. 1. Variable temperature ^{1}H NMR spectra of the allylic protons H(1), H(4), and H(5) of [η^3-$C_3H_5Pt(PCy_3)_2$]$^+$$PF_6^-$ in $CDCl_3$ solution.

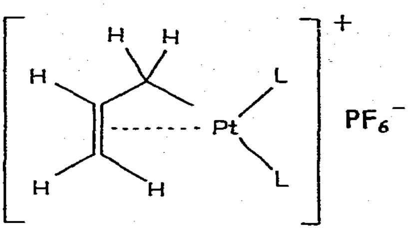
At room temperature in $CDCl_3$ or CD_2Cl_2, the *anti* protons H(2) and H(3) of III appear as a doublet of doublets accompanied by ^{195}Pt satellites [3] at τ7.52 [*J*(H(2,3)—H(5)) = 12.5 Hz, *J*(P—H(2,3)) = 8 Hz, *J*(Pt—H(2,3)) = 42 Hz]. The *syn* protons H(1) and H(4) appear as a broad doublet at τ5.61 [*J*(H(1,4)—H(5)) = 6 Hz]. Proton H(5) appears as a multiplet at τ5.05 [*J*(H(1,4)—H(5)) = 6 Hz, *J*(H(2,3)—H(5)) = 12.5 Hz, *J*(P—H(5)) = 12.5 Hz].

At +10 °C, the signals due to protons H(5) and H(1,4) broaden somewhat and the fine structure due to spin—spin coupling is lost. At −30 °C, the resonance due to protons H(1) and H(4) at τ5.61 disappears and two new broad resonances at τ5.05 and τ6.07 begin to appear. At −70 °C the new peaks at τ5.05 and τ6.07 sharpen and are in a ratio of 2/1. The ratio of 2/1 is observed because of overlap of the new peak at τ5.05 and the resonance of proton H(5) at τ5.05. Upon further cooling to −90 °C the spectrum sharpens somewhat; however, no fine structure due to spin—spin coupling is observed. The resonance of the *anti* protons H(2) and H(3) broadens upon cooling to −90 °C; however, the appearance of new peaks in this region was not observed, primarily because these protons appear as a shoulder of the large PCy_3 resonance.

The non-equivalence of the protons H(1) and H(4) cannot be attributed to the σ-allyl structure A since III was found to have a "static" structure at room temperature with no *syn—anti* proton exchange, and moreover the chemical shifts observed are not those of a σ-allyl group [4,5].



(A)



(B)

A π + σ structure (similar to B) has been reported for 2-methylallyl-PdCl(PPh_3) [6], in which the differences in the σ-donor abilities of the ligands *trans* to the allyl moiety can account for the slight perturbation of the symmetry of the allyl group (similar to B). However, in the present case the two ligands L are identical, so that there is no reason to postulate an asymmetric allyl group as in B.

The magnetic non-equivalence of the *syn* protons H(1) and H(4) can be attributed to the restricted rotation of the PCy_3 groups about the Pt—P bond. Restricted rotation about metal—phosphorus bonds has been observed for *trans*-$MX_2(PH\text{-}t\text{-}Bu_2)_2$ (M = Pt, Pd; X = Cl, Br, I) [7] and *trans*-MCl(CO)$(PR\text{-}t\text{-}Bu_2)_2$ (M = Rh, Ir; R = Me, Et, n-Pr) [8] by low-temperature NMR spectroscopy.

An idealized structure of III at −90 °C is shown in Fig. 2. The cyclohexyl groups of the two ligands are in a staggered configuration. A staggered configuration for *trans*-PCy_3 groups has been previously shown in the X-ray structures of *trans*-$PtI_2(PCy_3)_2$ [9] and *trans*-$PtH_2(PCy_3)_2$ [10]. An even greater interaction

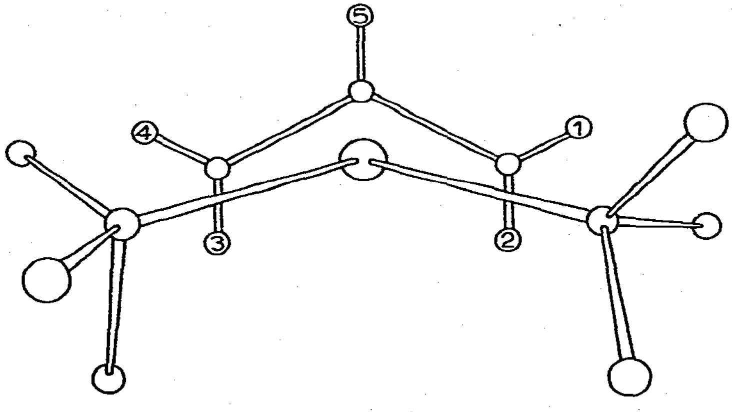


Fig. 2. Idealized structure of III at −90 °C viewed down the Pt—allyl bond axis. The cyclohexyl rings have been omitted for the sake of clarity.

between the PCy_3 ligands is expected in III since the P—Pt—P angle is much less than 180°. Because of the bulkiness of the ligands, the cyclohexyl groups are meshed together in a "cogwheel" type arrangement in which neither PCy_3 ligand can rotate independently of the other. At room temperature rotation is fast enough on the NMR time scale to average the magnetic environments of the *syn* protons H(1) and H(4) [as well as the *anti* protons H(2) and H(3)]. At −30 °C this rotation is slowed and protons H(1) and H(4) [and H(2) and H(3)] reside in different magnetic environments. One set of protons [H(1) and H(2) in Fig. 2] lie directly above a cyclohexyl substituent while the second set of protons [H(3) and H(4) in Fig. 2] lies between two cyclohexyl substituents of the second ligand. The *anti* protons H(2) and H(3) should exhibit a similar behavior at low temperatures. Because the *anti* protons appear as a shoulder of the PCy_3 resonance, we were unable to observe the non-equivalence of these protons.

We have examined the proton NMR spectrum of a similar η^3-allyl complex $[\eta^3\text{-}C_3H_5Pt(PPh_3)_2]^+ BF_4^-$ and a tricyclohexylphosphine platinum(0) complex $Pt(PCy_3)_2(CH_3CO_2C{\equiv}CCO_2CH_3)$. Magnetic non-equivalence of the *syn* or *anti* protons of the allyl complex was not observed from room temperature to −90 °C. The carbomethoxy groups of the platinum(0) complex were found to be magnetically equivalent at −90 °C. The interactions of the PCy_3 ligands in $Pt(PCy_3)_2(CH_3CO_2C{\equiv}CCO_2CH_3)$ are very similar to those in III and thus would be expected to have diastereotopic methyl groups at low temperatures. The differences in the chemical shifts of these diastereotopic methyl groups may be too small to be observed since the distance of the methyl groups to the PCy_3 ligands is much larger than the distance of the allylic protons to the PCy_3 ligands.

Acknowledgements

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