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The Crystal and Molecular Structure of Chloro(tri-*p*-tolylphosphine)(η^3-allyl)platinum(II)

A. DEL PRA and G. ZANOTTI

Centro Studi Biopolimeri del C.N.R., c/o Istituto di Chimica Organica, Università di Padova, Padua, Italy

G. CARTURAN

Centro Chimica Metallorganica Elementi di Transizione del C.N.R., c/o Istituto di Chimica Industriale, Via Marzolo 9, Padua, Italy

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Recent investigations on the reactivity and stability of allyl Pt(II) complexes [1, 2] demonstrate that the possibility of observing η^1- or η^3-allylic species is greatly affected by the nature of the solvent and of the ligands which may be simultaneously coordinated to the central metal. Moreover we observed that in the case of [(η^3-allyl)Pt(L)Cl] (1) (L = phosphine) complexes the ^{1}H and ^{31}P NMR behaviours are dependent on the phosphine nature and a linear relationship between J_{Pt-P} and the ^{1}H NMR patterns of the allyl protons was found in agreement with an intimate connection of the Pt–P with the Pt–allyl bond [3]. However the origin of these relationships remained unclear, so that we deemed it helpful to determine the crystal structure of some key compounds of the type (1). As a part of this study we report here the structure of the title compound which allows some comparison with the [(η^3-allyl)Pt(PBu^t_3)Cl] [4] and [(η^3-allyl)Pt($\mathrm{PCy_3}$)$_2$]$^+$ [5] structures.

Crystal Data

The complex {(η^3-allyl)Pt[P(*p*-Tol)$_3$]Cl} was obtained as previously described [3] and the crystals were formed from a solution of toluene/ether stored at –20 °C. The complex crystallizes in the orthorhombic system, with a = 17.277(8), b = 18.375(8), c = 14.290(6) Å, Z = 8, space group P *b c a*. Intensity data were collected on a four-circle diffractometer with MoK$\bar{\alpha}$ radiation from a crystal of approximate dimensions 0.4 × 0.3 × 0.2 mm. 2505 independent reflections up to θ = 27° having $I \geqslant 2.5\sigma(I)$ were measured and corrected for the Lorentz, polarization and absorption effects. The structure was determined by the heavy-atom technique and refined by full-matrix least-squares procedure. The final conventional R value is 0.052 (R_w = 0.054).

The molecular conformation of the {(η^3-allyl)Pt-[P(*p*-Tol)$_3$]Cl} complex and the atom-labeling scheme is illustrated in Figure 1.

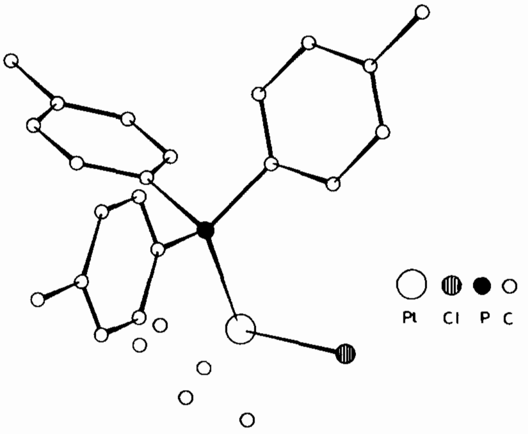

Fig. 1. Stereochemistry of the complex, as viewed along *c*.

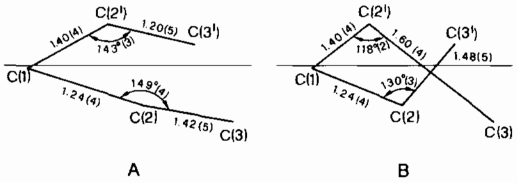

Fig. 2. The two possible allylic patterns named A and B.

The most important feature of the structure arises from the disorder found in the allyl moiety region as observed also for the [(η^3-allyl)Pt(PBu^t_3)Cl] structure [4]. Five carbon atom peaks were found in the electron density map instead of three with weights 1 for C(1) and 0.5 for C(2), C(2′), C(3) and C(3′) positions (see Fig. 1) indicating the occurrence of two statistically equivalent orientations for the allylic group. The low precision of allylic geometry allows four possible bond connections (see Fig. 2). Nonetheless the Pt–P bond distance is in the present case significantly shorter [2.272(4) Å] than in the PBu^t_3 derivative [2.333(4) Å]. This shortening parallels the lowering in the J_{Pt-P} observed on going from the PBu^t_3 (4548.3 Hz) to the title complex (4453.1 Hz) [3] in contrast with the well documented lowering of J_{Pt-P} as the Pt–P bond distance is increased [6, 7]. Also the Pt–Cl bond length [2.336(4) Å] determined here is shorter than for the [(η^3-allyl)Pt-(PBu^t_3)Cl] complex where it was found to be 2.367-(2) Å. The Pt–allyl carbon distances [Pt–C(1) = 2.23(2), Pt–C(2) = 2.15(4), Pt–C(3) = 2.17(2), Pt–C-

(2′) = 2.11(3), Pt–C(3′) = 2.16(3) Å] are comparable with those quoted for the PBu^t_3 analog [4] whereas the allylic carbon bond lengths, at variance with the PBu^t_3 case, do not favour possible 'symmetric' allylic geometries.

These facts might be related to the different ^1H NMR behaviour of these two complexes: the PBu^t_3 complex shows, at room temperature, a dynamic allyl proton spectrum while the $P(p\text{-Tol})_3$ analog displays a static spectrum. However, at present, owing to the fact that the comparison is made between only two compounds, a possible discussion based on the effect of the phosphine basicity and steric demand on the allyl bonding mode or configuration will be untenable.

On the other hand, Figures 1 and 2 show that the allyl group is considerably asymmetric and the terminal carbons C(3) or C(3′) are significantly out of the P–Pt–Cl plane at variance with the structure of the $[(\eta^3\text{-allyl})Pt(PCy_3)_2]^+$ complex [5] where two possible symmetric allyl geometries have been reported with both terminal allyl carbons lying approximately on the P–Pt–P plane. The difference in the allylic pattern with the present case where only asymmetric allylic geometries are allowed (see Figure 2), may be related to the presence of different ligands, *i.e.* Cl and $P(p\text{-Tol})_3$, bonded to the central metal atom.

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