Notes

Room-Temperature β-H Elimination in $(P_2P)Pt(OR)$ Cations: Convenient Synthesis of a Platinum Hydride

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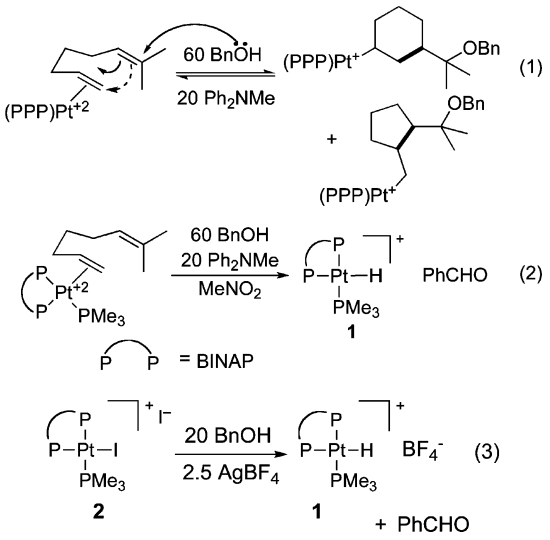
Received December 5, 2006

Summary: In situ-generated $[(BINAP)(PMe_3)Pt][BF_4]_2$ *reacts with benzyl alcohol at RT to yield* $[(BINAP)(PMe_3)Pt-H][BF_4]$ *and benzaldehyde. This reactivity contrasts similarly ligated platinum−alkyl species, which are stable to β-hydride elimination even at elevated temperatures. Protonolysis of the platinum hydride leads to a species that is readily substituted by weakly coordinating ligands (acetone, pentafluorobenzonitrile).*

Introduction

β-Hydride elimination is a well-established reaction in P_2PtR_2,[1] $P_2Pt(OR)R$,[2] and $P_2Pt(OR)_2$[2] complexes.[3] In the case of Pt alkyls it has been possible to inhibit these reactions using bidentate ligands (e.g., dppf and dppe)[1a,2c] that inhibit phosphine dissociation and thus block low-energy migratory deinsertion from three-coordinate intermediates.[1a] It has been possible to similarly inhibit β-H elimination in cationic structures using tridentate ligands (e.g., triphos (PPP) or pyridyl bisphosphine), which block the *cis* positions required for low-energy migratory deinsertion.[4] In fact, this strategy has been key to a number of processes where β-H elimination is undesirable,[5] including some catalytic Pt(II) alkene activation reactions.[4b,6,7] Our group recently reported that dicationic platinum catalysts containing a bidentate/monodentate (P_2P) ligand array could similarly block migratory deinsertion and improve diene cycloisomerization reaction profiles (e.g., yield, diastereo- and enantioselectivity) compared to first-generation PPP catalysts.[8]



Results and Discussion

A particularly useful experiment for probing the mechanism of the original $(PPP)Pt^{+2}$-catalyzed cycloisomerization reaction was to include *in situ* traps (benzyl alcohol) for putative carbocation intermediates (eq 1). Similar trapping experiments on second-generation P_2P cyclopropanation catalysts unexpectedly diverged, and no Pt alkyl species were observed. Instead, a new $(BINAP)(PMe_3)Pt$ species was generated with a J_{Pt-P} of 2200 Hz (^{31}P NMR) for the phosphorus *trans* to the new ligand (eq 2). When the alcohol was changed to either phenol or methanol, the same species was observed. Particularly informative was the ^1H NMR, which showed a diagnostic platinum hydride resonance at −5.2 ppm, suggesting $[(BINAP)(PMe_3)Pt-H][BF_4]_2$, **1**, as the structure (Figure 1).

To determine the source of the hydride, $[(BINAP)(PMe_3)PtI][I]$ (**2**) was taken with 2.5 equiv of $AgBF_4$ and 20 equiv of benzyl alcohol in nitromethane. The reaction cleanly generated **1** and benzaldehyde, indicating that benzyl alcohol likely served as the hydride source; ethanol and 2-propanol similarly afforded

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10.1021/om061105z CCC: $37.00
Publication on Web 04/07/2007

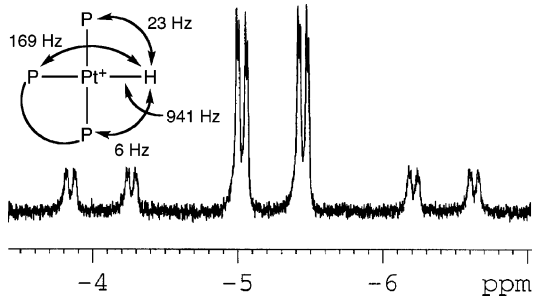


Figure 1. ^{1}H NMR spectrum of **1** in the hydride region ($\delta = -5.2$ ppm).

