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Molecular Structures of *trans*-Chlorocyanomethylbis(triphenylphosphine)platinum(II) and *trans*-Hydridocyanomethylbis(triphenylphosphine)platinum(II)

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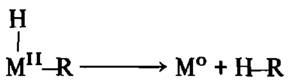
Spectroscopic and structural evidence indicates that the σ M–C bonds in organo-transition metal complexes increase in strength with increasing electronegativity of the alkyl chain (R_X), as dictated by alkyl substituents such as X = F, CN, NO_2, *etc.* [1, 2]. This enhanced bond strength has been often invoked to explain the existence and stability of many organotransition complexes: as a matter of fact, quantitative thermodynamic data on the strength of M–C bonds are rather scanty.

The Pt–R_X derivatives are among the most stable ones and have been more extensively investigated [3]. Recently some of us have reported on the preparation and reactivity of cyanoalkyl and fluoroalkyl complexes of Pt(II), [4, 5]. The enhanced strength of the Pt–R_X bond as compared to the parent alkyl complexes is reflected by the following findings: (i) insertion reactions across the Pt–C bond are unfavoured and (ii) the coexistence of σ Pt–C bonds along with other ligands that usually strongly destabilize these bonds (such as the hydride) becomes more likely [5]. In fact, the presence of both alkyl and hydrido groups in the same complex is not always feasible, easy reductive elimination occurring:



$$\overset{\displaystyle H}{\overset{|}{M^{II}}}\text{–}R \longrightarrow M^{\circ} + H\text{–}R$$

Hitherto, no complexes with simultaneous Pt–H and Pt–R_H bonds are known, although a number of dialkyl [1–3] and some dihydrido Pt(II) compounds with bulky phosphines [6] have been successfully isolated. Unsubstituted alkyl complexes (Pt–R_H) would facilitate reductive elimination compared to electronegatively substituted alkyl analogs (Pt–R_X), to the extent that this requires nucleophilic attack of an incipient carbanion on the adjacent group with which it is being eliminated, since R_H^- should be more nucleophile than the corresponding R_X^-.

Along these guidelines, we succeeded in isolating stable complexes of type [PtH(R_X)LL′] and [PtH(R_X)(L–L)] (R_X = cyanoalkyl or trifluoromethyl; L = L′ = PPh_3; L = PPh_3, L′ = isocyanide; L–L = diphosphine or diarsine) [5, 7]. The geometric configuration was elucidated by spectroscopic investigation.

The coexistence of two mutually affecting ligands – the R_X and the H – was thought to provide an ideal basis for a study of structural features with their possible implications in the more general subject of *cis*- and *trans*-influence. Moreover, in order to compare the effect of H and Cl ligands on the bond distances between platinum and the remaining ancillary groups, we also carried out an X-ray analysis on the title complexes.

Crystal Data

Both complexes crystallize in the monoclinic system, space group C^5_{2h}-$P2_1/n$ with four molecules in the unit cell; the lattice constants of **1** and **2** are a = 12.366(5), b = 23.019(8), c = 12.303(4) Å, β = 110.7(1)° and a = 14.610(6), b = 18.803(7), c = 12.083(5) Å, β = 93.1(1)° respectively. Intensity data were collected on a four-circle diffractometer with $MoK\bar{\alpha}$ radiaton. 4313 and 2544 independent reflections having $I \geqslant 3\sigma(I)$ were measured for **1** and **2**. Intensities were corrected for Lorentz, polarisation and absorption effects. The structures were determined by the heavy-atom technique and refined by full-matrix least squares procedure. The final conventional R value is 0.038 and 0.039 for **1** and **2**.

Perspective views of the molecules **1** and **2** are presented in Fig. 1 and 2, where thy most relevant bond lengths and angles are marked.

