

Synthesis and Properties of a Rhodium Complex Having a Novel β -Ketophosphenato Ligand, a Heavier Congener of a β -Ketoiminato Ligand[#]

Takahiro Sasamori, Teruyuki Matsumoto, Nobuhiro Takeda,[†] and Norihiro Tokitoh*

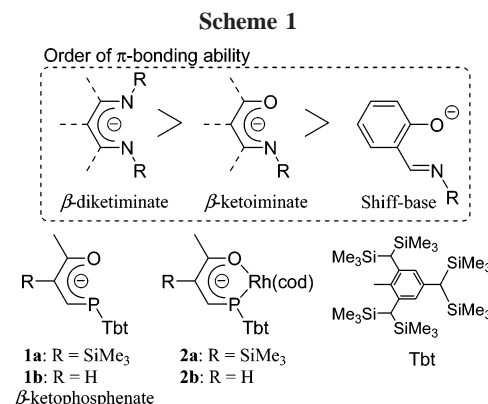
Institute for Chemical Research, Kyoto University, Gokasho, Uji, Kyoto 611-0011, Japan

Received April 28, 2007

Summary: The first stable rhodium complex having a β -keto-phosphenato ligand, which is a heavier congener of a β -ketoiminato ligand, has been synthesized and characterized. Comparison of properties between rhodium β -ketophosphenates **2** and rhodium β -ketoiminato **4** revealed the unique character of the β -ketophosphenato ligand, where the trans influence of the phosphorus atom should be stronger than the nitrogen atom of the β -ketoiminato ligand.

The coordination chemistry of β -diketiminato and β -ketoiminato ligands has attracted much interest especially in the field of olefin polymerization based on late transition metals.^{1,2} The principal advantage of β -diketiminato and β -ketoiminato ligands can be summarized as follows: (i) facile preparation, (ii) strong coordination ability to the transition metal center as a monovalent and bidentate ligand, and (iii) steric effect afforded by the substituent on the nitrogen atom(s). Particularly, a β -ketoiminato ligand features unique properties due to its moderate coordination ability toward a transition metal center lying between β -diketiminato (stronger) and Schiff base (weaker) ligands to the same metal center (Scheme 1) and its unsymmetrical trans effect based on the difference of the coordinating atoms (N and O).²

On the other hand, the coordination chemistry of phosphalkenes, which are heavier analogues of imines, has drawn a great deal of recent attention due to their unique electronic properties of the C=P double bond, whose characteristic low-lying π^* -orbital makes it possible to work as a good π -acceptor toward a transition metal center.³ However, it is difficult to isolate and handle such a low-coordinated phosphorus compound, since it is well-known that a double bond containing a heavier atom such as a P=C double bond is highly reactive to undergo facile oxidation, hydrolysis, and self-oligomerization. Since the first isolation of a stable phosphalkene (Bickelhaupt et al.),⁴ a disilene (West et al.),⁵ and a diphosphene (Yoshifuji et al.),⁶



etc., around 1980, the idea of kinetic stabilization afforded by bulky substituents has been proven to be very effective for the construction of doubly bonded systems containing (a) heavier atom(s).⁷ We have also reported the synthesis of a variety of unique low-coordinated species of main group elements, particularly a series of doubly bonded systems between heavier group 15 elements, ArE=EAR (E = P, Sb, Bi), as stable compounds by taking advantage of our original steric protection groups, Tbt and Bbt, and revealed their unique properties.^{8,9}

Recently, we have reported the application of a Tbt group toward the synthesis of an overcrowded β -diketiminato ligand

(7) It has been demonstrated that heavier main group elements can form a stable double-bond compound when they are appropriately protected by bulky substituents. For reviews, see: (a) Weber, L. *Chem. Rev.* **1992**, *92*, 1839–1906. (b) Power, P. P. *Chem. Rev.* **1999**, *99*, 3463–3503. (c) Tokitoh, N.; Okazaki, R. *Coord. Chem. Rev.* **2000**, *210*, 251–277.

