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Communications

Reversible Cleavage of the C−H Bond of Aldimine with Platinum Complexes

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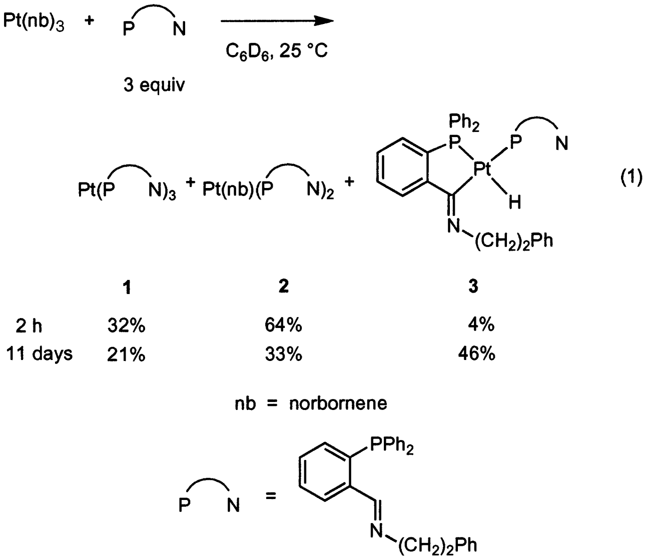
*Summary: The intramolecular oxidative addition of the C−H bond of N-(2-(diphenylphosphino)benzylidene)-2-phenylethylamine (PN) in Pt(PN)$_3$ (**1**) to give cis-Pt[η^2-o-P(Ph)$_2$C$_6$H$_4$C=N(CH$_2$)$_2$Ph](H)(PN) (**3**) proceeded reversibly under mild conditions. The enthalpy and the entropy of the equilibrium between **1** and (**3** + PN) ($\Delta H° = 38.0(8)$ kJ/mol, $\Delta S° = 23.2(6)$ eu) suggested that the oxidative addition of the imine C−H bond to Pt(0) is unfavorable in terms of the enthalpy but is driven by the contribution of the entropy.*

The scission of a C−H bond by transition-metal complexes[1] has received much interest, with oxidative addition of alkyl−H and aryl−H bonds being among the key issues.[2−5] For the cleavage of the C−H bond of aldimine, some examples have been reported in catalytic reactions,[6−9] but only a limited number of reports have been published on stoichiometric reactions.[10−12] According to these reports, for the C−H oxidative addition to occur a heteroatom capable of coordinating to the metal center is necessary in the aldimine molecule. In this paper we report the cleavage of the imine C−H bond of *N*-(2-(diphenylphosphino)benzylidene)-2-phenylethylamine (PN)[13] with a Pt(0) complex under mild conditions. Particularly notable is that the present system provides the rare case where C−H oxidative addition and reductive elimination proceed reversibly, thereby allowing access to thermodynamic and kinetic features of the C−H activation process.



Initially, the reaction of Pt(nb)$_3$ (nb = norbornene) with 3 equiv of PN at 25 °C was performed and monitored by ^{31}P NMR spectroscopy (eq 1). The formation of three complexes was confirmed after 2 h; there were observed two singlets at δ 42.5 ($J_{\mathrm{Pt-P}} = 4395$ Hz) and δ 29.8 ($J_{\mathrm{Pt-P}} = 3537$ Hz) and two doublets centered at δ 20.5 ($J_{\mathrm{Pt-P}} = 1891$ Hz, $J_{\mathrm{P-P}} = 8$ Hz) and δ 47.5 ($J_{\mathrm{Pt-P}} = 2078$ Hz, $J_{\mathrm{P-P}} = 8$ Hz). The first singlet was determined to be due to Pt(PN)$_3$ (**1**) by the elemental analysis of a sample isolated separately[14] and comparison of the ^{31}P NMR spectrum with that of Pt(PPh$_3$)$_3$ (δ 49.9, $J_{\mathrm{Pt-P}} = 4438$ Hz).[15] The second singlet was assumed to be due to Pt(nb)(PN)$_2$ (**2**) by the comparison of the ^{31}P NMR spectrum with that of Pt(nb)(PPh$_3$)$_2$ (δ 33.7, $J_{\mathrm{Pt-P}} = 3550$ Hz).[16] It is also assumed that in **1** and **2** the N atom of PN does not coordinate to platinum. The yields of **1** and **2** (32 and 64% based on platinum) decreased gradually to 21 and 33%, respectively, after 11 days. In contrast, the amount of the complex showing

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[14] The reaction of Pt(COD)$_2$ with PN was used for the isolation of **1** and **3**. This reaction proceeded faster than eq 1 to give **1** (80%) and **3** (20%) in 2 h, but no ^{31}P signal assignable to Pt(COD)(PN)$_x$ ($x = 1, 2$) was observed in the course of the reaction. The complex **1** was obtained by repeated recrystallization from the mixture of Pt(COD)$_2$ and 3 equiv of PN (reaction time 30 min). The complex **3** was obtained by recrystallization from a reaction mixture of Pt(COD)$_2$ and 3 equiv of PN, which had been heated at 60 °C for 24 h. See the Supporting Information for more details.