In both compounds the Pt atom is four-coordinate and is surrounded in a approximately planar fashion by two *trans* phosphorus atoms of the PPh_3 ligands, a chlorine (or H) atom and a σ-bonded carbon of the CH_2CN group. In addition the latter ligand is approximately linear and is tilted with respect to the σ Pt–C bond of 111.1 and 106.0° in **1** and **2** respectively. The triphenylphosphine geometry in both molecules, as judged by P–C distances and C–P–C and P–C–C angles is nearly identical with the geometry of the triphenylphosphine and its derivatives in other platinum(II) complexes with the same *trans* configuration [8]. The Pt–P distances in **2** (2.274 Å, av.) are significantly shorter than those found in **1** (2.309 Å, av.).

This provides a quantitative assessment of relative structural *cis*-influences, *i.e.* Cl > H, in agreement

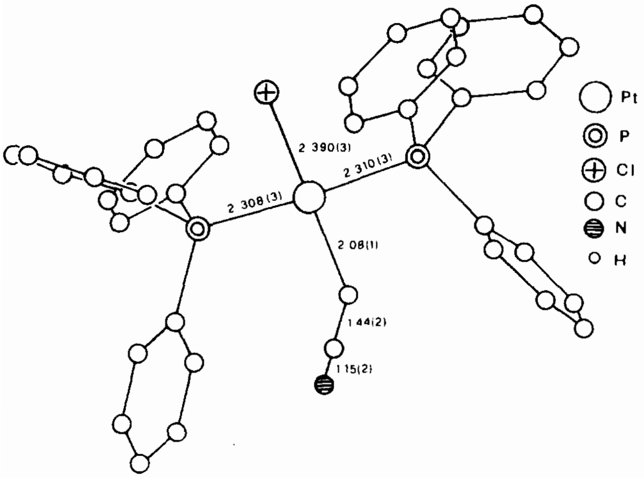


Figure 1. Structure of *trans*-[PtCl(CH$_2$CN)(PPh$_3$)$_2$] (1). Hydrogen atoms are omitted.

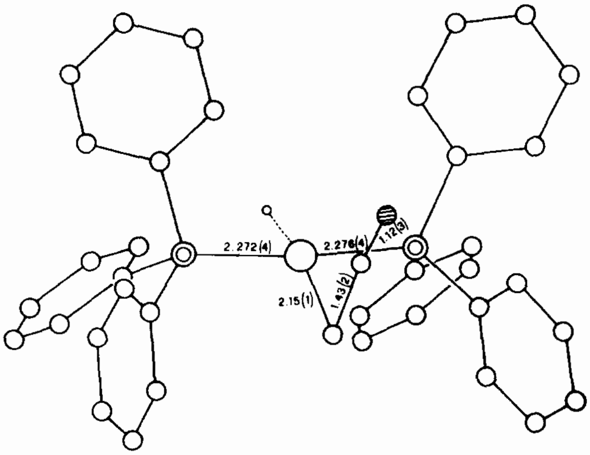


Figure 2. Structure of *trans*-[PtH(CH$_2$CN)(PPh$_3$)$_2$] (2). Phenyl and methylene hydrogen atoms are omitted.

with nmr *cis*-influences as determined by ^{1}J(PtP) data (2850 and 3034 Hz for 1 and 2 respectively) [4, 5]. The electronic mechanism by which the *cis*-influence manifests itself on the Pt–P bond length is still a subject of debate [8]. The Pt–C distances, 2.08(1) and 2.15(1) Å in 1 and 2 respectively, are typical of Pt(II)–C(sp^3) bonds (*cf.* the values of 2.090(4) Å in *trans*-[PtCl(η^1-allyl)(PPh$_3$)$_2$] and 2.120(7) Å in *trans*-[Pt(I–SO$_2$)(CH$_3$)(PPh$_3$)$_2$] [9] and are approximately the values expected from the sum of covalent radii. However, the significantly longer Pt–C distance in 2 confirms the high *trans*-influence of the hydrido ligand as compared with the halide in platinum(II) compounds [10].

Acknowledgments

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