

Intramolecular C–H and C–O Bond Activation of Dimethylplatinum(II) Complexes Having the PN Ligand

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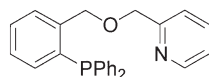
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Reaction of (cod)PtMe₂ with 1 equiv and 2 equiv of the PN ligand (PN = *o*-Ph₂PC₆H₄CH₂OCH₂C₅H₄N-2) (**1**) gave *cis*-(PN-*κ*P:*κ*N)PtMe₂ (**2**) and *cis*-(PN-*κ*P)₂PtMe₂ (**3**) respectively. The complex **2** underwent activation of the benzylic C–H bond in toluene at 110 °C to afford (PCN-*κ*P:*κ*C:*κ*N)PtMe (**4**). Toluene solution of **3** was refluxed for 42 h in the presence of 2 equiv of the PN ligand to afford the C–O bond cleavage product *cis*-(PN-*κ*P)(Ph₂PC₆H₄CH₂-*κ*P:*κ*C)PtMe (*cis*-**5**) along with *cis*-(PN-*κ*P)(PCN-*κ*P:*κ*C)PtMe (*cis*-**6**).

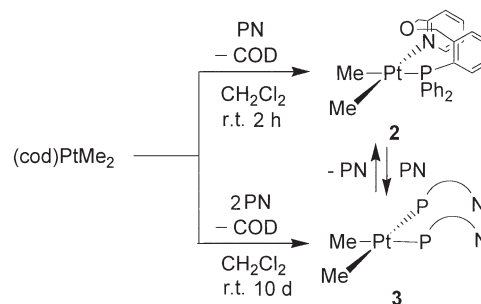
Transition metal coordination chemistry of hemilabile ligands has been an extremely active research area due to their unusual switching functions for supplying an open coordination site at the metal center or closing an unnecessary site under an appropriate condition.¹ Different coordination ability between the coordination atoms of the hemilabile ligands is also important in a stereo-discriminating step in asymmetric reactions; especially some PN chelate ligands are efficiently used as chiral ligands in palladium catalyzed reactions.² We have paid much attention to the hemilabile ligands and prepared a unique hetero-chelate PN hybrid ligand (**1**), which is able to act as a P–N bidentate, a P–O–N tridentate or a P–C–N tridentate ligand.³ Through our iridium chemistry of **1**, the flexibility inherent in the PN ligand is found to play an important role for stabilizing reactive species: we have succeeded in isolations of both Ir(I) and Ir(III) complexes before and after C–H bond activation by employing the PN ligand.^{3a}



PN Ligand (**1**)
Chart 1.

Redox systems between Pt(II) and Pt(IV) have been of interest in recent years, e.g., activation of hydrocarbon at a cationic Pt(II) species and reductive elimination from a Pt(IV) species.⁴ Compared to remarkable results on the C–H bond activation, there are only few examples on Pt-mediated C–O bond activation.⁵ Herein we report the preparation of several Pt(II) complexes having our PN ligand and show not only intramolecular C–H bond activation but also novel C–O bond activation of the Pt(II) complexes.

Reaction of (cod)PtMe₂ with a little excess of PN ligand **1** (1.1 equiv) in CH₂Cl₂ at room temperature for 2 h gave the dimethyl complex, *cis*-(PN-*κ*P:*κ*N)PtMe₂ (**2**), as white powders in 75% isolated yield (Scheme 1). The structure of **2** was fully characterized by elemental analysis as well as spectral data.⁶ The PN ligand acts as a P–N bidentate ligand and coordinates to the Pt

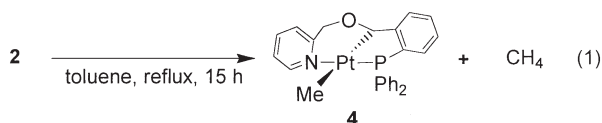


Scheme 1.

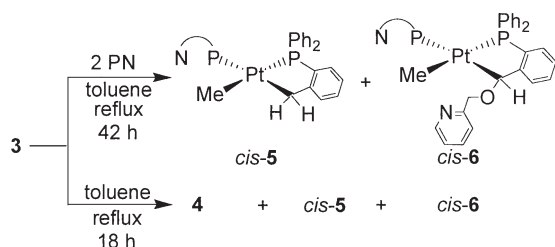
center with the *cis*-configuration. The ³¹P NMR spectrum in CDCl₃ showed a singlet at δ 22.7 with ¹⁹⁵Pt satellites (¹J_{Pt-P} = 1949 Hz), which was typical of a phosphorus atom *cis* to a nitrogen atom in platinum complexes.⁷ The ¹H NMR signal for the proton at the 6-position of the pyridine ring in the PN ligand showed a characteristic shape for that of the *cis*-coordinated PN ligand.^{3b} Reaction of (cod)PtMe₂ with 2 equiv of **1** in CH₂Cl₂ at room temperature for 10 days gave another dimethyl complex, *cis*-(PN-*κ*P)₂PtMe₂ (**3**), as white powders in 83% isolated yield (Scheme 1).⁸ The signal shape of the ¹H NMR for the proton at the 6-position of the pyridine ring in the PN ligand was similar to that of the free PN ligand.^{3b} All spectral data indicated that the complex **3** had the *cis*-configuration, in which the two PN ligands act as a P-coordinated monodentate ligand. The ¹H and ³¹P NMR analyses showed that the complex **3** was stable in toluene at room temperature but above 40 °C dissociated one of the PN ligands easily to give an equilibrium mixture with **2**.

