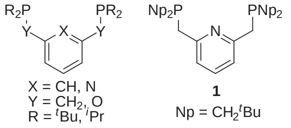
Neopentyl-substituted PNP-pincer Ligand: Complexation with Iridium to Form an Iridacycle via Alkyl C–H Activation

Toshiyuki Yano, Yoshiki Moroe, Makoto Yamashita,* and Kyoko Nozaki*
Department of Chemistry and Biotechnology, Graduate School of Engineering, The University of Tokyo,
7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656

(Received August 7, 2008; CL-080767; E-mail: makotoy@chembio.t.u-tokyo.ac.jp, nozaki@chembio.t.u-tokyo.ac.jp)

A new PNP-pincer ligand **1** bearing neopentyl substituents reacted with $[Ir(cod)_2]BF_4$ to form hydridoiridacycle **3** via oxidative addition of a C–H bond of a neopentyl group to Ir^I. Addition of π-acceptor ligands induced C–H reductive elimination to form cationic iridium(I) complexes **5** ligated by the π-acceptor ligand. Although **3** did not give a benzene adduct, reaction of **3** with nitrobenzene or acetophenone afforded the C–H activated **7a** or **8a**.

Recent advances in the chemistry of late-transition-metal complexes ligated by phosphine-based pincer ligands provide a wide variety of interesting reactivities.[1] Among them, some iridium complexes have been reported to react with alkane[2] and benzene.[3,4] Recent studies on the reaction of pincer-ligated Ir complexes with benzene[3,4] concluded that a facile formation of a low-coordinate Ir^I center, which has been originally suggested as an intermediate in alkane dehydrogenetion,[5] is a key step to give aryliridium(III) hydride complexes via C–H oxidative addition. So far, substituents of phosphine-based pincer ligands on iridium complexes, which can activate C–H bonds of hydrocarbons, are limited to *t*-Bu or *i*-Pr groups as described in Figure 1.[6] Since it was reported that *i*-Pr-substituted pincer ligand exhibited higher activity than *t*-Bu-substituted one in the Ir-catalyzed dehydrogenation of alkanes,[2i] the modification of the R groups in pincer ligand is expected to induce significant changes on the catalytic activity of their complexes. Such assumption prompted us to introduce neopentyl (Np) groups as R. The neopentyl groups have sufficient bulkiness to generate a low-coordinate iridium complex and less bulky methylene chains around the central iridium to keep a large space. Herein, we report synthesis of a new PNP-pincer ligand **1** possessing neopentyl groups on the phosphorus atoms, its complexation with iridium to form an iridacycle **3**, and oxidative addition of a C–H bond of arene rings to **3**.

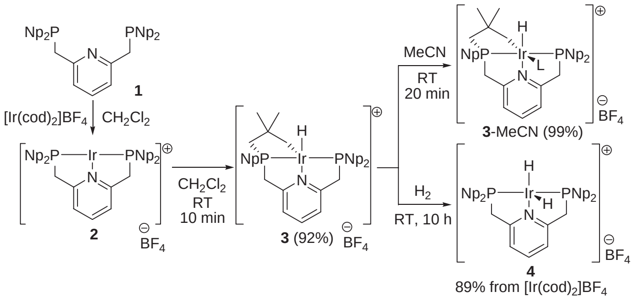


X = CH, N
Y = CH_2, O
R = ^tBu, ^iPr

1
Np = $CH_2{}^tBu$

Figure 1. PXP-pincer ligand.

A neopentyl-substituted PNP-pincer ligand **1**, which could be prepared in an analogous manner to *t*-Bu-substituted PNP ligand[7] (see Supporting Information),[8] reacted with cationic iridium complex $[Ir(cod)_2]BF_4$ in CH_2Cl_2 to afford the corresponding hydridoiridacycle **3** (Scheme 1). The formation of **3** should result from a facile intramolecular oxidative addition of a C–H bond of one of the methyl groups of neopentyl substituents in a reactive T-shape complex **2** generated by a ligand exchange.[9]



Scheme 1. Synthesis and reactions of **3**.

