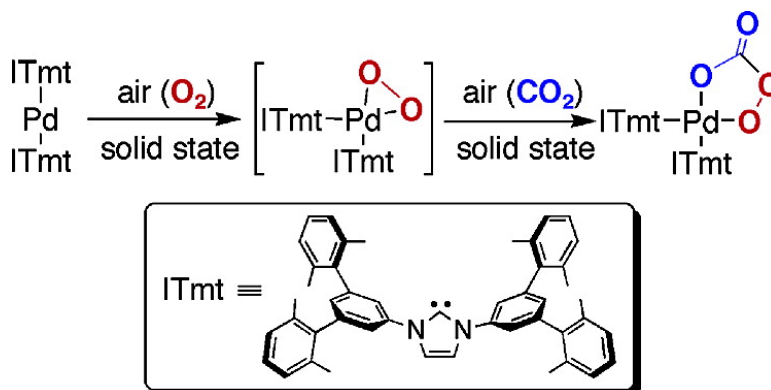


Fixation of Both O and CO from Air by a Crystalline Palladium Complex Bearing *N*-Heterocyclic Carbene Ligands

Makoto Yamashita, Kei Goto, and Takayuki Kawashima

J. Am. Chem. Soc., **2005**, 127 (20), 7294-7295 • DOI: 10.1021/ja051054h • Publication Date (Web): 27 April 2005

Downloaded from <http://pubs.acs.org> on March 25, 2009



More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Links to the 10 articles that cite this article, as of the time of this article download
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

[View the Full Text HTML](#)



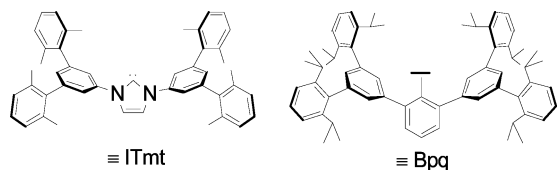
Fixation of Both O₂ and CO₂ from Air by a Crystalline Palladium Complex Bearing *N*-Heterocyclic Carbene Ligands

Makoto Yamashita, Kei Goto,* and Takayuki Kawashima*

Department of Chemistry, Graduate School of Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, 113-0033 Tokyo, Japan

Received February 18, 2005; E-mail: goto@chem.s.u-tokyo.ac.jp; takayuki@chem.s.u-tokyo.ac.jp

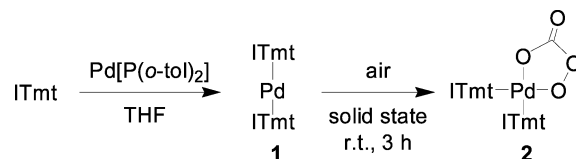
Fixation of CO₂ is generally achieved in biological systems through the dark reaction (Calvin–Benson cycle)¹ of photosynthesis. This process can fix a low concentration (0.035%) of CO₂² from air at room temperature. Many elemental reactions of CO₂ with transition metal complexes^{3,4} and catalytic reactions of CO₂ with organic substrates^{5–9} as well as CO₂ sensing by use of lithium-ion conductor^{10,11} have been developed to date. Most of these reactions, however, usually require a high pressure of CO₂ or a CO₂ atmosphere in a reaction vessel, in contrast to the case of biological CO₂ fixation. Otherwise, a high temperature of the device is necessary. Here we report a rapid fixation reaction of both O₂ and CO₂ from air to the palladium(0) complex **1** bearing the novel *N*-heterocyclic carbene (NHC) ligands, ITmt [1,3-bis(2,2'',6,6''-tetramethyl-*m*-terphenyl-5'-yl)imidazol-2-ylidene]. This reaction rapidly proceeds even in the solid state to produce the corresponding palladium(II) peroxocarbonate complex **2**.



