Oxygen-atom-transfer Reactions of a Palladium(II) Peroxocarbonate Complex

Shohei Sase, Maki Hashimoto, and Kei Goto*

Department of Chemistry, Graduate School of Science and Engineering, Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro-ku, Tokyo 152-8551

2-12-1 Обкауата, тедиго-ка, 10куб 152-855.

(E-mail: goto@chem.titech.ac.jp)

Reactivity of a palladium(II) peroxocarbonate complex was investigated. It was found that a bis(*N*-heterocyclic carbene) palladium(II) peroxocarbonate acts as an oxygen-atom-transfer (OAT) reagent toward a phosphine and a sulfoxide. In these OAT reactions, the peroxocarbonate was converted to the corresponding palladium(II) carbonate. While the OAT reaction toward triphenylphosphine proceeded only sluggishly, addition of lithium chloride remarkably facilitated the reaction. It was proposed that the chloride ion induces the liberation of the peroxocarbonate moiety from the coordination sphere of palladium.

Transition-metal peroxocarbonate complexes represent an interesting class of compounds in view of their ability as oxygen-atom-transfer reagents as well as their potential for application to oxidative CO_2 fixation to organic molecules.¹ They can be synthesized by the reaction of low-valent transition-metal complexes with O_2 and CO_2 . To date, the syntheses of peroxocarbonates containing various transition metals such as iron(III),² rhodium(III),³ palladium(II),⁴ and platinum(II)⁵ have been reported. However, information on the reactivity of transition-metal peroxocarbonates has been limited only to rhodium(III) and platinum(II) complexes, which were found to behave as oxygen-atom-transfer reagents toward organic molecules such as phosphines^{3a-3c,5a,5b} and olefins.^{3d-3f}

As for the palladium(II) counterpart, while there is a report on the synthesis of a bis(phosphine) peroxocarbonate complex, the reactivity has not been investigated due to its instability in solution.⁴ It is desirable to elucidate the reactivity of a welldefined palladium(II) peroxocarbonate complex. Recently, we have reported that the palladium(0) complex **1** bearing *N*heterocyclic carbene (NHC) ligands (denoted as ITmt) bearing *m*-terphenyl groups on the nitrogen atom captures both O₂ and CO₂ from air in the solid state to produce the bis(*N*-heterocyclic carbene) palladium(II) peroxocarbonate complex **2** (Scheme 1), which represents the first example of the solid-state fixation of O₂ and CO₂ from air to a transition metal complex.⁶ In contrast to the aforementioned bis(phosphine) palladium(II) peroxocarbonate, the NHC-ligated complex **2** is stable enough to manipulate under laboratory conditions. In this communication,



Scheme 1. Solid-state fixation of O_2 and CO_2 from air by Pd(0) complex 1 to produce the palladium(II) peroxocarbonate complex 2.

we report the reactivity of the palladium(II) peroxocarbonate as an oxygen-atom-transfer reagent toward a phosphine and a sulfoxide.

In the literature, there has been no example of an oxygenatom-transfer reaction from a transition-metal peroxocarbonate complex to a sulfur compound.⁷ During the course of our studies on the properties of 2, it was found that 2 was quantitatively transformed to the $[Pd^{II}(CO_3)(NHC)_2]$ complex 3 in DMSO- d_6 at room temperature. In a mixed solvent of benzene/dimethyl sulfoxide (1:1 v/v), the transformation also proceeded to afford 3, which was isolated in 82% yield (Scheme 2). GC-MS analysis of the reaction mixture confirmed the formation of dimethyl sulfone (m/z = 94), proving the oxygen-atom transfer from 2 to dimethyl sulfoxide. The amount of dimethyl sulfoxide was able to be reduced to 100 equivalents without decreasing the yield of 3 (Table 1, Entry 1). The reaction of 2 with diphenyl sulfoxide (30 equiv) resulted in no reaction, while that with dimethyl sulfoxide under the same conditions produced 3 in 39% yield (Entries 2 and 3). These results indicate that the oxygen-atom transfer from 2 to a sulfoxide is sensitive to the steric bulkiness of the substrate.

