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Chemistry of Metal–Diene Complexes: Preparation and Structure of σ-Bonded Cyclopentadienyl Platinum(II) Complexes

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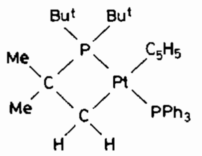
There has been a considerable current interest in the chemistry of cyclopentadienyl complexes of platinum and palladium [1–3]. Although a variety of π-cyclopentadienyl (η^5-C_5H_5) complexes of platinum have been reported, only a small number of σ-bonded cyclopentadienyl platinum (η^1-C_5H_5Pt) complexes are known. Almost all of the monohaptocyclopentadienyl complexes of platinum(II) known to date are stable only at low temperatures and undergo rapid decomposition during attempted isolation. The structural configuration of these complexes have been proposed mainly on the basis of their ^{1}H NMR spectral data and to the best of our knowledge no X-ray structure of such η^1-C_5H_5–Pt complex has been reported. In the course of our present investigations on metal–diene complexes, we have been able to prepare some air stable monohaptocyclopentadienyl platinum complexes containing mixed phosphine ligands, [(η^1-C_5H_5)Pt(P–C)L] (I) [where (P–C) = $Bu^t_2PCMe_2CH_2$ and L = Ph_3P, (p-$CH_3C_6H_4$)$_3$P, Cy_3P and $(PhO)_3P$]. These show unusual ^{1}H and ^{31}P NMR spectra and on the basis of the informations obtained from the spectral analysis only, it is difficult to assign the correct structure. We wish to present here a brief account of these studies and the X-ray structure for these complexes.

The pentaheptocyclopentadienyl platinum complex, [(η^5-C_5H_5)Pt(P–C)] (II), is obtained conveniently in high yield from the reaction of cyclopentadienylthallium with the chloro-bridged dinuclear platinum complex, [Pt–(μ-Cl)(P–C)]$_2$ [6]. It reacts smoothly with tertiary phosphines or phosphites in benzene leading to the formation of monohaptocyclopentadienyl platinum complexes of the type [(η^1-C_5H_5)Pt–(P–C)L] (I).

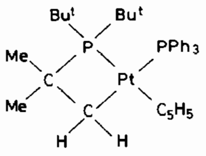
$$[(\eta^5\text{-}C_5H_5)Pt\text{–}(P\text{–}C)] + L \rightarrow [(\eta^1\text{-}C_5H_5)Pt(P\text{–}C)L] \qquad (1)$$

These complexes are obtained as air stable crystalline solids and are readily soluble in benzene or toluene but only sparingly soluble in pentane or hexane.

Stable pale-yellow crystals are isolated in approximately 70% yield from the reaction of Ph_3P with complex II in 1:1 molar ratio in benzene. Elemental analyses and the molecular weight correspond to [(C_5H_5)Pt–(P–C)(Ph_3P)]. The proton NMR spectrum of this complex I consists of resonances due to the protons of the metalated tri-t-butyl phosphine at δ 1.06 (d; JPH = 12.5 Hz), 1.38 (d; JPH = 13.2 Hz) and 0.38 ppm (dd; JPH = 8.8 and 1.6 Hz) in approximately 9/3/0.7 ratio, corresponding to the di-t-butyl (t-Bu_2P), dimethyl (P–Me_2) and methylene (CH_2–Pt) protons respectively. The signals due to the methylene protons display ^{195}Pt-satellites (JPtH = 85 Hz) confirming that methylene is bonded to platinum. Signals due to Ph_3P protons appear as two sets of multiplets centered at δ 7.01 and 7.95 ppm. In addition, the spectrum shows a well-resolved symmetrical triplet centered at δ 6.24 (JPH = 3.4 Hz) associated with platinum satellites (JPtH = 30.8 Hz) due to the cyclopentadienyl protons. The large magnitude of the platinum coupling constant is consistent with the σ-bonded cyclopentadienyl platinum complexes reported previously by Cross and Wardle [2]. The overall ratio between the signals due to the protons of the metallated t-butyl phosphine, Ph_3P and the cyclopentadienyl groups is approximately 5:3:1. Low temperature NMR spectrum carried out at –70 °C in d_8-toluene does not show any further splitting in the signals of the Cp ring suggesting a fluxional behavior [7]. The appearance of the resonances due to cyclopentadienyl protons as a triplet suggests a symmetrical arrangement of cyclopentadienyl with respect to both phosphorus nuclei. In other words the two phosphines should be *trans* to each other and *cis* to the Cp group. (Structure A). This is consistent with the arguments used to rationalize the configuration of σ-bonded complexes