In the course of our study on the stabilization of highly reactive species, we previously developed a novel steric protection group, a Bpq group, with a denderimer-type framework.^{12–14} The ligand ITmt was designed as its NHC analogue, which is expected to facilitate the formation of low-coordinate species. As a whole molecule, ITmt has a much higher degree of bulkiness than other diaryl NHC ligands such as 1,3-bis(2,4,6-trimethylphenyl)imidazoline-2-ylidene (IMes).¹⁵ On the other hand, the steric congestion in the vicinity of the carbene center is less severe in ITmt because of the absence of any substituent in the ortho positions of nitrogen. The ligand ITmt can be readily prepared by the usual procedures.¹⁶ The Pd(0)(ITmt)₂ complex **1** was synthesized by the reaction of Pd[P(*o*-tol)]₂¹⁷ with ITmt (Scheme 1). The neutral complex **1** showed a similar crystal structure (Figure 1a) to those of other reported Pd(NHC)₂ complexes.^{18–21}

Exposure of the crystalline palladium(0) complex **1** to air at room temperature for 3 h caused a dramatic color change from deep red to pale yellow, and the formation of the palladium(II) peroxocarbonate complex **2** was confirmed by NMR, IR spectroscopy, and elemental analysis. Complete structural characterization of **2** as a peroxocarbonate complex^{22,23} was achieved by X-ray crystallography (Figure 1c). In the solid state, **2** has a palladium atom on the C₂ axis and two disordered peroxocarbonate groups, forming a palladacycle with an occupancy of 0.5 for each. The two NHC ligands are placed at cis positions to each other, although these ligands have considerable steric bulkiness and occupy the trans

Scheme 1



positions in the Pd(0) complex **1**. All four *m*-terphenyl units are in gear with one another, forming a cavity to accommodate the peroxocarbonate chelate ring. There have been some reports of the formation of group 10 peroxocarbonate complexes by the reaction with O₂ and CO₂ gases,^{22,23} and one report about a reversible CO₂ absorption reaction from air to a solution of transition metal alkoxide complex.²⁴ However, the present reaction is the first example of the solid-state fixation of O₂ and CO₂ from air to a transition metal complex.

Several control experiments for the reaction of the palladium(0) complex **1** with O₂ or CO₂ revealed that the intermediate of the reaction is the palladium(II) peroxy complex **3** (Scheme 2). Direct treatment of a THF solution of **1** with dry ice under an argon atmosphere caused no change in its ¹H NMR spectrum. On the other hand, the subsequent reaction of the resulting solution containing **1** and CO₂ with O₂ gas produced the peroxocarbonate complex **2** within seconds. In the reaction of crystalline **1** with O₂ gas, the peroxy complex **3** formed, with a color change from red to brownish-yellow. A recent report about the formation of bis(NHC)-ligated palladium peroxy complex (IMes)₂PdO₂ (**7**) by the solid-state reaction of (IMes)₂Pd (**4**) with air also supports the formation of peroxy complex **3**.^{18,25,26} The peroxy complex **3** was independently synthesized by reaction of **1** with O₂ in C₆D₆, and was fully characterized by ¹H NMR, ¹³C NMR, IR spectroscopy, and X-ray crystallography (Figure 1b).

The solid-state reactions of other two-coordinate palladium(0) complexes bearing bulky phosphines or carbenes with O₂ and air were carried out as control experiments, but none of these reactions produced a palladium(II) peroxocarbonate complex. Solid Pd(PCy₃)₂, Pd(P^{*t*}Bu₃)₂, and Pd(IPr)₂ (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazoline-2-ylidene)²⁷ did not react with O₂ in air at all, although Pd(PCy₃)₂ was converted to the corresponding peroxocarbonate complex by treatment with O₂ and CO₂ gases in toluene.²² Whereas (IMes)₂Pd (**4**) was reported to react with O₂ in air to form the corresponding peroxy complex (IMes)₂PdO₂ (**6**) in the solid state,¹⁷ no carbonyl band was observed in the IR spectrum when solid **4** was exposed to air for 12 h at room temperature, indicating that **6** does not undergo further reaction with CO₂ (Scheme 2).