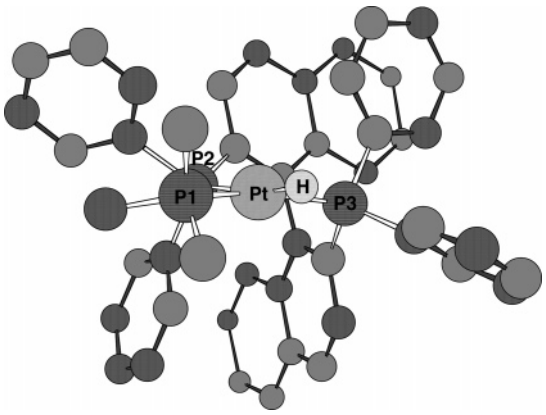
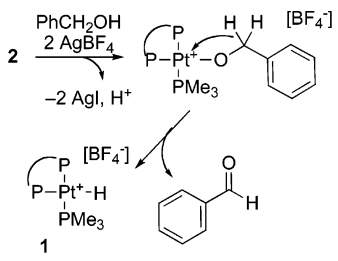


Figure 2. Chem3D representation of **1**. BF_4^- counterion is not shown. Selected bond lengths (Å): Pt−H = 1.682, Pt−P_1 = 2.2944(12), Pt−P_2 = 2.3472(12), Pt−P_3 = 2.2966(12). Selected bond angles (deg): P_1−Pt−P_2 = 92.17, P_2−Pt−P_3 = 101.45.

Scheme 1. Proposed Mechanism for Hydride Formation from BnOH



the hydride. A generic mechanism for hydride formation is shown in Scheme 1, with the key step being β-hydride elimination from an alkoxide (or an alcohol) intermediate.[9]

In contrast to the *in situ* carbocyclization trapping experiments in eq 2, direct reactions of phenol and methanol with $(P_2P)Pt^{2+}$ did not yield **1**. The source of the hydride in the former cases was separately traced to the amine base (Ph_2NMe), which, in the absence of alcohol, generates **1** on reacting with the dication. In this case a β-H elimination to generate the *N*,*N*′-diphenylimminium ion is envisioned[10] (Scheme 2); switching to Ph_2NH completely suppresses hydride formation (no β-H's).

An X-ray structure of **1** was obtained (Figure 2) by slow vapor diffusion of pentane to an acetone solution. Chlorinated solvents were not suitable for crystallization because **1** was readily converted to the platinum chloride. Pt−H and Pt−P bond lengths are similar to related platinum hydride structures.[11] The Pt−P bond *trans* to the hydride is about 0.1 Å longer than the Pt−P bond *trans* to the chloride in the analogous chloride structure.[12]

Interestingly, this route to the hydrides seems to be limited to compounds containing biaryl-linked diphosphine ligands. Platinum complexes containing BINAP/PMe_3, xyl-BINAP/PMe_3, and SEGPHOS/PMe_3 ligand arrays all successfully generated the respective platinum hydrides on reacting with benzyl alcohol, while dppm/PMe_3, dppe/PMe_3, and triphos did not. Phosphorus−platinum coupling constants suggest that these species weakly coordinate the alcohol[13] but do not facilitate the subsequent β-elimination. Table 1 collects the diagnostic J_{P-Pt} for the phosphine *trans* to the variable site; the PMe_3 chemical shift was sensitive to the charge on the fourth ligand and is also included.

Scheme 2. Proposed Mechanism for Hydride Formation from Ph_2NMe

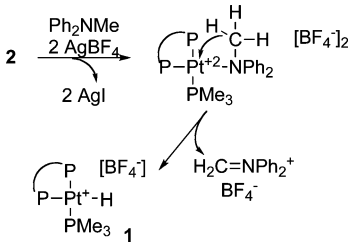


Table 1. Selected J_{P-Pt} Coupling Constants for the Phosphine *trans* to X/L

$(BINAP)(PMe_3)Pt^{2+}$−X/L	J_{P-Pt} (Hz)	chemical shift of PMe_3 (ppm)[a,b]
X = alkyl$^-$	1700	−10
H^-	2200	−15.6
I^-	3510	−13.9[c]
L = NCC_6F_5	3650	−3.5
acetone	4020	2.1
"MeOH"[d]	4100	3.8

[a] In CD_3NO_2 unless otherwise noted; the counterion is BF_4^-. [b] Externally referenced to 85% H_3PO_4. [c] In $CDCl_3$. [d] Tentative assignment based on J_{P-Pt}.