(8) 2,4,6-Tris[bis(trimethylsilyl)methyl]phenyl and 2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl are denoted as Tbt and Bbt, respectively.

(9) (a) Tokitoh, N.; Arai, Y.; Okazaki, R.; Nagase, S. *Science* **1997**, *277*, 78–80. (b) Tokitoh, N.; Arai, Y.; Sasamori, T.; Okazaki, R.; Nagase, S.; Uekusa, H.; Ohashi, Y. *J. Am. Chem. Soc.* **1998**, *120*, 433–434. (c) Sasamori, T.; Arai, Y.; Takeda, N.; Okazaki, R.; Furukawa, Y.; Kimura, M.; Nagase, S.; Tokitoh, N. *Bull. Chem. Soc. Jpn.* **2002**, *75*, 661–675. (d) Sasamori, T.; Arai, Y.; Takeda, N.; Okazaki, R.; Furukawa, Y.; Kimura, M.; Nagase, S.; Tokitoh, N. *Bull. Chem. Soc. Jpn.* **2002**, *75*, 661–675. (e) Sasamori, T.; Takeda, N.; Fujio, M.; Kimura, M.; Nagase, S.; Tokitoh, N. *Angew. Chem., Int. Ed.* **2002**, *41*, 139–141. (f) Sasamori, T.; Takeda, N.; Tokitoh, N. *Chem. Commun.* **2000**, 1353–1354. (g) Sasamori, T.; Takeda, N.; Tokitoh, N. *J. Phys. Org. Chem.* **2003**, *16*, 450–462. (h) Nagahora, N.; Sasamori, T.; Takeda, N.; Tokitoh, N. *Chem.-Eur. J.* **2004**, *10*, 6146–6151. (i) Sasamori, T.; Mieda, E.; Nagahora, N.; Takeda, N.; Takagi, N.; Nagase, S.; Tokitoh, N. *Chem. Lett.* **2005**, *34*, 166–167. (j) Sasamori, T.; Tsurusaki, A.; Nagahora, N.; Matsuda, K.; Kanemitsu, Y.; Watanabe, Y.; Furukawa, Y.; Tokitoh, N. *Chem. Lett.* **2006**, *35*, 1382–1383. (k) Nagahora, N.; Sasamori, T.; Tokitoh, N. *Chem. Lett.* **2006**, *35*, 220–221. (l) Sasamori, T.; Mieda, E.; Nagahora, N.; Sato, K.; Shiomi, D.; Takui, T.; Hosoi, Y.; Furukawa, Y.; Takagi, N.; Nagase, S.; Tokitoh, N. *J. Am. Chem. Soc.* **2006**, *128*, 12582–12588. For reviews, see: (m) Tokitoh, N. *Acc. Chem. Res.* **2004**, *37*, 86–94. (n) Okazaki, R.; Tokitoh, N. *Acc. Chem. Res.* **2000**, *33*, 625–630. (o) Tokitoh, N.; Okazaki, R. *Coord. Chem. Rev.* **2000**, *210*, 251–277.

[#] Dedicated to the late Prof. Yoshihiko Itoh.

* To whom correspondence should be addressed. Phone: +81-774-38-3200. Fax: +81-774-38-3209. E-mail: tokitoh@boc.kuicr.kyoto-u.ac.jp.

[†] Present address: Department of Chemistry and Chemical Biology, Graduate School of Engineering, Gunma University, 1-5-1, Tenjin-cho, Kiryu, Gunma 376-8515, Japan.

(1) Bourget-Merle, L.; Lappert, M. F.; Severn, J. R. *Chem. Rev.* **2002**, *102*, 3031–3065.