The structure of the palladium(II) carbonate **3** was unambiguously determined by X-ray crystallographic analysis (Figure 1).⁸ The coordination geometry around the Pd atom is distorted square planar with two carbene ligands in the *cis* configuration and one η^2 -coordinated carbonate ligand. The structural parameters for the palladium carbonate moiety are in the range typical for palladium(II) carbonate complexes.⁹ The C–Pd–C bond angle (98.1(2)°) in **3** is slightly larger than that of the related palladium(II) carbonate **4** (Chart 1) bearing two NHC



Scheme 2. Oxygen-atom-transfer reaction from 2 to dimethyl sulfoxide to form the palladium(II) carbonate complex 3.

Table 1.	Oxygen-atom	transfer	from	2	to	sulfoxides
		0				

	2		→ 3	
Entry	Sulfoxide	equiv	Time/h	Yield of $3^a/\%$
1	R = Me	100	13	quant.
2	R = Me	30	39	39
3	R = Ph	30	39	N.R. ^b

^aEstimated by ¹H NMR. ^bN.R.: No reaction.



Figure 1. ORTEP drawing of the palladium(II) carbonate 3 (50% probability). Selected bond lengths (Å) and angles (degree): Pd(1)–O(1) 2.063(4); Pd(1)–O(2) 2.023(5); Pd(1)–C(2) 1.971(6); Pd(1)–C(3) 2.025(7); C(2)–Pd(1)–C(3) 98.1(2); O(1)–Pd(1)–O(2) 65.04(17).







Scheme 3. Oxygen-atom-transfer reaction from 2 to phosphines.

ligands (91.1°) .^{9a} This is probably because of the steric repulsion between the *m*-terphenyl groups of the ITmt ligands.

Upon treatment of **2** with triphenylphosphine (2 equiv) in C_6D_6 at room temperature, **2** was slowly converted to **3** with the concomitant formation of triphenylphosphine oxide (Scheme 3). After 7 d, both **3** and triphenylphosphine oxide were formed in 24% NMR yield, and the rest of **2** remained unreacted. When tributylphosphine was employed under identical reaction conditions, the reduction of **2** proceeded somewhat faster to afford **3** in 34% yield after 4 d. The rate enhancement would be attributable to the higher nucleophilicity of tributylphosphine and its smaller steric demand. These results demonstrate that a palladium(II) peroxocarbonate complex works as an oxygenatom-transfer reagent toward phosphines, which is in line with the reactivity of the rhodium(III) and platinum(II) congeners.

It is notable that oxygen-atom transfer from 2 to triphenylphosphine is remarkably facilitated in the presence of lithium



Scheme 4. Oxidation of triphenylphosphine by 2 in the presence of lithium chloride.



Figure 2. ORTEP drawing of the palladium(II) dichloride **5** (50% probability). Selected bond lengths (Å) and angles (degree); Pd(1)–C(1) 1.997(3); Pd(1)–C(2) 1.999(3); Pd(1)–Cl(1) 2.3483(7); Pd(1)–Cl(2) 2.3442(8); C(1)–Pd(1)–C(2) 93.95(11); Cl(1)–Pd(1)–Cl(2) 91.30(3).



Scheme 5. Reaction of 2 with lithium chloride to form 5.

chloride. Reaction of **2** with triphenylphosphine (2 equiv) in the presence of lithium chloride (7 equiv) completed in 5.5 h at room temperature to produce triphenylphosphine oxide in 75% yield (Scheme 4). It was found that the palladium species formed in this reaction was not the palladium carbonate **3** but the *cis*-palladium(II) dichloride complex **5** bearing two ITmt ligands, the yield of which was 96% as estimated by ¹HNMR spectroscopy. The geometrical arrangement of **5** was confirmed by X-ray crystallographic analysis (Figure 2).¹⁰ The palladium atom was found to have a square-planar geometry with two chlorine atoms in mutual *cis* positions. The structural parameters around the palladium atom were similar to those reported for the *cis*-palladium(II) dichloride complexes bearing NHC ligands.¹¹