The utility of **1** to function as a convenient (Ag^+-free) precursor to highly reactive $(P_2P)Pt^{2+}$ catalysts was investigated. HBF_4 and $HNTf_2$ were each able to protonolyze off the hydride in the presence of a suitable trapping ligand (acetone or pentafluorobenzonitrile) (Scheme 3), though similar protonolysis experiments on $(P_2P)Pt^+-CH_3$ were very sluggish under these conditions.[14] $[Ph_2NH_2][BF_4]$ (pK_a = 0.8)[15] was not acidic enough to initiate similar reactivity.

(9) We are unable, as of yet, to distinguish between these two possibilities, as the reaction is fast both with and without the added weak base (Ph_2NH). We favor the alkoxide route simply because hydride migration from a coordinated alcohol would generate aldehyde bound to both an electrophilic Pt Lewis acid and H^+. A counterpoint to this notion is the observation that dicationic P_2Pt^{2+} Lewis acids can function with a Brønsted co-catalyst in certain electrophilic activation reactions on aldehydes; see: Mullen, C. A.; Gagné, M. R. *Org. Lett.* **2006**, *8*, 665−668. Regardless, the discussion explicitly assumes a key alkoxide intermediate.

(10) The imminium ion was not observed.

(11) Selected, similar platinum hydride structures: (a) Clark, H. C.; Dymarski, M. J.; Oliver, J. D. *J. Organomet. Chem.* **1978**, *154*, C40−C42. (b) Manojlovic-Muir, L.; Jobe, I. R.; Ling, S. S. M.; McLennan, A. J.; Puddephatt, R. J. *J. Chem. Soc., Chem. Commun.* **1985**, 1725−1726. (c) Alonso, E.; Fornies, J.; Fortuno, C.; Martin, A.; Orpen, A. G. *Organometallics* **2001**, *20*, 850−859. (d) Jaska, C. A.; Lough, A. J.; Manners, I. *Dalton Trans.* **2005**, 326−331. (e) Packett, D. L.; Syed, A.; Trogler, W. C. *Organometallics* **1988**, *7*, 159−166.

(12) See supporting information for details on the $[(BINAP)(PMe_3)PtCl][BF_4]$ X-ray structure.

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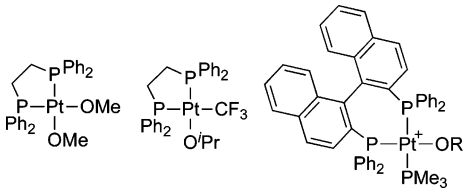
(15) Measured in aqueous HCl. See: (a) Dolman, D.; Stewart, R. *Can. J. Chem.* **1967**, *45*, 903−910. (b) Stewart, R.; Dolman, D. *Can. J. Chem.* **1967**, *45*, 925−928.

Scheme 3. Protonolysis of Pt−H

HA = HBF_4, $HNTf_2$
L = acetone, NCC_6F_5

Chart 1



The rapid β-hydride elimination of the described platinum−alkoxides significantly contrasts with comparably ligated platinum−alkyl compounds, which do not β-eliminate up to 70 °C.[6a,7] Bercaw and Bryndza have previously noted the polarizing influence of electronegative substituents on β-H elimination from 16-electron neutral P_2PtX_2 complexes: (dppe)$Pt(OMe)_2$ (25 °C) ≫ (dppe)Pt(OMe)Et (100 °C) > (dppe)$PtEt_2$ (160 °C).[2c] Mechanistic studies implicated a pre-equilibrium β-H elimination to an 18-electron, five-coordinate (dppe)Pt(H)OMe(H_2C═O) intermediate, which reacted by competitive loss of MeOH or formaldehyde. Similarly, Strukul has shown that β-H elimination is rapid at RT in (dppe)(CF_3)Pt(OR) complexes, which act as efficient oxidation catalysts in the presence of H_2O_2.[16] The electron-deficient CF_3 ligand presumably increased the metal's electrophilicity, which increased the rate of β-H elimination (cf. (dppe)Pt(OMe)Et, which does react until 100 °C). We hypothesize, on the basis of these studies and our own, that the combination of a cationic metal and an alkoxide ligand generates a sufficiently electrophilic complex to enable rapid β-H eliminate and provide **1** at RT. The analogous alkyl complexes lacking such an electronegative substituent do not readily β-eliminate. The situation may be more complex than this, since not all $(P_2P)Pt^{2+}$ complexes generated the hydride. The complexes known to β-hydride eliminate at RT are collected in Chart 1.