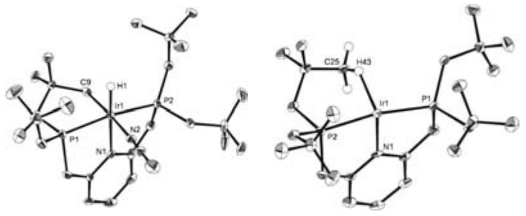
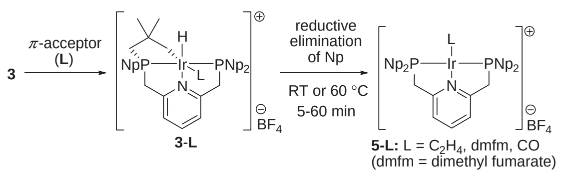


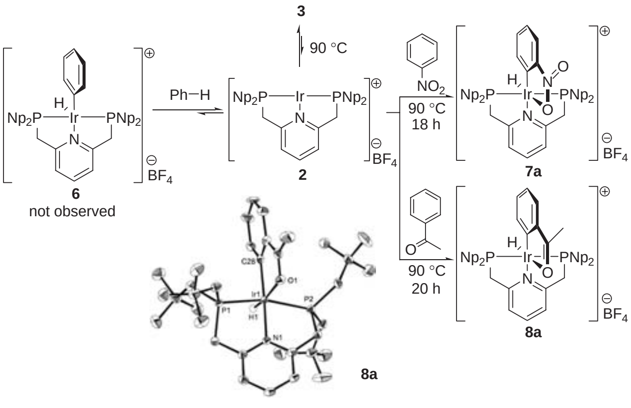
Figure 2. ORTEP drawings of **3**–MeCN (left) and **4** (right) with 50% thermal ellipsoids (hydrogen atoms except hydrido ligand in **3**–MeCN, agostic methyl group in **4**, and anionic parts are omitted for clarity).

The ^{31}P NMR spectrum of **3** showed two doublets with a coupling constant of $^2J_{PP} = 314$ Hz which indicates trans configuration of two phosphorus atoms.[4] In the ^1H NMR spectrum of **3**, a triplet signal of the hydride located trans to the pyridine nitrogen atom resonated at δ -16.87 with a coupling of $^2J_{PH} = 12$ Hz to two nearly equivalent phosphorus atoms. The H–H COSY experiments revealed three distinct neopentyl groups, one C–H activated neopentyl group, two AB quartets of methylene protons connected to a pyridine ring, and an unsymmetrical pyridine ring in **3**. The cyclic structure of **3** was further confirmed by addition of MeCN to form six-coordinate **3**–MeCN using X-ray crystallography (Figure 2, left). On the other hand, a reaction of **3** with dihydrogen afforded the corresponding cationic dihyride complex **4**[10] (Figure 2, right) accompanied by a reproduction of the neopentyl group.

In the crystal of **3**–MeCN, the central iridium atom has typical octahedral geometry with a cis relationship between the activated neopentyl group having a C9–Ir1 bond of 2.114(6) Å and hydride ligand. The pyridine ring was slightly twisted from the PNP–Ir plane to abate the metallacyclic strain. In **4**, C25–Ir1 distances in **4** (2.729 and 2.828 Å) are longer than the covalent C–Ir bond in **3**–MeCN, indicating the existence of C–H agostic interaction between a methyl C–H bond and the cationic iridium(III) center. Although the two hydrido ligands could not be assigned by Fourier map, the ^1H NMR spectrum showed two dd signals in the hydride region. They may be located cis and



Scheme 2. Reaction of **3** with π-acceptor molecules.



Scheme 3. Reaction of **3** with aromatic compounds (bottom: ORTEP drawing of **8a** with 50% thermal ellipsoids).

trans to the nitrogen atom to form an octahedral geometry with the C–H agostic interaction of C25–H43.

A reductive elimination of a neopentyl group induced by π-acceptor ligand was examined to generate a coordinatively unsaturated iridium(I) complex (Scheme 2). Addition of excess ethylene, dimethyl fumarate, or carbon monoxide to **3** led to reductive elimination of a neopentyl group to form the cationic complexes **5**–L.[11] In a reaction with carbon monoxide, neopentyl-activated π-acceptor complex **3**–CO has been detected by ^{1}H and ^{31}P NMR spectroscopy as a reaction intermediate. All the resulting complexes **5**–L could be considered as 16-electron square-planar iridium(I) species. In the crystal of **5**–C_2H_4 (see Supporting Information), no apparent C–H agostic interaction from a neopentyl group to the central iridium atom was observed in contrast to the case of dihydridoiridium(III) complex **4**.