To confirm the solid-state fixation of O₂ and CO₂ by **1**, microscopic IR spectra were recorded during the course of the reaction of **1** with air.²⁸ Exposure of **1** to air at room temperature for 1 h led to a disappearance of its red color from the edge of the crystals in the early stage of the reaction. Subsequently, new bands

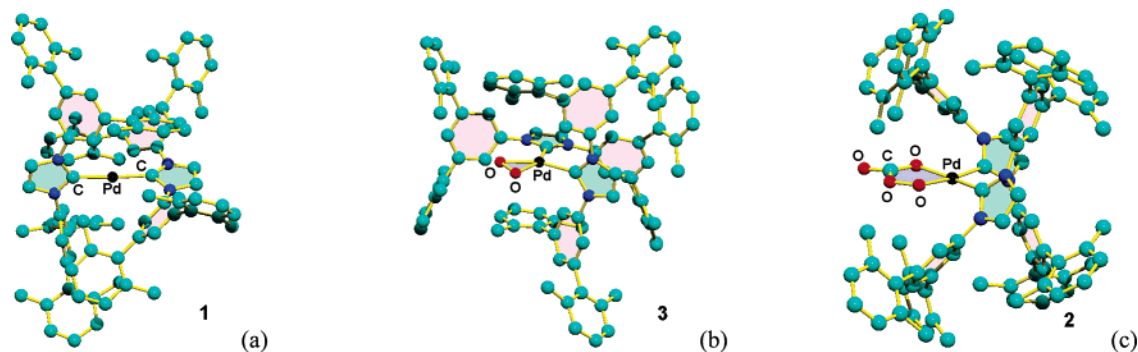
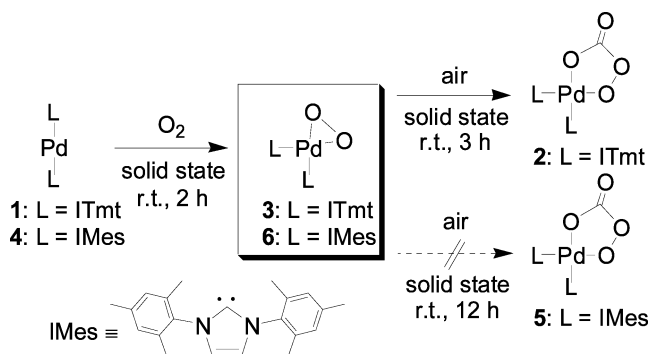


Figure 1. Solid-state structures of (a) palladium bis(NHC) complex **1**, (b) peroxo complex **3**, and (c) peroxocarbonate complex **2**. Hydrogens, disordered aromatic rings, and solvents are omitted for clarity. All carbene rings, phenyl rings on each nitrogen, and palladacycles are illustrated as colored planes.

Scheme 2



due to the C=O vibration at 1637 and 1673 cm^{-1} began to develop. After 3 h, the complete formation of the peroxocarbonate complex **2** was confirmed by comparison of IR spectrum with that of the independently synthesized **2**. During the solid-state reaction, a characteristic peak of the palladium peroxo complex **3** was observed at 1260 and 1300 cm^{-1} although most of the signals due to the NHC ligands showed no significant changes.

The difference in reactivity among these PdL_2 species can be explained in terms of the difference in the steric factor between ITmt and other monodentate ligands. $\text{Pd}(\text{PCy}_3)_2$, $\text{Pd}(\text{P}^t\text{Bu}_3)_2$, and $\text{Pd}(\text{IPr})_2$, which do not react with O_2 in air in the solid state, would cause large steric repulsion between the two cis-positioned ligands if they formed the corresponding peroxo complexes. Furthermore, $(\text{IMes})_2\text{PdO}_2$ (**6**)¹⁸ is likely to have too little space around the central palladium atom to react with CO_2 , because the IMes ligand has four methyl groups in close vicinity of the coordination site. In contrast, there is a larger space around the central palladium atom in the peroxo complex **3** without any alkyl groups around the coordination site, as is apparent from the comparison of the crystal structures of **3** and **6**.²⁹ Further investigations on the application of ligand ITmt with such structural features to catalytic reactions are currently in progress.

Acknowledgment. We thank Prof. Shigehiro Yamaguchi and Dr. Atsushi Wakamiya at Nagoya University for the measurement of X-ray crystallography of **3**. This work was partly supported by Grants-in-Aid for The 21st Century COE Program (T.K.) and for Scientific Research (K.G. and T.K.) from the Ministry of Education, Culture, Sports, Science and Technology. M.Y. thanks JSPS for a postdoctoral fellowship.