(2) (a) Li, X. F.; Dai, K.; Ye, W. P.; Pan, L.; Li, Y. S. *Organometallics* **2004**, *23*, 1223–1230. (b) Zhang, D.; Jin, G. X.; Weng, L. H.; Wang, F. S. *Organometallics* **2004**, *23*, 3270–3275. (c) Liu, B. Y.; Tian, C. Y.; Zhang, L.; Yan, W. D.; Zhang, W. J. *J. Polym. Sci. Polym. Chem.* **2006**, *44*, 6243–6251.

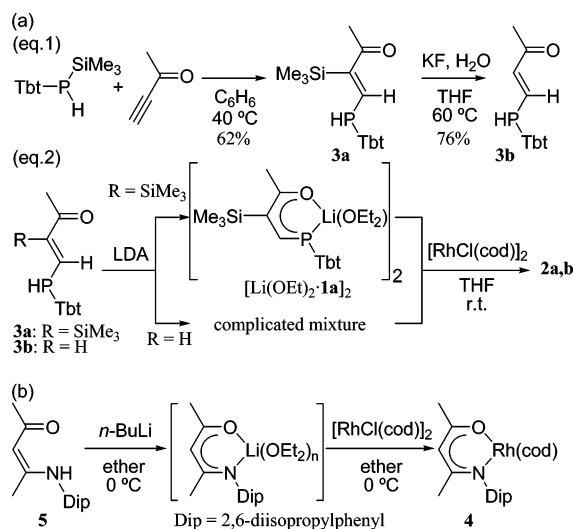
(3) (a) For a review, see: Floch, P. L. *Coord. Chem. Rev.* **2006**, *250*, 627–681. (b) Ozawa, F.; Kawagishi, S.; Ishiyama, T.; Yoshifuji, M. *Organometallics* **2004**, *23*, 1325–1332.

(4) Klebach, T. C.; Lourens, R.; Bickelhaupt, F. *J. Am. Chem. Soc.* **1978**, *100*, 4886–4888.

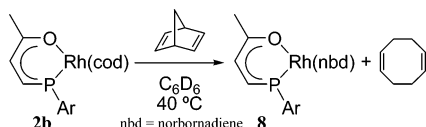
(5) West, R.; Fink, M. J.; Michl, J. *Science* **1981**, *214*, 1343–1344.

(6) Yoshifuji, M.; Shima, I.; Inamoto, N.; Hirotsu, K.; Higuchi, T. *J. Am. Chem. Soc.* **1981**, *103*, 4587–4589.

Scheme 2



Scheme 3



and its group 4 metal complexes.¹⁰ During the course of our investigations on the low-coordinated species of heavier group 15 elements and the extremely bulky β -diketiminato ligand, we designed novel β -ketophosphenato ligands **1**, which have features of both β -ketoiminato and low-coordinated phosphorus ligands.^{11,12} We report here the synthesis and properties of stable rhodium-cod β -ketophosphenates **2** as touchstones for the elucidation of the properties of β -ketophosphenato ligands **1a,b**.

Precursors **3a,b** were synthesized as shown in Scheme 2 [(a), eq 1].¹³ Deprotonation reaction of **3a** with LDA in THF afforded lithium β -ketophosphenate $[\text{Li}(\text{OEt}_2) \cdot \text{1a}]$, which was characterized by spectroscopic and X-ray crystallographic analyses.¹⁴ It was found that the C=C moiety of **3a** rotated to form a cyclic structure with the central lithium atom coordinated by P and O atoms through lithiation. The reaction of $[\text{Li}(\text{OEt}_2) \cdot \text{1a}]$ with $[\text{RhCl}(\text{cod})]_2$ resulted in the formation of rhodium β -ketophosphenate **2a** in 98% yield [Scheme 2 (a), eq 2]. In contrast to the case of lithiation of **3a**, the reaction of **3b** with LDA under the same conditions afforded a complicated mixture, as judged by the ¹H and ³¹P NMR spectra. Although the purification and identification of the resulting products were unsuccessful, the addition of $[\text{RhCl}(\text{cod})]_2$ to the reaction mixture in situ gave

(10) (a) Hamaki, H.; Takeda, N.; Tokitoh, N. *Inorg. Chem.* **2007**, *46*, 1795–1802. (b) Hamaki, H.; Takeda, N.; Yamasaki, T.; Sasamori, T.; Tokitoh, N. *J. Organomet. Chem.* **2007**, *692*, 44–54. (c) Hamaki, H.; Takeda, N.; Tokitoh, N. *Organometallics* **2006**, *25*, 2457–2464. (d) Takeda, N.; Hamaki, H.; Tokitoh, N. *Chem. Lett.* **2004**, *33*, 134–135.