In summary, we report a convenient method for the synthesis of chiral $(P_2P)Pt-H$ cations and additionally extend the compound types known to β-H eliminate at RT to several cationic triphosphine structures.

Experimental Section

General Methods. Synthetic procedures were performed in a dinitrogen-filled MBraun Labmaster 100 glovebox. CH_2Cl_2 was sparged with dry argon and passed through a column of activated alumina. Acetone was distilled from $CaSO_4$ and freeze−pump−thaw degassed. $MeNO_2$ was purified according to literature procedures, which removes trace propionitrile from the commercial material.[17] CD_3NO_2 and Ph_2NMe were distilled from CaH_2 and freeze−pump−thaw degassed prior to use. $HNTf_2$ and phenol were sublimed under vacuum. Anhydrous benzyl alcohol, methanol, ethanol, and 2-propanol were used as received from Aldrich. P_2PtI_2 was prepared by stirring equimolar quantities of the bidentate phosphine with $(COD)PtI_2$ (COD = 1,5-cyclooctadiene) in CH_2Cl_2 and then precipitating with pentane. [(*R*)-BINAP(PMe_3)PtI][I] was prepared by adding 1 equiv of PMe_3 to ((*R*)-BINAP)PtI_2 in $MeNO_2$ as previously reported.[8] NMR spectra were recorded on either a Bruker 400 MHz DRX or a Bruker 300 MHz AMX spectrometer; chemical shifts are given in ppm and are referenced to residual solvent resonances (^1H, ^{13}C) or an external 85% H_3PO_4 standard (^{31}P). Elemental analysis was performed by Robertson Microlit Labs.

[((*R*)-BINAP)(PMe_3)PtH][BF_4] (1). To a solution of 70 mg of [((*R*)-BINAP)(PMe_3)PtI][I] (61 μmol) in 0.5 mL of $MeNO_2$ was added 126 μL of benzyl alcohol (1.22 mmol) and 30 mg of $AgBF_4$ (152 μmol). The mixture was stirred for 15 min at 23 °C, diluted with CH_2Cl_2, and filtered through a 0.45 μm PTFE syringe filter. The solution was then washed three times with distilled water. The organic fraction was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude material was dissolved in CH_2Cl_2 and precipitated with *n*-pentane five times until no benzyl alcohol remained by ^1H NMR. The purified solid was dried under vacuum to yield 45 mg (64%) of a white solid: ^1H NMR (400 MHz, $CDCl_3$) δ 7.97−6.49 (m, 32H), 1.33 (m, 9H); ^{31}P NMR (161 MHz, $CDCl_3$) δ 28.56 (dd, 1P, J_{P-P} = 21, 352 Hz, $^1J_{P-Pt}$ = 2616 Hz), 17.46 (dd, 1P, J_{P-P} = 20, 21 Hz, $^1J_{P-Pt}$ = 2020 Hz), −17.65 (dd, 1P, J_{P-P} = 20, 352 Hz, $^1J_{P-Pt}$ = 2464 Hz). Anal. Calcd for $C_{47}H_{42}BF_4P_3Pt$: C, 57.51; H, 4.31. Found: C, 57.23; H, 4.12.

[((*rac*)-BINAP)(PMe_3)PtCl][BF_4] (2). Slow vapor diffusion of *n*-pentane to a solution of **1** in $CDCl_3$ yielded X-ray quality crystals of [((*rac*)-BINAP)(PMe_3)PtCl][BF_4].[18]

Platinum−Hydride Cleavage Reactions. In a typical reaction, to 15 mg of [((*R*)-BINAP)(PMe_3)PtH][BF_4] (15.3 μmol) in CD_3NO_2 was added 1 equiv of acid ($HNTf_2$, HBF_4, $[Ph_2NH_2][BF_4]$, or $[Ph_3C][BF_4]$) and 5 equiv of NCC_6F_5 or acetone. Disappearance of the hydride resonance was monitored by ^1H NMR, and the appearance of a new platinum species (either the nitrile or acetone adduct) was observed by ^{31}P NMR.

Acknowledgment. The National Institute of General Medicine (GM-60578) is gratefully acknowledged for support.

Supporting Information Available: X-ray data and tables and NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

OM061105Z

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(18) During crystallization attempts of **1**, the presence of chlorinated solvents (particularly chloroform and dichloromethane) led to the formation of **2**, which selectively crystallized.