To gain insight into the effect of lithium chloride, some control experiments were performed. In the absence of triphenyl-phosphine, the reaction of 2 with lithium chloride (7 equiv) afforded 5 quantitatively (Scheme 5). This indicates that



Scheme 6. Plausible mechanism of oxidation of triphenylphosphine by 2 in the presence of lithium chloride.

triphenylphosphine has little effect on the conversion of **2** to **5** and that chloride ions remove the peroxocarbonate moiety from the coordination sphere of palladium. In addition, monitoring of the reaction of **2** with triphenylphosphine in the presence of lithium chloride by ¹HNMR spectroscopy revealed that **5** and triphenylphosphine oxide were formed at almost the same rate. Based on these observations, we propose a plausible mechanism depicted in Scheme 6. The reaction starts with the nucleophilic attack of chloride ions to the palladium atom of **2** to form **5** with the concomitant liberation of the peroxocarbonate moiety,¹² which readily oxidizes triphenylphosphine to the corresponding oxide. The liberated peroxocarbonate moiety incorporated in **2**.

In summary, we demonstrated that a palladium(II) peroxocarbonate complex undergoes an oxygen-atom-transfer reaction toward a phosphine and a sulfoxide, in which the peroxocarbonate was converted to the corresponding palladium(II) carbonate. It was also found that lithium chloride induces the liberation of the peroxocarbonate moiety from the palladium complex, which remarkably accelerates the oxidation of a phosphine. Oxygen-atom transfer to other organic molecules, such as olefins, by utilizing the palladium(II) peroxocarbonate is currently under investigation.

This work was partly supported by Grants-in-Aid for The Global COE Program for Education and Research, Center for Emergence of New Molecular Chemistry and for Scientific Research on Innovative Areas "Molecular Activation Directed toward Straightforward Synthesis" from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

Supporting Information is available electronically on J-STAGE.

References and Notes

- a) M. Aresta, A. Dibenedetto, *Dalton Trans.* 2007, 2975. b) T. Sakakura, J.-C. Choi, H. Yasuda, *Chem. Rev.* 2007, 107, 2365.
- 2 a) K. Hashimoto, S. Nagatomo, S. Fujinami, H. Furutachi, S. Ogo, M. Suzuki, A. Uehara, Y. Maeda, Y. Watanabe, T. Kitagawa, *Angew. Chem., Int. Ed.* **2002**, *41*, 1202. b) H. Furutachi, K. Hashimoto, S. Nagatomo, T. Endo, S. Fujinami, Y. Watanabe, T. Kitagawa, M. Suzuki, *J. Am. Chem. Soc.* **2005**, *127*, 4550.
- 3 a) Y. Wakatsuki, M. Maniwa, H. Yamazaki, *Inorg. Chem.* 1990, 29, 4204. b) M. Aresta, A. Dibenedetto, I. Tommasi, *Eur. J. Inorg. Chem.* 2001, 1801. c) G. Meier, T. Braun, *Angew. Chem., Int. Ed.* 2012, 51, 12564. d) M. Aresta, E. Quaranta, A. Ciccarese, *J. Mol. Catal.* 1987, 41, 355. e) M. Aresta, C. Fragale, E. Quaranta, I. Tommasi, *J. Chem. Soc., Chem. Commun.* 1992, 315. f) M. Aresta, A. Dibenedetto, *J. Mol. Catal. A: Chem.* 2002, 182–183, 399. g) L. Dahlenburg, C.

Prengel, Organometallics 1984, 3, 934. h) L. Dahlenburg, C. Prengel, J. Organomet. Chem. 1986, 308, 63.

