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Fixation of Both O_2 and CO_2 from Air by a Crystalline Palladium Complex Bearing *N*-Heterocyclic Carbene Ligands

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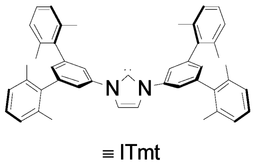
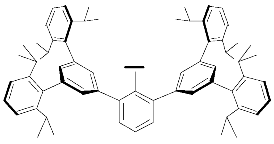
Fixation of CO_2 is generally achieved in biological systems through the dark reaction (Calvin−Benson cycle)[1] of photosynthesis. This process can fix a low concentration (0.035%) of CO_2[2] from air at room temperature. Many elemental reactions of CO_2 with transition metal complexes[3,4] and catalytic reactions of CO_2 with organic substrates[5−9] as well as CO_2 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 CO_2 or a CO_2 atmosphere in a reaction vessel, in contrast to the case of biological CO_2 fixation. Otherwise, a high temperature of the device is necessary. Here we report a rapid fixation reaction of both O_2 and CO_2 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**.



≡ ITmt

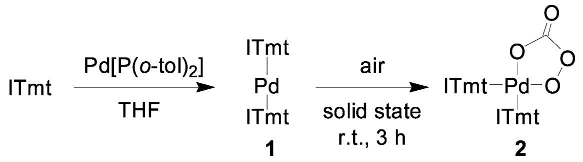


≡ Bpq

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)$_3$]$_2$[17] 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 C_2 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 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 O_2 and CO_2 gases,[22,23] and one report about a reversible CO_2 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 O_2 and CO_2 from air to a transition metal complex.

Scheme 1



Several control experiments for the reaction of the palladium(0) complex **1** with O_2 or CO_2 revealed that the intermediate of the reaction is the palladium(II) peroxo complex **3** (Scheme 2). Direct treatment of a THF solution of **1** with dry ice under an argon atmosphere caused no change in its ^{1}H NMR spectrum. On the other hand, the subsequent reaction of the resulting solution containing **1** and CO_2 with O_2 gas produced the peroxocarbonate complex **2** within seconds. In the reaction of crystalline **1** with O_2 gas, the peroxo complex **3** formed, with a color change from red to brownish-yellow. A recent report about the formation of bis(NHC)-ligated palladium peroxo complex (IMes)$_2$PdO$_2$ (**7**) by the solid-state reaction of (IMes)$_2$Pd (**4**) with air also supports the formation of peroxo complex **3**.[18,25,26] The peroxo complex **3** was independently synthesized by reaction of **1** with O_2 in C_6D_6, and was fully characterized by ^{1}H NMR, ^{13}C 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 O_2 and air were carried out as control experiments, but none of these reactions produced a palladium(II) peroxocarbonate complex. Solid Pd(PCy$_3$)$_2$, Pd(P^{t}Bu$_3$)$_2$, and Pd(IPr)$_2$ (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazoline-2-ylidene)[27] did not react with O_2 in air at all, although Pd(PCy$_3$)$_2$ was converted to the corresponding peroxocarbonate complex by treatment with O_2 and CO_2 gases in toluene.[22] Whereas (IMes)$_2$Pd (**4**) was reported to react with O_2 in air to form the corresponding peroxo complex (IMes)$_2$PdO$_2$ (**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 CO_2 (Scheme 2).

To confirm the solid-state fixation of O_2 and CO_2 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

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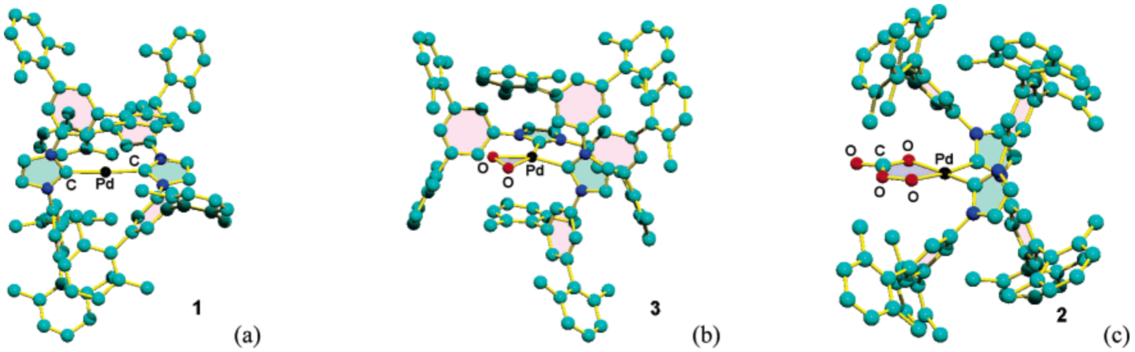
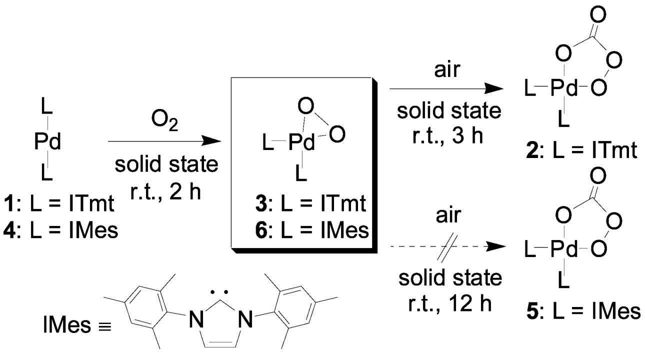


Figure 1. Solid-state structures of (a) palladium bis(NHC) complex **1**, (b) peroxo complex **3**, and (c) peroxocarbonate complex **2**. Hydrogens, disordered aromatic rings, and solvents are omitted for clarity. All carbene rings, phenyl rings on each nitrogen, and palladacycles are illustrated as 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. $Pd(PCy_3)_2$, $Pd(P^tBu_3)_2$, and $Pd(IPr)_2$, 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, $(IMes)_2PdO_2$ (**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.

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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.

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(28) The microscopy images and IR spectra are shown in Figures S1−S3 in the Supporting Information.
(29) The space-filling models of **3** and **6** are shown in Figure S4 in the Supporting Information.

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