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# Preparation and X-Ray Structure of the σ-allylic Compound [(σ-allyl)Pt($CH_3NC$)($PPh_3Cl$]

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A series of σ-allyl complexes of type [(σ-allyl)-Pt($CNR)_2Cl$] (1) (R = $CH_3$, $C_6H_{11}$, p-$ClC_6H_4$ and 2,6-dimethylphenyl) was obtained on reacting [($\eta^3$-allyl)Pt(CNR)Cl] (2) with the stoichiometric amount of isocyanide [1]. Under the same experimental conditions used on preparing complexes (1), [($\eta^3$-allyl)Pt($PPh_3$)Cl] (3) reacts with $CH_3CN$ to give a pale yellow compound having the elemental composition corresponding to [($C_3H_5$)Pt($CH_3NC$)($PPh_3$)Cl] (4). (*Anal.*: Found: C, 47.55; H, 4.05; N, 2.61; Cl, 5.98%; $PtC_{23}H_{23}NPCl$ requires: C, 48.06; H, 4.00; N, 2.43; Cl, 6.16). Its IR spectrum (nujol mull) shows $\nu_{C\equiv N}$ at 2260 $cm^{-1}$, $\nu_{Pt-Cl}$ at 325 $cm^{-1}$ and a medium absorption at 1615 $cm^{-1}$ attributable to $\nu_{C=C}$ of uncoordinated double bond. Therefore in the solid state a σ-allyl structure can be proposed and that was definitely proven by determining the crystal and molecular structure of compound (4).

## Crystal Structure

$PtCl_{23}NPH_{23}$, $M$ = 575.0, triclinic, $a$ = 13.38(1), $b$ = 9.626(8), $c$ = 9.188(8) Å, $\alpha$ = 99.8(1), $\beta$ = 81.8(1), $\gamma$ = 107.3(1)°; $u$ = 1107.8 Å$^3$, $D_c$ = 1.72, Z = 2, $\mu$(Mo-K$\alpha$) = 68.6 $cm^{-1}$, $\mu\cdot r \sim 0.5$. Space group P$\bar{1}$ (from structure determination).

The conventional R-factor was 0.055 for 2166 independent reflections after the last anisotropic least-squares refinement including the hydrogen atom contribution held constant. Absorption correction was not applied because of the small size of the crystal used during the data collection. The crystal is built up by monomeric units [Pt$^{II}$(σ-allyl)($CH_3NC$)($PPh_3$)Cl] where the metal atom has a square-planar arrangement with a slight (± 0.04 Å) tetrahedral distortion. The ligands are arranged as shown in Figure 1. The most outstanding feature is the σ-bonded allyl group. Although the allyl ligand undergoes a large termal motion, which affects the accuracy of its geometry, the overall structure is unequivocally established. The value of the Pt–$CH_2$ distance is close to those usually found for σPt–C bonds whereas the bond lengths and angles of allyl group would suggest a double bond mainly concentrated between the terminal atoms [2]. The orientation of the allyl group may be defined by the torsional angle around the Pt$CH_2$–CH$CH_2$ bond, which is 131° and by the dihedral angle between the coordination and the allyl planes, which is 67°. Non bonded intra- and inter-molecular interactions are probably responsible for such an orientation.

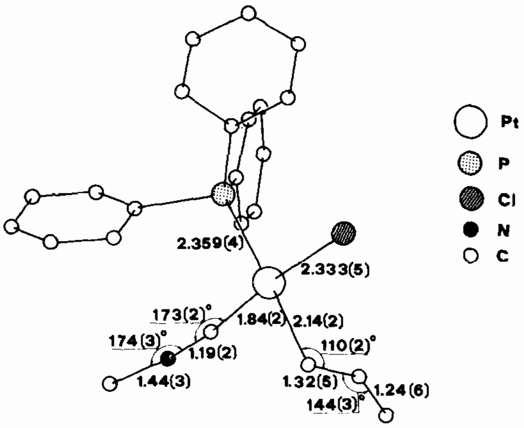

Fig. 1. Molecular structure of [(σ-allyl)Pt($CH_3NC$)($PPh_3$)Cl].

To our knowledge, the value of the Pt–P bond length of 2.359(4) Å is the greatest value so far reported [3, 4]. This is indicative of the strong *trans*-influence of the allyl group.

The geometry of the RNC–Pt unit in the present case is virtually the same as that found for other isocyanide platinum(II) complexes [5, 6]. The Pt–Cl distance (2.333(5) Å) is also close to those normally found in these species [7].

At variance with the solid state, the behaviour in solution at room temperature of compound (4) shows that it is an electrolyte in $CH_2Cl_2$ and the solution smells of free isocyanide. Its PMR spectrum is quite complex: the allyl protons appear as unresolved broad multiplets, whereas the protons of methylisocyanide were observed at 6.55 τ and at 7.08 τ, this latter corresponding to free isocyanide protons resonance [8]. Ring closure by the chelating tooth of the olefinic end is probably responsible for this behaviour, leading to displacement of either isocyanide or chloride *cis* ligands. On the other hand the allylic structure is probably present in solution at low temperature. In fact the PMR spectrum strongly varies with the temperature and at –70 °C the $CH_3NC$ is completely coordinated, the signal appearing at 6.55 τ with $J_{Pt-H}$ = 19Hz. As for the allylic protons the fine structure still remains lost although the spectrum is quite similar to that of the σ-allylic compounds (**1**). In fact at –70 °C these signals were observed at 7.10–7.30 τ, 4.80–5.20 τ and 3.50–3.90 τ with integration ratios 2:2:1.

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