(11) Although there have been a few reports on the theoretical calculations for a phosphorus analogue of a Schiff base ligand from the viewpoint of catalytic activities, no example of such a unique ligand has been synthesized so far. See: (a) Chan, M. S. W.; Deng, L. Q.; Ziegler, T. *Organometallics* **2000**, *19*, 2741–2750. (b) Zhang, T. Z.; Guo, D. W.; Jie, S. Y.; Sun, W. H.; Li, T.; Yang, X. Z. *J. Polym. Sci. Polym. Chem.* **2004**, *42*, 4765–4774.

(12) The intermediacy of a β -iminophosphenato complex, which is a phosphorus analogue of a β -diketiminato complex, was proposed to be generated; see: Basuli, F.; Tomaszewski, J.; Huffman, J. C.; Mindiola, D. J. *J. Am. Chem. Soc.* **2003**, *125*, 10170–10171.

(13) The 1,2-addition reaction of a silylphosphine with an alkyne has been reported; see ref 11b.

(14) The experimental procedures and spectral data for the newly obtained compounds are shown in the Supporting Information.

Table 1. Observed and Calculated Structural Parameters for **2b**, **4**, **6**, and **7**

bond lengths/Å	observed		calculated ^a		
	2b	4	6	2b	7
Rh–E	2.2404(8)	2.098(1)	2.300	2.332	2.136
E–C ₁	1.698(3)	1.325(2)	1.723	1.708	1.331
C ₁ –C ₂	1.396(5)	1.419(3)	1.398	1.405	1.416
C ₂ –C ₃	1.387(5)	1.372(3)	1.409	1.398	1.393
C ₃ –O ₁	1.278(4)	1.289(2)	1.280	1.286	1.281
O ₁ –Rh	2.043(2)	2.040(1)	2.095	2.089	2.064
Rh–C ₄	2.108(3)	2.116(2)	2.152	2.146	2.167
Rh–C ₄ '	2.119(4)	2.140(2)	2.171	2.174	2.191
Rh–C ₅	2.195(4)	2.152(2)	2.263	2.252	2.201
Rh–C ₅ '	2.173(4)	2.125(2)	2.242	2.214	2.174

^a Optimized at B3LYP/6-31G(d) (6-31G(3d) for Si, P; lan12DZ for Rh).

stable rhodium β -ketophosphenate **2b** in 26% yield (from **3b**) [Scheme 2 (a), eq 2]. In order to make a comparison of properties between β -ketophosphenato and β -ketoiminato ligands, rhodium β -ketoiminato **4** was synthesized by the reaction of the corresponding lithium β -ketoiminato, which was generated from β -enaminoketone **5**,¹⁵ with $[\text{RhCl}(\text{cod})]_2$ [Scheme 2 (b)].