- 4 C. Di Bugno, M. Pasquali, P. Leoni, *Inorg. Chim. Acta* **1988**, *149*, 19.
- 5 a) P. J. Hayward, D. M. Blake, C. J. Nyman, G. Wilkinson, J. Chem. Soc. D 1969, 987b. b) P. J. Hayward, D. M. Blake, G. Wilkinson, C. J. Nyman, J. Am. Chem. Soc. 1970, 92, 5873.
 c) H. C. Clark, A. B. Goel, C. S. Wong, J. Organomet. Chem. 1978, 152, C45. d) D. A. Clarke, R. D. W. Kemmitt, M. A. Mazid, P. McKenna, D. R. Russell, M. D. Schilling, L. J. S. Sherry, J. Chem. Soc., Dalton Trans. 1984, 1993. e) F. Porta, F. Ragaini, S. Cenini, O. Sciacovelli, M. Camporeale, Inorg. Chim. Acta 1990, 173, 229.
- 6 M. Yamashita, K. Goto, T. Kawashima, J. Am. Chem. Soc. 2005, 127, 7294.
- 7 Oxidation of sulfur compounds by a peroxymonocarbonate salt that does not contain transition metal was reported. D. E. Richardson, H. Yao, K. M. Frank, D. A. Bennett, *J. Am. Chem. Soc.* 2000, *122*, 1729.
- 8 Crystal data for **3**·6.5DMSO- d_6 : fw: 1987.27, T = 120 K, monoclinic, $P2_1/c$, a = 12.748(2), b = 27.956(4), c = 29.439(5) Å, $\beta = 96.801(3)^\circ$, V = 10418(3) Å³, Z = 4, $D_{calcd} = 1.242$ g cm⁻³, $\mu = 0.366$ mm⁻¹, No. of indep reflns (parameters) = 15905 (1149), GOF = 0.927, R ($I > 2\sigma(I)$) = 0.1031, wR_2 (all data) = 0.2357. CCDC1040118. Crystallographic data reported in this manuscript have been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-1040118. Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/ retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).
- 9 a) Y.-M. Liu, Y.-C. Lin, W.-C. Chen, J.-H. Cheng, Y.-L. Chen, G. P. A. Yap, S.-S. Sun, T.-G. Ong, *Dalton Trans.* 2012, 41, 7382. b) P. W. G. Ariyananda, G. P. A. Yap, J. Rosenthal, *Dalton Trans.* 2012, 41, 7977. c) S. K. Mandal, M. S. Sigman, J. Org. Chem. 2003, 68, 7535. d) J. Pushkar, O. F. Wendt, *Inorg. Chim. Acta* 2004, 357, 1295. e) J. T. Bagdanoff, B. M. Stoltz, *Angew. Chem., Int. Ed.* 2004, 43, 353.
- 10 Crystal data for $5 \cdot 6.5 C_6 D_6 \cdot 0.5 C_6 H_{14}$: fw: 2041.11, T = 120 K, monoclinic, $P2_1/n$, a = 24.960(3), b = 18.203(3), c = 25.430(4) Å, $\beta = 104.1382(18)^\circ$, V = 11204(3) Å³, Z = 4, $D_{calcd} = 1.187$ g cm⁻³, $\mu = 0.266$ mm⁻¹, No. of indep reflns (parameters) = 19539 (1315), GOF = 1.050, R ($I > 2\sigma(I)$) = 0.0541, wR_2 (all data) = 0.1526. CCDC1040119. Crystallographic data reported in this manuscript have been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-1040119. Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/ retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).
- 11 a) A. Sinha, S. M. W. Rahaman, M. Sarkar, B. Saha, P. Daw, J. K. Bera, *Inorg. Chem.* **2009**, *48*, 11114. b) C.-F. Fu, C.-C. Lee, Y.-H. Liu, S.-M. Peng, S. Warsink, C. J. Elsevier, J.-T. Chen, S.-T. Liu, *Inorg. Chem.* **2010**, *49*, 3011.
- 12 Preparation of dilithium peroxocarbonate monohydrate has been reported, see: a) T. P. Firsova, V. I. Kvlividze, A. N. Molodkina, T. G. Morozova, *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1975**, *24*, 1318. b) D. P. Jones, W. P. Griffith, *J. Chem. Soc., Dalton Trans.* **1980**, 2526.