Supporting Information Available: All experimental procedures and spectroscopic data of ITmt and **1–3**; IR monitoring of the reaction of **1** with air; space filling model of **3** and **6**; CIF files for **1–3**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- Calvin, M. *Angew. Chem., Int. Ed. Engl.* **1962**, *1*, 65–75.
- Emsley, J. *The Elements*, 3rd ed.; Oxford University Press: New York, 1998.
- Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Application of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987.
- Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*; John Wiley & Sons: New York, 2001.
- Jessop, P. G.; Ikariya, T.; Noyori, R. *Chem. Rev.* **1995**, *95*, 259–272.
- Behr, A. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 661–678.
- Inoue, S.; Koinuma, H.; Tsuruta, T. *J. Polym. Sci., Part B: Polym. Lett.* **1969**, *7*, 287–292.
- Darensbourg, D. J.; Holtcamp, M. W. *Coord. Chem. Rev.* **1996**, *153*, 155–174.
- Braunstein, P.; Matt, D.; Nobel, D. *Chem. Rev.* **1988**, *88*, 747–764.
- Zhang, Y. C.; Kaneko, M.; Uchida, K.; Mizusaki, J.; Tagawa, H. *J. Electrochem. Soc.* **2001**, *148*, H81–H84.
- Maruyama, T.; Ye, X. Y.; Saito, Y. *Solid State Ion.* **1987**, *23*, 113–117.
- Goto, K.; Yamamoto, G.; Tan, B.; Okazaki, R. *Tetrahedron Lett.* **2001**, *42*, 4875–4877.
- Goto, K.; Hino, Y.; Takahashi, Y.; Kawashima, T.; Yamamoto, G.; Takagi, N.; Nagase, S. *Chem. Lett.* **2001**, 1204–1205.
- Shimada, K.; Goto, K.; Kawashima, T.; Takagi, N.; Choe, Y.-K.; Nagase, S. *J. Am. Chem. Soc.* **2004**, *126*, 13238–13239.
- Arduengo, A. J., III; Dias, H. V. R.; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1992**, *114*, 5530–5534.
- The details of preparation of **1** are given in the Supporting Information.
- Bohm, V. P. W.; Gstottmayr, C. W. K.; Weskamp, T.; Herrmann, W. A. *J. Organomet. Chem.* **2000**, *595*, 186–190.
- Konnick, M. M.; Guzei, I. A.; Stahl, S. S. *J. Am. Chem. Soc.* **2004**, *126*, 10212–10213.
- Gstottmayr, C. W. K.; Bohm, V. P. W.; Herdtweck, E.; Grosche, M.; Herrmann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1363–1365.
- Altenhoff, G.; Goddard, R.; Lehmann, C. W.; Glorius, F. *Angew. Chem., Int. Ed.* **2003**, *42*, 3690–3693.
- Arnold, P. L.; Cloke, F. G. N.; Geldbach, T.; Hitchcock, P. B. *Organometallics* **1999**, *18*, 3228–3223.
- Dibugno, C.; Pasquali, M.; Leoni, P. *Inorg. Chim. Acta* **1988**, *149*, 19–20.
- Hayward, P. J.; Blake, D. M.; Nyman, C. J.; Wilkinson, G. *J. Chem. Soc., Chem. Commun.* **1969**, 987–988.
- Mandal, S. K.; Ho, D. M.; Orchin, M. *Organometallics* **1993**, *12*, 1714–1719.
- Yoshida, T.; Tatsumi, K.; Matsumoto, M.; Nakatsu, K.; Nakamura, A.; Fueno, T.; Otsuka, S. *Nouv. J. Chim.* **1979**, *3*, 761–774.
- Stahl, S. S.; Thorman, J. L.; Nelson, R. C.; Kozee, M. A. *J. Am. Chem. Soc.* **2001**, *123*, 7188–7189.
- Jafarpour, L.; Stevens, E. D.; Nolan, S. P. *J. Organomet. Chem.* **2000**, *606*, 49–54.
- The microscopy images and IR spectra are shown in Figures S1–S3 in the Supporting Information.
- The space-filling models of **3** and **6** are shown in Figure S4 in the Supporting Information.

JA051054H