

### Platinum(II) Induced Cleavage of P–C Bond of Tri-*t*-Butylphosphine and Isolation of a Novel Low Symmetry Phosphido- and Hydrido-Bridged Dinuclear Platinum Complex

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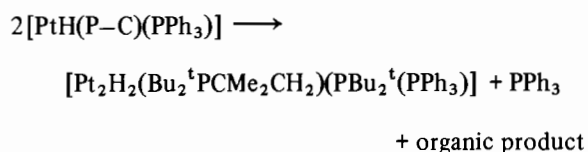
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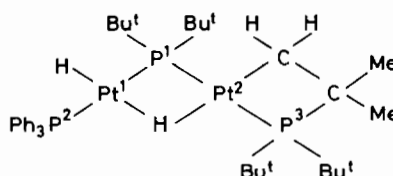
Studies concerning the process of catalyst deactivation, generally occurring via an undesired interaction of the metal with the ligands in the course of homogeneous transition metal catalyzed organic synthesis, have become a very important field of research in recent years [1, 2]. We, recently, reported a similar unexpected interaction of triaryl phosphine and stibene with palladium(II) salts resulting in the cleavage of P–C bonds [2]. Formation of biaryls in these systems has been considered as the result of a bimolecular mechanism although no such dinuclear complex could be isolated. Now we wish to report for the first time the cleavage of P–C bond of tri-*t*-butylphosphine induced by platinum(II) and isolation of an unusual mixed hydrido- and phosphido-bridged dinuclear platinum complex.

In the course of our studies on the mixed ligands containing hydrido-platinum complexes [3] that might be useful catalysts in the homogeneous catalyzed hydrogenation and polymerization reactions of unsaturated organic substrates, we synthesized a series of low symmetry complexes containing carbon-platinum and platinum-hydrogen bonds, [PtH(P–C)L] (1) (P–C = Bu<sup>t</sup>PCMe<sub>2</sub>CH<sub>2</sub>). It is noteworthy that while these complexes are reasonably stable in solid state, they decompose gradually in solution. This process of decomposition can be observed by the proton NMR spectroscopic means. When the solution of 1 (L = PPh<sub>3</sub>) in benzene is kept at room temperature, a complete decomposition results within 2 weeks. The solution provides needle shaped colorless crystals (m.p. = 185 °C), the elemental analyses, molecular weight and mass-spectral data of which correspond to [Pt<sub>2</sub>H<sub>2</sub>(Bu<sub>2</sub><sup>t</sup>PCMe<sub>2</sub>CH<sub>2</sub>)(PBu<sub>2</sub><sup>t</sup>)(PPh<sub>3</sub>)] (2). Infrared spectrum shows the presence of terminal and bridging

platinum-hydrides ( $\nu$ PtH = 2080(s) and 1570–1720 cm<sup>-1</sup> (br.)).



The proton NMR spectrum of the complex (2) consists of resonances due to the protons of metalated tri-*t*-butylphosphine, (Bu<sub>2</sub><sup>t</sup>PCMe<sub>2</sub>CH<sub>2</sub>), as two sets of sharp doublets at  $\delta$  1.64 ( $J_{\text{PH}} = 14.6$  Hz), 1.54 ( $J_{\text{PH}} = 12.7$  Hz) in the ratio 3:1 corresponding to the di-*t*-butyl (PBu<sub>2</sub><sup>t</sup>) and dimethyl (P–CMe<sub>2</sub>) protons respectively. The methylene protons appear at  $\delta$  2.31 ppm ( $J_{\text{PH}} = 15.5$  Hz) associated with <sup>195</sup>Pt satellites with  $J(\text{PtH})$  82 Hz confirming that methylene is bonded to platinum [4]. The protons of di-*t*-butylphosphido-group appear as doublet at  $\delta$  1.19 ppm ( $J_{\text{PH}} = 11.7$  Hz) and phenyl group protons as two multiplets at  $\delta$  7.06 and 7.78 ppm. In addition, proton NMR spectrum, in the hydride region, consists of two sets of signals each corresponding to terminal and bridging hydrides. The terminal hydride ligand appears as four doublets centered at  $\delta$  -4.74 ppm ( $J^{\text{PtH}} = 19.1$  and 5.15 Hz,  $n = 1$  and 2 and  $J_{\text{HH}} = 13$  Hz) flanked by two sets of <sup>195</sup>Pt-satellites ( $J^{\text{Pt}^1\text{H}} = 1368$  Hz and  $J^{\text{Pt}^2\text{H}} = 71$  Hz). The platinum satellite ( $J^{\text{Pt}^1\text{H}} = 1368$  Hz) appears to be larger compared to a platinum-dihydride complex (e.g., in (R<sub>3</sub>P)<sub>2</sub>PtH<sub>2</sub>,  $J^{\text{PtH}} = 780$  Hz) [5], however, is in agreement with the value ( $J^{\text{PtH}} = 1090$ –1316 Hz) observed recently by Venanzi and co-workers [6] in several dinuclear platinum(II) complexes. The bridging hydride displays signals as five sets of multiplets centered at  $\delta$  -6.61 ppm [ $J_{\text{HH}}$  and  $J^{\text{Pt}^n\text{H}} = 12.5$ –13.3 Hz ( $n = 1, 2$  or 3) and  $J^{\text{Pt}^n\text{H}} = 460$  Hz ( $n = 1$  or 2)] in the approximate ratio of 1/8/18/8/1. Although due to the presence of dissimilar groups on the two platinum, non-equivalent coupling constants are expected [6, 7], however, a similar pattern with equal platinum satellites has been observed by Paonessa *et al.* [8] in the case of [Pt<sub>2</sub>( $\mu$ -H)HPh(PEt<sub>3</sub>)<sub>4</sub>]<sup>+</sup>. On the basis of above evidence, the following structure can be assigned to complex 2.