(A)



(B)

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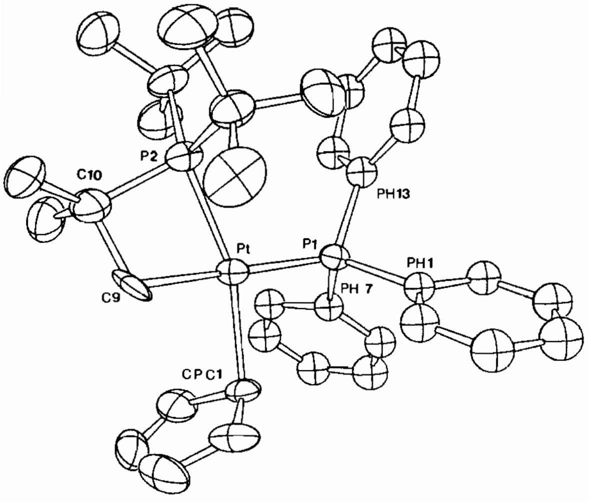

Fig. 1. ORTEP diagram $[(\eta^1\text{-}C_5H_5)Pt(Bu^t_2PCMe_2CH_2)\text{-}PPh_3]$. Principal bond lengths (Å): Pt–P = 2.313, $Pt–P_2$ = 2.284, Pt–C9 = 2.100, $Pt–C_1Cp$ = 2.211, and bond angles (°): $P_1–Pt–P_2$ = 111.4, $P_1–Pt–C_9$ = 177.0, $P_1–Pt–C_1Cp$ = 87.9, $P_2–Pt–C_9$ = 68.1, $P_2–Pt–C_1Cp$ = 160.7, $C_9–Pt–C_1Cp$ = 92.8.

previously [2]. However the JPH value (3.4 Hz) observed for this complex is rather unusually high for *cis*-coupling of mutually *trans* phosphines. Interestingly, the ^{31}P NMR spectrum shows signals due to metallated phosphine at ($\delta P = -14.27$ ppm) and Ph_3P ($\delta P' = 24.33$ ppm) as sharp singlets, each associated with platinum satellites JPtP = 2060 and 1963 Hz respectively. The occurrence of signals as singlets suggests no coupling between two nonequivalent phosphorus nuclei, and the small magnitude of JPtP (of the order of ≈2000 Hz) is consistent with the structure (B) where both phosphorus are *cis*- to each other and *trans* to carbons [8]. For the complex having structure (A) with two non-equivalent phosphorus nuclei at *trans*-to each other, one would expect to see a phosphorus–phosphorus coupling showing two doublets each associated with platinum satellites *i.e.* a 12 line spectrum is expected as we have reported earlier for complexes, *trans*-[PtCl-(P–C)L] [6]. These ^{31}P NMR results are not in agreement with that of ^1H NMR data. In order to assign the correct configuration, the X-ray crystal structure has been determined and is reproduced in Fig. 1.

The compound crystallized in the orthorhombic space group *P*ca2, with unit cell parameters a = 17.968(3) Å, b = 9.656(3) Å, c = 18.709(3) Å, and $Z = 4$. Intensity data were collected on a Syntex $P2_1$ four circle diffractometer. A semi-empirical absorption correction (μ = 42.49) was applied and 2560 reflections having $F \geqslant 3(F)$ were used in the final refinement. The structure was solved by locating the platinum from a Patterson function and using subsequent difference Fouriers to locate the remaining atoms. Phenyl rings were refined as rigid groups with isotopic thermal parameters assigned to the carbons. The temperature factors of the remaining non-hydrogen atoms were varied anisotropically. The full-matrix least squares refinement converged at R = 0.037. The results show this molecule to possess a distorted square planar geometry with two phosphines at *cis*-positions to each other which is consistent with Structure B and the ^{31}P NMR spectral analyses. It is surprising that although the two phosphorus nuclei are not symmetrically disposed with respect to the cyclopentadienyl group, they show coupling of the same magnitude. This unusual NMR behavior is perhaps due to the different electronic parameters of the two phosphines.

Similar ^1H and ^{31}P NMR features are observed for other complexes of type I containing different phosphine ligands. In conclusion, this report represents the first X-ray structure determination of a stable σ-bonded cyclopentadienyl platinum(II) complex and also the first example of a structure of a metallated tri-*t*-butylphosphine complex with a four membered ring.

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