Intramolecular C–H bond activation at the benzylic position of the PN ligand occurred by heating a toluene solution of **2** at 110 °C for 15 h to produce the monomethyl Pt(II) complex, (PCN-*κ*P:*κ*C:*κ*N)PtMe (**4**), as whitish yellow powders in 79% isolated yield (equation 1).⁹ The ³¹P NMR spectrum of **4** showed a singlet at δ 29.9 with ¹⁹⁵Pt satellites (¹J_{Pt-P} = 4400 Hz), which was a typical value for the presence of a weak *trans* donor ligand. The ¹H NMR signal for the proton at the 6-position of the pyridine ring displayed a characteristic shape for that of the *trans*-coordinated PN ligand.^{3b} The ¹H NMR signal of the benzylic proton of the PN ligand at δ 5.62 has Pt satellites, indicating that the benzylic carbon is attached to the platinum metal directly. Only one methyl signal was observed at δ 0.17 with ¹⁹⁵Pt satellites. Generation of CH₄ was confirmed by the ¹H NMR (δ 0.18). All experimental data were consistent with the conclusion that the complex **4** had a square planar geometry and the PN ligand acted as a P–C–N tridentate ligand. From the kinetic studies using ¹H NMR, the activation parameters for the C–H bond activation were determined; at 110 °C ΔG[‡] = 126 kJ/mol, ΔH[‡] = 111 kJ/mol, ΔS[‡] = –39 J/Kmol. The negative activation entropy indicates

that the approach of the benzylic C–H bond to the Pt center is the rate-determining step, which is similar to that obtained in the intramolecular C–H bond activation of $[\text{Ir}(\text{cod})(\text{PN-}\kappa\text{P}:\kappa\text{N})][\text{PF}_6]$.^{3a}



Unexpected C–O bond activation was observed in the reaction of **3**. A toluene solution of **3** was refluxed for 42 h in the presence of 2 equiv of the PN ligand to afford the C–O bond cleavage product, *cis*-(PN- κ P)(Ph₂PC₆H₄CH₂- κ P: κ C)PtMe (*cis*-**5**) in 95% along with *cis*-(PN- κ P)(PCN- κ P: κ C)PtMe (*cis*-**6**) in 5% (Scheme 2).¹⁰ The complex *cis*-**6** was confirmed to be a C–H bond activation product by the separate experiment, in which the reaction of **4** with the PN ligand under reflux conditions afforded *cis*-**6** quantitatively after isomerization of intermediate complex *trans*-(PN- κ P)(PCN- κ P: κ C)PtMe (*trans*-**6**).¹¹ When a similar reaction was conducted in the absence of additional PN ligand, the products derived from the C–H bond activation (**4** and *cis*-**6**) were obtained mainly (**4** : *cis*-**5** : *cis*-**6** = 35 : 36 : 29) (Scheme 2). The structure of *cis*-**5** was fully characterized by elemental analysis as well as spectral data. The ³¹P NMR spectrum displayed one set of two doublet signals (²J_{P-P} = 7.8 Hz) with ¹⁹⁵Pt satellites (¹J_{Pt-P} = 1988 and 1880 Hz), indicating the two phosphorus atoms were coordinated to the Pt with the *cis*-configuration. The ¹³C NMR spectrum displayed two kinds of carbon directly bound to the Pt metal at δ 4.8 for Pt–CH₃ and 38.0 for the benzyl carbon. In the ¹H NMR spectrum, two kinds of benzylic protons with equal intensity (2H) appear; one is a singlet signal at δ 5.24 and another one is a doublet signal at δ 3.90 with ¹⁹⁵Pt satellites. These spectra indicate that the cleavage of the C(benzyl)–O bond in only one of the two PN ligands in **3** resulted in the formation of the Pt–C bond.¹²



Scheme 2.

The C–H bond activation would proceed through a 14-electron species such as (PN- κ P)PtMe₂ after dissociation of the nitrogen donor from **2** or the PN ligand from **3**.^{4a} The fact that the C–H bond activation of **3** in the presence of the PN ligand was suppressed compared to that in the absence of the ligand strongly suggests that the formation of the 14-electron species is an important step for the C–H bond activation. On the contrary, the intramolecular C–O bond of **3** has been accelerated by addition of excess ligands; the fact is inconsistent with the presence of the 14-electron species. Prof. Komiya reported the C–O bond cleavage via β -aryloxy elimination from an aryloxyethylplatinum(II) complex and suggested an associative mechanism involving a five-coordinated intermediate.^{5a} Our system also has a possibility that contains a similar five-coordinated intermediate such as (PN-

κ P)₃PtMe₂, but at present we could not observe the evidence in the NMR analyses.