Structures of the rhodium complexes, **2b** and **4**, were revealed by the X-ray crystallographic analysis,¹⁶ and the observed structural parameters are shown in Table 1. Complex **2b** was found to possess an sp^2 -hybridized phosphorus atom on the basis of the almost planar geometry (the sum of the angles around the P atom is 359.6°). In addition, it was found that both **2b** and **4** possessed an almost planar structure for the central six-membered ring moiety $[-\text{Rh}-\text{O}-\text{C}-\text{C}-\text{C}-\text{E}-]$ (E = N and P), where every bond length of the central hexagonal rings was in the range of values between those of the corresponding single and double bonds, suggesting their delocalized cyclic π -electron systems. It should be noted that the two kinds of Rh–C(cod) distances of **2b** were apparently different from each other; that is, Rh–C₄ and Rh–C₄' were shorter than Rh–C₅ and Rh–C₅', although those of **4** were similar to each other. These structural features suggested the stronger trans influence of the phosphorus moiety of β -ketophosphenato ligand **1b** as compared with its oxygen moiety, in contrast to the similar degree of trans influence of N and O atoms in the β -ketoiminato ligand. Such a unique unsymmetrical electronic feature of β -ketophosphenato ligand **1b** suggests the high σ -donating ability due to the electropositive phosphorus atom and the low-lying π^* -orbital of the sp^2 -hybridized phosphorus atom, making the back-donation from the rhodium stronger.

Theoretical calculations have been performed for the model molecules bearing a less hindered substituent (Dmp = 2,6-dimethylphenyl) instead of a Tbt or Dip group, i.e., rhodium

(15) Yu, R. C.; Hung, C. H.; Huang, J. H.; Lee, H. Y.; Chen, J. T. *Inorg. Chem.* **2002**, *41*, 6450–6455.

(16) In the case of X-ray crystallographic analysis of **2b**, inevitable disorder was observed for several single crystals. The disorder was reasonably solved by using the SHELXL program. Sheldrick, G. M. *SHELXL-97*, Program for Crystal Structure Solution and Refinement of Crystal Structures; Institut für Anorganische Chemie der Universität Göttingen: Göttingen, Germany, 1997.

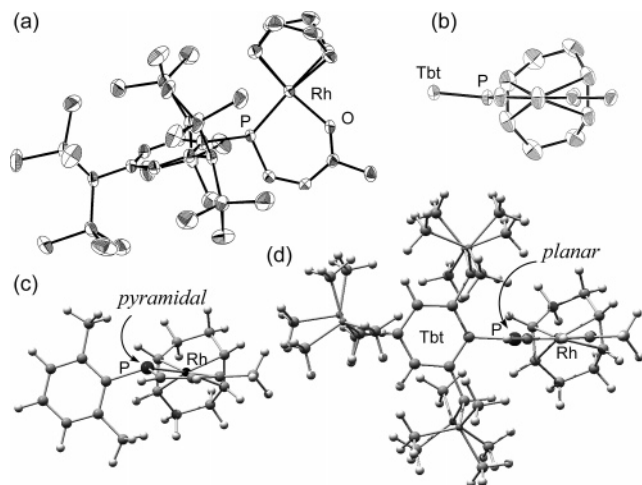


Figure 1. (a, b) ORTEP drawing of **2b** with thermal ellipsoid plots (50% probability). Hydrogen atoms are omitted for clarity. (c) Optimized structure of **6**. (d) Optimized structure of **2b**.

β -ketophosphenate **6** and rhodium β -ketoiminate **7**.¹⁷ The optimized structural parameters of **7** were similar to those observed for **4**, indicating that the relatively bulky Dip group have a lesser effect on the structure of the rhodium β -ketoiminate skeleton. However, the optimized structure of **6** showed a bent structure for the central six-membered ring moiety, in contrast to the observed planar structure of **2b**. Although the C–C and C–O bonds of **6** were found to be highly conjugated, as judged by their bond lengths, the phosphorus atom showed a pyramidal geometry (the sum of the angles around the P atom is 347.1°), which is indicative of its sp^3 hybridization. Therefore, it can be concluded that the extremely bulky Tbt group plays two important roles as follows: (i) kinetic stabilization for the reactive sp^2 phosphorus center and (ii) steric effect of the upright geometry of the two CH(SiMe₃)₂ moieties at *ortho* positions for keeping the planar structure of the β -ketophosphenato ligand with an sp^2 -hybridized phosphorus atom and preventing the phosphorus atom from pyramidalization. Actually, the theoretically optimized structure of the real molecule **2b** showed structural parameters similar to the planar skeleton experimentally observed for the central six-membered ring of **2b** (the sum of angles around the P atom is 359.8°).^{17,18} The ³¹P NMR spectra of **2a,b** showed doublet signals at relatively low field, 129 (¹J_{PRh} = 174 Hz) and 120 (¹J_{PRh} = 175 Hz) ppm, respectively, which

(17) B3LYP/6-31G(d) (6-31G(3d) for Si, P; lanl2DZ for Rh) level.