Heating **3** in benzene did not afford the corresponding phenyl(hydrido)iridium complex **6** (Scheme 3), although there is a possible formation of T-shape intermediate **2** in equilibrium with **3**. This result is in contrast to that [(*t*-Bu)PNP–Ir(coe)]PF_6 provided [(*t*-Bu)PNP–Ir(H)(Ph)]PF_6 via activation of the C–H bond of benzene at 60 °C.[12] However, the reaction of **3** with nitrobenzene or acetophenone at 90 °C afforded C–H activated complexes **7a** and **8a** with intramolecular coordination of a nitro or an acetyl group to the central iridium, with the aryl rings being located trans to the nitrogen atom.[13] The difference in reactivity of **3** with benzene or nitrobenzene/acetophenone may be explained by the order of thermal stabilities from the most stable **7a** or **8a** > **3** > **6** (See Supporting Information for further discussion). Thus, the iridacycle **3** can be considered as an equivalent to the T-shape intermediate **2**.

In conclusion, a neopentyl-substituted PNP-pincer ligand **1** reacted with [Ir(cod)$_2$]BF_4 to form hydridoiridacycle **3** via C–H activation of a neopentyl group. Addition of π-acceptor ligand induced C–H reductive elimination of a neopentyl group. Although **3** did not give a benzene adduct, reaction of **3** with nitrobenzene or acetophenone afforded the C–H activated complexes **7a** or **8a**. Further reactivity of iridacycle **3** is under investigation.

This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas (No. 17065005, "Advanced Molecular Transformations of Carbon Resources" and No. 19028011, "Chemistry of Concerto Catalysis") from MEXT, Japan.

Dedicated to Professor Ryoji Noyori on the occasion of his 70th birthday.

References and Notes

1 a) M. E. van der Boom, D. Milstein, *Chem. Rev.* **2003**, *103*, 1759. b) *The Chemistry of Pincer Compounds*, Elsevier, Oxford, **2007**.

2 a) M. Gupta, C. Hagen, R. J. Flesher, W. C. Kaska, C. M. Jensen, *Chem. Commun.* **1996**, 2083. b) M. Gupta, C. Hagen, W. C. Kaska, R. E. Cramer, C. M. Jensen, *J. Am. Chem. Soc.* **1997**, *119*, 840. c) M. Gupta, W. C. Kaska, C. M. Jensen, *Chem. Commun.* **1997**, 461. d) W.-W. Xu, G. P. Rosini, K. Krogh-Jespersen, A. S. Goldman, M. Gupta, C. M. Jensen, W. C. Kaska, *Chem. Commun.* **1997**, 2273. e) C. M. Jensen, *Chem. Commun.* **1999**, 2443. f) F. Liu, E. B. Pak, B. Singh, C. M. Jensen, A. S. Goldman, *J. Am. Chem. Soc.* **1999**, *121*, 4086. g) D. Morales-Morales, D. W. Lee, Z. Wang, C. M. Jensen, *Organometallics* **2001**, *20*, 1144. h) M. W. Haenel, S. Oevers, K. Angermund, W. C. Kaska, H. J. Fan, M. B. Hall, *Angew. Chem., Int. Ed.* **2001**, *40*, 3596. i) F. Liu, A. S. Goldman, *Chem. Commun.* **1999**, 655. j) K. Krogh-Jespersen, M. Czerw, M. Kanzelberger, A. S. Goldman, *J. Chem. Inf. Comput. Sci.* **2001**, *41*, 56. k) K. Krogh-Jespersen, M. Czerw, A. S. Goldman, *J. Mol. Catal. A: Chem.* **2002**, *189*, 95. l) K. Krogh-Jespersen, M. Czerw, N. Summa, K. B. Renkema, P. D. Achord, A. S. Goldman, *J. Am. Chem. Soc.* **2002**, *124*, 11404. m) S. Niu, M. B. Hall, *J. Am. Chem. Soc.* **1999**, *121*, 3992. n) S. Li, M. B. Hall, *Organometallics* **2001**, *20*, 2153. o) K. B. Renkema, Y. V. Kissin, A. S. Goldman, *J. Am. Chem. Soc.* **2003**, *125*, 7770. p) I. Göttker-Schnetmann, M. Brookhart, *J. Am. Chem. Soc.* **2004**, *126*, 9330. q) I. Göttker-Schnetmann, P. White, M. Brookhart, *J. Am. Chem. Soc.* **2004**, *126*, 1804. r) I. Göttker-Schnetmann, P. S. White, M. Brookhart, *Organometallics* **2004**, *23*, 1766. s) K. Zhu, P. D. Achord, X. Zhang, K. Krogh-Jespersen, A. S. Goldman, *J. Am. Chem. Soc.* **2004**, *126*, 13044. t) A. S. Goldman, A. H. Roy, Z. Huang, R. Ahuja, W. Schinski, M. Brookhart, *Science* **2006**, *312*, 257.