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- 2**: IR (KBr tablet): 1604 cm⁻¹ ($\nu_{\text{C=N}}$). ¹H NMR (CDCl₃): δ 8.57–8.70 (m, 1H), 6.35–8.10 (m, 17H), 5.77 (d, ²J_{H-H} = 11.8 Hz, 1H), 5.46 (d, ²J_{H-H} = 11.5 Hz, 1H), 4.63 (d, ²J_{H-H} = 11.8 Hz, 1H), 4.22 (d, ²J_{H-H} = 11.8 Hz, 1H), 0.88 (d, ²J_{Pt-H} = 94.8 Hz, ³J_{P-H} = 7.4 Hz, 3H), 0.41 (d, ²J_{Pt-H} = 77.2 Hz, ³J_{P-H} = 7.4 Hz, 3H). ³¹P{¹H} NMR (CDCl₃): δ 22.7 (s, ¹J_{Pt-P} = 1949 Hz). Found: C, 53.01; H, 4.42; N, 2.39%; Calcd for C₂₇H₂₈NOPPt: C, 53.29; H, 4.64; N, 2.30%.
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- 3**: IR (KBr tablet): 1590, 1571 cm⁻¹ ($\nu_{\text{C=N}}$). ¹H NMR (CDCl₃): δ 8.36–8.50 (m, 2H), 6.80–7.95 (m, 34H), 4.85 (s, 4H), 4.41 (s, 4H), 0.41 (dd, ²J_{Pt-H} = 69.8 Hz, ³J_{P-H} = 8.5 Hz, 8.2 Hz, 6H). ³¹P{¹H} NMR (CDCl₃): δ 24.2 (s, ¹J_{Pt-P} = 1818 Hz). FABMS: *m/z* 994 (M⁺+2), 977 (M⁺-Me), 962 (M⁺-2Me).
- 4**: IR (KBr tablet): 1605 cm⁻¹ ($\nu_{\text{C=N}}$). ¹H NMR (CDCl₃): δ 8.88–9.06 (m, ³J_{Pt-H} = 35.2 Hz, 1H), 6.85–8.00 (m, 17H), 5.62 (s, ²J_{Pt-H} = 73.1 Hz, 1H), 4.93 (d, ²J_{H-H} = 12.4 Hz, 1H), 4.67 (d, ²J_{H-H} = 12.6 Hz, 1H), 0.17 (d, ²J_{Pt-H} = 45.9 Hz, ³J_{P-H} = 1.9 Hz, 3H). ³¹P{¹H} NMR (CDCl₃): δ 29.9 (s, ¹J_{Pt-P} = 4400 Hz). Found: C, 52.66; H, 4.00; N, 2.34%; Calcd for C₂₆H₂₄NOPPt: C, 52.70; H, 4.08; N, 2.36%.
- cis*-**5**: IR (KBr tablet): 1590, 1571 cm⁻¹ ($\nu_{\text{C=N}}$). ¹H NMR (C₆D₆): δ 8.36–8.48 (m, 1H), 6.55–8.05 (m, 31H), 5.24 (s, 2H), 4.40 (s, 2H), 3.90 (d, ²J_{Pt-H} = 78.4 Hz, ³J_{P-H} = 9.1 Hz, 2H), 1.02 (dd, ²J_{Pt-H} = 67.3 Hz, ³J_{P-H} = 8.5 Hz, 8.2 Hz, 3H). ³¹P{¹H} NMR (C₆D₆): δ 44.6 (d, ¹J_{Pt-P} = 1988 Hz, ²J_{P-P} = 7.8 Hz, 1P), 24.1 (d, ¹J_{Pt-P} = 1880 Hz, ²J_{P-P} = 7.8 Hz, 1P). Found: C, 62.21; H, 4.76; N, 1.61%; Calcd for C₄₅H₄₁NOP₂Pt: C, 62.16; H, 4.70; N, 1.57%.
- cis*-**6**: ³¹P{¹H} NMR (C₆D₆): δ 47.3 (d, ¹J_{Pt-P} = 2030 Hz, ²J_{P-P} = 5.6 Hz, 1P), 22.5 (d, ¹J_{Pt-P} = 1678 Hz, ²J_{P-P} = 5.6 Hz, 1P). *trans*-**6**: ³¹P{¹H} NMR (C₆D₆): δ 47.6 (d, ¹J_{Pt-P} = 3343 Hz, ²J_{P-P} = 440 Hz, 1P), 26.8 (d, ¹J_{Pt-P} = 3062 Hz, ²J_{P-P} = 440 Hz, 1P).
- Generation of 2-pyridylmethanol and CH₄ was confirmed by the GCMS and the ¹H NMR respectively.