(18) It has been reported that the bulky substituents induced the planar geometry of the phosphorus atom in the phosphole ring; see: Cloke, F. G. N.; Hitchcock, P. B.; Hunnabell, P.; Nixon, J. F.; Nyulaszi, L.; Niecke, E.; Thelen, V. *Angew. Chem., Int. Ed.* **1998**, *37*, 1083–1086.

should be characteristic of sp^2 -hybridized phosphorus atoms.¹⁹ In the ¹³C NMR spectra of **2a,b**, the chemical shifts of C₅ and C_{5'} (96.5 for **2a**, 96.0 for **2b**) were observed at lower field region than those of C₄ and C_{4'} (64.7 for **2a**, 64.4 for **2b**) (the atom numberings are according to those shown in Table 1). Thus, the NMR spectra of **2a,b** also demonstrated the stronger trans influence of the P atom than that of the O atom in β -ketophosphenato ligands **1**. On the other hand, the ¹³C NMR spectra of rhodium β -ketoiminate **4** showed the signals for its C₄ (C_{4'}) and C₅ (C_{5'}) atoms at 75.9 and 81.6 ppm, respectively, indicating the similar degree of the trans influence of the O and N atoms in the β -ketoiminate ligand.

Heating of rhodium β -ketophosphenate **2b** in the presence of norbornadiene (10 equiv) in C₆D₆ at 40 °C for 5 h afforded the corresponding diene-exchange product **8** almost quantitatively, though no diene-exchange reaction was observed in the case of heating of rhodium β -ketoiminate **4** under the same conditions. The lower barrier of the diene-exchange reaction of **2b** than that of **4** would be due to the strong trans effect of the P atoms of the β -ketophosphenato ligand **1b**.

In conclusion, the first stable rhodium β -ketophosphenates **2a,b** have been synthesized, and their unique properties due to the intrinsic nature of the sp^2 -hybridized P atom have been revealed on the basis of the comparison with those of rhodium β -ketoiminate **4**. The unique unsymmetrical trans influence of β -ketophosphenato ligands **1** was suggested by spectroscopic and crystallographic analyses, where that of the phosphorus moiety should be stronger than the oxygen moieties, in contrast to the similar degree of trans influence of both sides of N and O in the β -ketoiminate ligand. The β -ketophosphenato ligands **1a,b** should be unique and useful ligands. Further investigation of their chemical reactivity and catalytic abilities of the newly obtained metal complexes is currently in progress.

Acknowledgment. This work was partially supported by Grants-in-Aid (Nos. 17GS0207, 12CE2005, and 18750030) and the 21st Century COE, Kyoto University Alliance for Chemistry, from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

Supporting Information Available: X-ray crystallographic data of **2b**, **4**, and [Li(OEt₂)·**1a**]₂·(0.5hexane) in CIF format, experimental procedures, and spectral data. These materials are available free of charge via the Internet at <http://pubs.acs.org>.

OM700412G

(19) The observed coupling constants [¹J(¹⁰³Rh–³¹P)] of **2a,b** were in the typical range of those for rhodium–phosphine or –phosphide complexes. (a) Naaktgeboren, A. J.; Nolte, R. J. M.; Drenth, W. *J. Am. Chem. Soc.* **1980**, *102*, 3350–3354. (b) Lee, I.; Dahan, F.; Maisonnat, A.; Poilblanc, R. *Organometallics* **1994**, *13*, 2743–2750.