3 a) M. Kanzelberger, B. Singh, M. Czerw, K. Krogh-Jespersen, A. S. Goldman, *J. Am. Chem. Soc.* **2000**, *122*, 11017. b) E. Ben-Ari, M. Gandelman, H. Rozenberg, L. J. W. Shimon, D. Milstein, *J. Am. Chem. Soc.* **2003**, *125*, 4714. c) E. Ben-Ari, R. Cohen, M. Gandelman, L. J. W. Shimon, J. M. L. Martin, D. Milstein, *Organometallics* **2006**, *25*, 3190.

4 E. Ben-Ari, G. Leitus, L. J. W. Shimon, D. Milstein, *J. Am. Chem. Soc.* **2006**, *128*, 15390.

5 D. W. Lee, W. C. Kaska, C. M. Jensen, *Organometallics* **1998**, *17*, 1.

6 In chapter 19 of ref 1b, W. D. Jones commented "*The variability in the ligand structure is immense*."

7 M. Kawatsura, J. F. Hartwig, *Organometallics* **2001**, *20*, 1960.

8 Supporting Information for all the experimental procedure and spectral data is available free of charge on the web at http://www.csj.jp/journals/chem-lett/.

9 Relatively slower C–H activations of a *tert*-butyl group on the phosphorus atom of phosphine-based pincer iridium complex have been reported. See: a) W. Weng, C. Guo, C. Moura, L. Yang, B. M. Foxman, O. V. Ozerov, *Organometallics* **2005**, *24*, 3487. b) H. A. Y. Mohammad, J. C. Grimm, K. Eichele, H.-G. Mack, B. Speiser, F. Novak, M. G. Quintanilla, W. C. Kaska, H. A. Mayer, *Organometallics* **2002**, *21*, 5775. Similar C–H activations of alkyl chains of pincer ligand for Rh and Ru complexes have also been reported. See: c) S. Nemeh, C. Jensen, E. Binamira-Soriaga, W. C. Kaska, *Organometallics* **1983**, *2*, 1442. d) A. Walstrom, M. Pink, N. P. Tsvetkov, H. Fan, M. Ingleson, K. G. Caulton, *J. Am. Chem. Soc.* **2005**, *127*, 16780.

10 The complex **4** was characterized as dihydride complex according to their high-field shifted hydride signal (δ −23.2, $^2J_{PH} = 13.7$ Hz) similar to that of previously reported [(*t*-Bu)PNP–IrH_2]PF_6 complex (δ −28.7, $^2J_{PH} = 12.5$ Hz). See: S. M. Kloek, D. M. Heinekey, K. I. Goldberg, *Organometallics* **2006**, *25*, 3007.

11 Similar reductive elimination of dihydrogen molecule from pincer-ligated iridium complex induced by an addition of carbon monoxide. See: ref 10.

12 The difference between **3** and [(*t*-Bu)PNP–Ir(coe)]PF_6 could be explained as follows: (1) Formation of iridacycle to give iridium(III) could stabilize the complex **3** more efficiently than a coordination of COE ligand to [(*t*-Bu)PNP–Ir]$^+$ core. (2) Loss of COE ligand from [(*t*-Bu)PNP–Ir(coe)]PF_6 led to entropy gain to stabilize the phenyl(hydride)iridium complex.

13 Complexes **7a** and **8a** may be a thermodynamically stable isomer, which could be isomerized from the other intermediate formed via nonchelation-assisted mechanism as Goldman et al. have reported on *t*-Bu-substituted PCP iridium system. See: X. Zhang, M. Kanzelberger, T. J. Emge, A. S. Goldman, *J. Am. Chem. Soc.* **2004**, *126*, 13192. Mechanism for the formation of **7a** and **8a** is still unclear; however, dissociative mechanism via T-shape intermediate **2** may be the most reasonable mechanism. Associative pathway by a coordination of acetyl or nitro group to the metal center may be ruled out because these groups should not be considered as π acid to accelerate reductive elimination.

Published on the web (Advance View) December 5, 2008; doi:10.1246/cl.2008.1300