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Preliminary communication

PREPARATION AND FACILE INTRAMOLECULAR METALATION REACTIONS OF BIS(TRI-t-BUTYLPHOSPHINE)PLATINUM(II) HYDRIDES

HOWARD C. CLARK*, ANIL B. GOEL, RAM G. GOEL* and WILLIAM O. OGINI
Guelph-Waterloo Centre for Graduate Work in Chemistry, Department of Chemistry, University of Guelph, Guelph, Ontario N1G 2WI (Canada)

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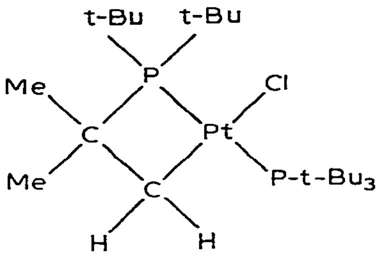
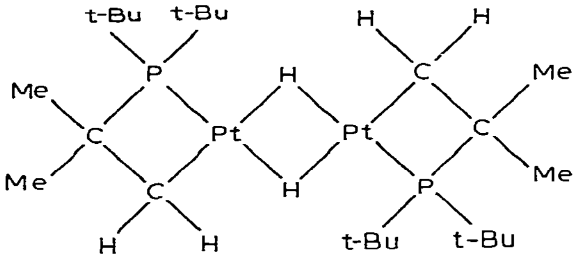
Summary

Bis(tri-t-butylphosphine)platinum(II) hydrides, *trans*-$HPtX(P\text{-}t\text{-}Bu_3)_2$ (where X = Cl, Br, I and CF_3CO_2) and *trans*-$H_2Pt(P\text{-}t\text{-}Bu_3)_2$, have been prepared and characterized. These hydrides, unlike platinum(II) hydrides containing less bulky phosphines, undergo facile intramolecular metalation to form the internally metalated complexes $[t\text{-}Bu_2PC(CH_3)_2\overline{CH_2]Pt}X(P\text{-}t\text{-}Bu_3)$ and $[\{t\text{-}Bu_2PC(CH_3)_2\overline{CH_2\}Pt}H]_2$, respectively.

Recently there has been considerable interest in the stabilization of transition metal hydrides [1—6] by bulky phosphines. For example, while attempts to reduce *trans*-$HPtCl(PR_3)_2$ complexes to the dihydride complexes lead to decomposition with less bulky phosphines such as PPh_3 and PEt_3, stable dihydride complexes $(R_3P)_2PtH_2$ are obtained with bulky phosphines such as $P(cyclo\text{-}C_6H_{11})_3$, $P\text{-}i\text{-}Pr_3$ and $P\text{-}t\text{-}Bu_2Ph$. Hence, it is now generally believed [5] that the stability of the hydride increases with increasing steric bulk of the phosphine. We have prepared the previously unknown dihydride complex *trans*-$H_2Pt(P\text{-}t\text{-}Bu_3)_2$ (I) as well as the monohydride complexes *trans*-$HPtX(P\text{-}t\text{-}Bu_3)_2$ (II) (where X = Cl, Br, I or CF_3CO_2 and have found that these hydrides undergo facile intramolecular metalation reactions at room temperature to form the internally metalated complexes $[\{t\text{-}Bu_2PC(CH_3)_2\overline{CH_2\}Pt}\text{-}H]_2$ (III) or $[t\text{-}Bu_2PC(CH_3)_2\overline{CH_2]Pt}X(P\text{-}t\text{-}Bu_3)$ (IV). Although intramolecular metalation of tri-t-butylphosphine [7] as well as other bulky phosphines [8] in platinum(II) and palladium(II) chloride complexes is now well recognized, to our knowledge intramolecular metalation of a phosphine ligand has hitherto not been observed for any hydride complex.



(III)



(IV)

The preparation of the platinum(0) complex, $(t\text{-}Bu_3P)_2Pt$ [3,4] (V) from the reaction of $t\text{-}Bu_3P$ and $Pt(COD)_2$ [9] (COD = cycloocta-1,5-diene) has been reported recently. We have prepared complex V in over 70% yield by refluxing commercially available potassium tetrachloroplatinate(II) with two equivalents of tri-t-butylphosphine in the presence of two equivalents of potassium hydroxide in ethanol.