[15] Sen, A.; Halpern, J. *Inorg. Chem.* **1980**, *19*, 1073.

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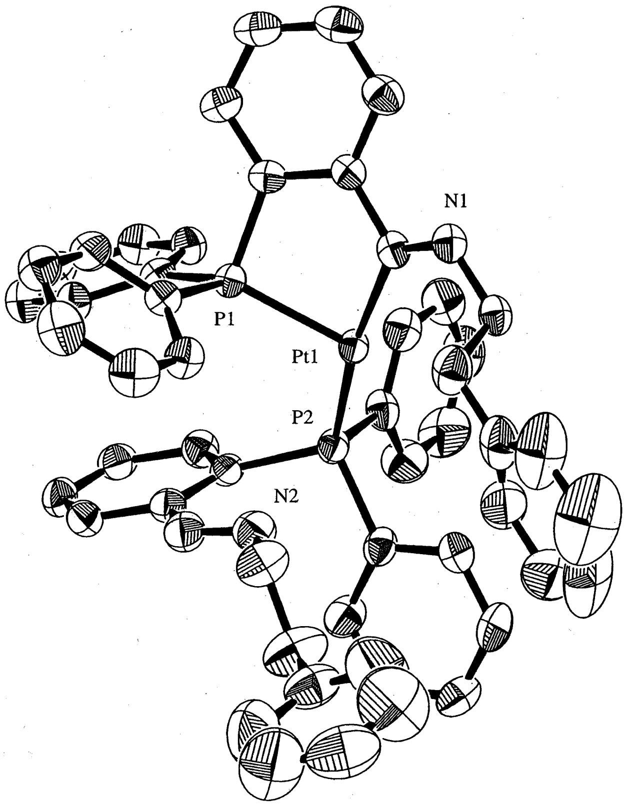
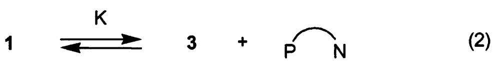


Figure 1. ORTEP diagram of **3**.

the two doublets (4% at 2 h) increased gradually and reached 46% after 11 days. Its ^{1}H NMR spectrum showed a doublet of doublets centered at δ −1.7 with satellites due to coupling to ^{195}Pt (J_{H-P} = 28, 172 Hz, J_{H-Pt} = 1242 Hz), suggesting formation of a Pt−H bond.[17] An analytically pure sample of this complex was isolated[14] and structurally characterized as *cis*-Pt[η^2-*o*-P(Ph)$_2$C$_6$H$_4$C=N(CH$_2$)$_2$Ph](H)(PN) (**3**, ν(Pt−H) 2043 cm^{-1}). A crystal of **3** suitable for X-ray diffraction was obtained after recrystallization from toluene/hexane, and Figure 1 confirmed that the oxidative addition of the imine C−H bond of PN occurred.[18]

When an isolated sample of **1** was dissolved in C$_6$D$_6$, it gradually afforded **3** (50% yield at 25 °C for 2 h) accompanied by the liberation of PN. After 2 days, no further change of the ratio of **1**, **3**, and PN was observed, suggesting that an equilibrium between **1** and (**3** + PN) is attained (eq 2). To confirm the equilibrium, we



monitored the reaction of **3** with 1 equiv of PN at 25 °C by ^{31}P NMR spectroscopy. The formation of **1** was observed in 7% and 28% yields (based on **3**) after 5 h and 8 days, respectively. The equilibrium constant (K) of eq 2 was determined to be $K = 2.2 \times 10^{-2}$ mol/L (25 °C in C$_6$D$_6$).[19] The temperature dependence of the