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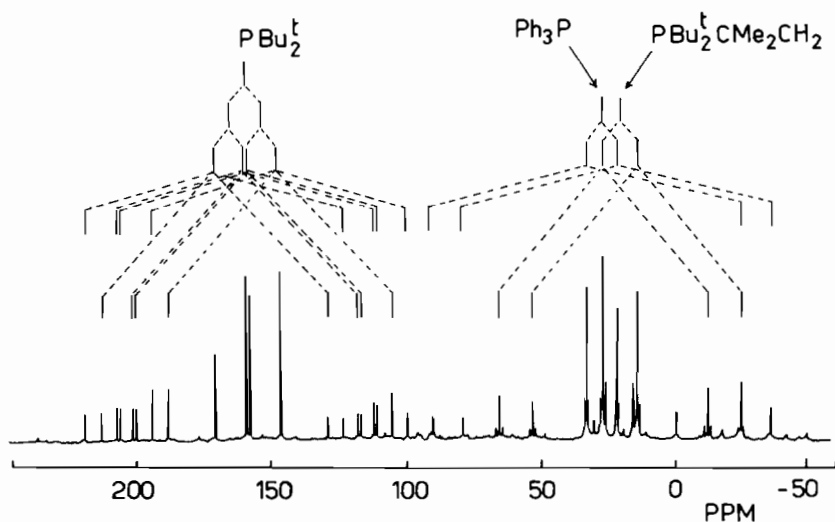


Fig. 1.  $^{31}\text{P}$  NMR spectrum of complex  $[\text{Pt}_2(\mu\text{-H})(\mu\text{-PBu}_2^t)\text{H}(\text{Bu}_2^t\text{PCMe}_2\text{CH}_2)(\text{PPh}_3)]$  in  $\text{CH}_2\text{Cl}_2/\text{C}_6\text{D}_6$  at room temperature.

This structure is further supported by the  $^{31}\text{P}$  NMR spectrum which shows a complex but easily interpretable pattern (Fig. 1). The phosphorus nuclei of the bridging phosphido-group is observed as a double-doublet centered at  $\delta$  159.93 ppm ( $J^{\text{P}^1\text{P}^2} = 274$  Hz and  $J^{\text{P}^1\text{P}^3} = 308$  Hz) associated with two sets of platinum satellites ( $J^{\text{Pt}^1\text{P}^1} = 2019$  Hz and  $J^{\text{Pt}^2\text{P}^1} = 2300$  Hz). The signals due to metalated tri-*t*-butylphosphine and triphenylphosphine consist of main doublets at  $\delta$  20.86 ppm ( $J^{\text{P}^1\text{P}^3} = 310$  Hz) and  $\delta$  27.49 ppm ( $J^{\text{P}^1\text{P}^2} = 276$  Hz) each associated with two sets of platinum satellites ( $J^{\text{Pt}^1\text{P}^3} = 54$  Hz and  $J^{\text{Pt}^2\text{P}^3} = 1904$  Hz;  $J^{\text{Pt}^1\text{P}^2} = 2812$  Hz and  $J^{\text{Pt}^2\text{P}^2} = 31$  Hz). The relatively lower platinum–phosphorus coupling constant ( $J^{\text{PtP}} = 1904$  and 2812 Hz) compared to that in the starting complex (1) ( $J^{\text{PtP}} = 2407$  and 2920 Hz)<sup>3</sup> and in the diphenylphosphido-bridged dinuclear platinum complex,  $[\text{Pt}(\mu\text{-H})\text{Ph}(\text{PPh}_2)(\text{PPh}_3)_3]^+$  ( $J^{\text{PtP}^n} = 2509$  and 2895 Hz where  $\text{P}^n =$  phosphorus *trans*- to phosphido-group) [7] is probably due to the higher *trans*-effect of di-*t*-butyl phosphido-group as well as higher steric parameters.

The above observations provide the first example of the platinum(II) induced cleavage of P–C bond of tri-*t*-butylphosphine under mild conditions yielding the low symmetry mixed hydrido and di-*t*-butylphosphido-bridged dinuclear platinum complex containing mixed ligands.

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