Complex V readily undergoes oxidative addition reactions with protic acids such as HCl, HBr, HI and CF_3COOH to give complexes II (reaction 1).

$$\underset{\text{(V)}}{(t\text{-}Bu_3P)_2Pt} + HX \rightarrow \underset{\text{(II)}}{\textit{trans}\text{-}HPtX(P\text{-}t\text{-}Bu_3)_2} \qquad (1)$$

$(X = Cl, Br, I, O_2CCF_3)$

Complex I is obtained by the reactions of complexes II with $NaBH_4$ in ethanol. The infrared spectrum of I shows a strong band at 1820 cm^{-1} due to the Pt—H stretching vibration and its ^1H NMR spectrum consists of one triplet due to the t-butyl protons (τ 8.48 ppm, J(P—H) 5.8 Hz) and another triplet due to the hydrogens bonded to platinum. (τ 12.95 ppm, J(P—H) 15.5 Hz; J(Pt—H) 774 Hz). The Pt—H stretching frequencies for complexes II occur in the 2382 to 2402 cm^{-1} region. Thus the Pt—H stretching frequencies for these hydrides are significantly higher than those for other hydrides [6] of platinum(II) containing less bulky phosphines. Proton NMR spectra for these complexes showed the expected 1/2/1 triplets in the τ 25.70 to 31.71 ppm region (J(Pt—H) 996—1104 Hz, J(P—H) 12.5—13.5 Hz) due to the hydride proton. ^{31}P NMR spectra for the dihydride as well as the monohydride complexes consisted of a main peak (δ 99.2 and 73.0—75.0 ppm) and two satellite peaks due to ^{195}Pt—^{31}P spin—spin coupling ($J(^{195}Pt—^{31}P)$ 3003 and 2952—2904 Hz).

$$\underset{\text{(I)}}{\textit{trans}\text{-}H_2Pt(P\text{-}t\text{-}Bu_3)_2} \rightarrow \underset{\text{(III)}}{[\{t\text{-}Bu_2PC(CH_3)_2\overline{CH_2\}\,Pt}H]_2} + H_2 + P\text{-}t\text{-}Bu_3 \qquad (2)$$

$$\underset{\text{(II)}}{\textit{trans}\text{-}HPtX(P\text{-}t\text{-}Bu_3)_2} \rightarrow \textit{trans}\text{-}[t\text{-}Bu_2PC(CH_3)_2\overline{CH_2]\,Pt}X(P\text{-}t\text{-}Bu_3) + H_2 \qquad (3)$$

$(X = Cl, Br, I \text{ or } O_2CCF_3)$

I and II are stable at room temperature, in the solid state. However, in solution, they undergo facile intramolecular metallation (reactions 2 and 3).

The rate of metallation of complexes II is markedly increased by the presence of trace amounts of alcohol or acids and follows the order I > Br > Cl > O_2CCF_3. The ^1H NMR spectrum of III consists of two doublets at τ 8.83 ppm (J(P—H) 12 Hz) and τ 8.84 ppm (J(P—H) 11.7 Hz) in the intensity ratio of 3/1 which can be assigned, respectively, to the protons of the two t-butyl groups and protons of the two methyl groups attached to the third tertiary carbon of the metallated phosphine. In addition to these doublets, a few very low intensity peaks are also present in the spectrum which can be assigned to the protons of the CH_2 group bonded to platinum. Further evidence for the formulation of III is provided by the disappearance of the hydride resonance in the NMR spectrum. The infrared spectrum of III does not contain any band in the 1800—2300 cm^{-1} region but shows a broad band at ca. 1550 cm^{-1} similar to that reported for hydride dinuclear platinum(II) complexes [10]. No infrared band due to Pt—H stretching is observed in the infrared spectra of complexes IV. Their ^1H and ^{31}P NMR spectra are similar to those observed for $[t\text{-}Bu_2PC(CH_3)_2\overline{CH_2]Pt}Cl(P\text{-}t\text{-}Bu_3)$ [7].

Acknowledgments

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