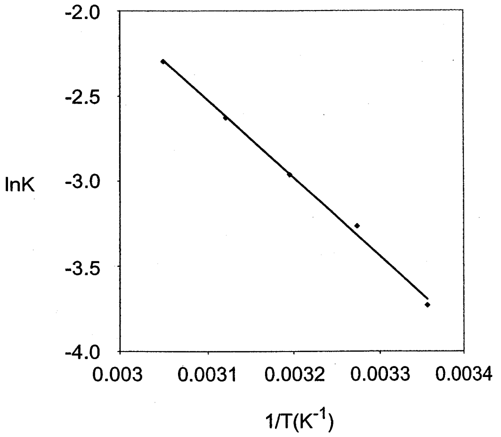
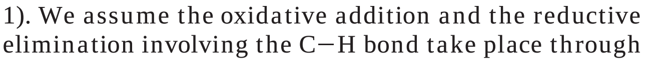


Figure 2. van't Hoff plot for the equilibrium between **1** and (**3** + PN).

equilibrium constant from 25 to 55 °C (Figure 2) allowed the determination of the enthalpy and the entropy as $\Delta H° = 38.0(8)$ kJ/mol and $\Delta S° = 23.2(6)$ eu. Thus, it is evident that the oxidative addition of the imine C−H bond to Pt(0) is unfavorable in terms of the enthalpy[20] but is driven by the contribution of the entropy.

A precise kinetic study on the conversion of **1** into **3** in the presence of added PN was difficult, because the solubility of PN was not sufficiently high to maintain PN concentrations constant during the course of the reaction. Nevertheless, it was found that the initial rate of the disappearance of **1** (2.0×10^{-5} mol/(L·min) without added PN) decreases with the increase of added PN (5.0×10^{-6}, 2.8×10^{-6}, and 1.7×10^{-6} mol/(L·min) at 8.3×10^{-3} mol/L of **1** and 8.3×10^{-3}, 1.7×10^{-2}, and 2.5×10^{-2} mol/L of PN, respectively). This fact suggests that the dissociation of PN from **1** would occur to produce Pt(PN)$_2$ (**4**) before the oxidative addition of the imine C−H bond of PN to Pt(0) takes place.[21,22]

The reaction of **3** with dibenzylideneacetone (dba) resulted in quantitative formation of Pt(dba)(PN)$_2$ (**5**) (eq 3). This reaction obeyed first-order kinetics with



respect to **3**, and the rate constant (3.3×10^{-4} min^{-1}) was independent of the amount of the added dba (0.025−0.10 mol/L, initial concentration of **3** 0.005−0.015 mol/L). This suggests the rate-determining step of eq 3 to be the reductive elimination from **3** to form **4**, followed by rapid quenching by dba to give **5** (Scheme 1). We assume the oxidative addition and the reductive elimination involving the C−H bond take place through a planar transition state, as shown in Chart 1, in accord with a theoretical prediction.[23]

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(17) For comparison, the hydride peak of Pt(H)(Ph)(DPPE) was observed at δ −1.0 (J_{H-P} = 16, 195 Hz, J_{H-Pt} = 1272 Hz): Crespo, M.; Sales, J.; Solans, X.; Altaba, M. F. *J. Chem. Soc., Dalton Trans.* **1988**, 1617.

(18) Crystal data of **3**: space group $P2_1/n$ (No. 14) with a = 9.2410(2) Å, b = 19.6169(4) Å, c = 24.4580(5) Å, β = 96.9851(8)°, Z = 4, ρ = 1.48 g/cm^3, R = 0.032, R_w = 0.060.

(19) The average of three measurements for mixtures containing different concentrations of **1** and PN.

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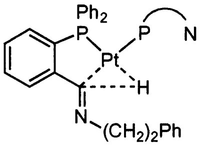
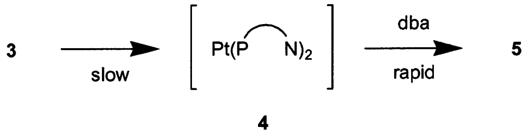
(22) The dependence of the rate of the disappearance of **1** on [PN] may be similar for two kinetic schemes; one involves a rapid preequilibrium for dissociation of PN from **1** to form **4** followed by slow C−H oxidative addition, and the other, steady-state formation of **4**. No discrimination is possible at the moment.

(23) Sakaki, S.; Mizoe, N.; Musashi, Y.; Biswas, B.; Sugimoto, M. *J. Phys. Chem. A* **1998**, *102*, 8027.

Chart 1



Scheme 1



In summary, the oxidative addition of an imine C−H bond to Pt(0) and the reductive elimination from **3** proceeded under mild conditions. Further systematic examinations on the thermodynamics and kinetics of both C−H bond oxidative addition and reductive elimination and catalytic application using **3** are now under way.

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Supporting Information Available: Text, figures, and tables giving experimental procedures, analysis data for the compounds, and X-ray crystal data for **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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