

The First Isolation and Characterization of a Palladium–Copper Heterometallic Complex Bearing μ_4 -Oxo Atom Derived from Molecular Oxygen

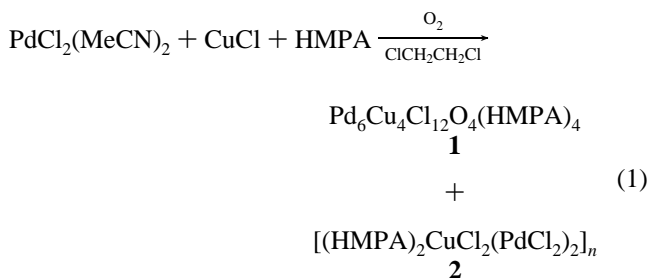
Takahiro Hosokawa,* Minoru Takano, and Shun-Ichi Murahashi*

Department of Chemistry, Faculty of Engineering Science
Osaka University, Machikaneyama
Toyonaka, Osaka 560, Japan

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In the organic chemistry of palladium, one of the important reactions is the oxidation of alkenes with Pd(II) catalysts, and various catalyst systems for this transformation have been developed.¹ In particular, copper salts such as CuCl, CuCl₂, and Cu(OAc)₂ are commonly used together with O₂ in order to make the reaction catalytic in palladium. With regard to this catalysis, we have proposed that a Pd–Cu heterometallic species derived from O₂ participates in the reaction as the catalyst and that the formal oxidation state of palladium(II) remains constant throughout the reaction.^{2–5} This is in contrast to the well-known redox catalysis of palladium and copper.⁶ In line with this study, we now wish to report the first isolation of Pd–Cu μ_4 -oxo complex Pd₆Cu₄Cl₁₂O₄(HMPA)₄ (**1**) (HMPA = hexamethylphosphoramide) derived from O₂. This result not only fundamentally agrees with our proposal but also provides information on the interaction of copper salts and O₂ in this type of oxidations.

The oxidation of terminal alkenes proceeds catalytically when PdCl₂(MeCN)₂ and CuCl are used together with O₂ and HMPA in anhydrous, aprotic solvents.^{4,5} Study of the catalyst system has now allowed us to isolate a Pd–Cu heterometallic μ_4 -oxo-bridged complex. Thus, the reaction of PdCl₂(MeCN)₂ (5 mmol) and CuCl (5 mmol) with HMPA (10 mmol) in ClCH₂-CH₂Cl (20 mL) under O₂ atmosphere (50 °C, 1 h) (eq 1) gave a brown precipitate (35%), the composition of which was



determined to be Pd₆Cu₄Cl₁₂O₄(HMPA)₄ (**1**) by elemental analysis. From the filtrate, a red–brown complex (32%) of [(HMPA)₂CuCl₂(PdCl₂)₂]_n (**2**) was obtained. Recrystallization

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of each complex of **1** and **2** from CH₂Cl₂, MeOH, and ether gave a single crystal suitable for X-ray analyses, respectively.⁷

The ORTEP presentation of **1** (Figure 1)⁸ shows that the μ_4 -O atom is bonded to three Pd and one Cu such as seen in O(3). The structure has a crystallographic three-fold axis through the O(1)–Cu(1)–O(3) atoms. The prime- and nonprime-numbered atoms are thus related by a three-fold symmetrical operation. The four Cu atoms involved lie on the apices of the tetrahedron with pseudo-*T_d* symmetry, and six Pd atoms are located in the middle of each edge. Each of the Cu atoms is arranged in trigonal bipyramidal structure by three μ -Cl atoms and two O atoms. Two axial sites of Cu are occupied by the O atom of O=P(NMe₂)₃ (HMPA) and μ_4 -O atom [e.g. O(3)] derived from O₂. Three Pd atoms are bound to the μ_4 -O atom, and each of the Pd atoms is situated in a square plane with two mutually *cis* Cl ligands and two mutually *cis* μ_4 -O atoms. Thus, Cu and Pd atoms are linked to each other by the μ -Cl and the μ_4 -O atoms. The geometry around the μ_4 -O atom is a distorted sp³ form with bond angles of Cu–O–Pd equal to 102.4(4)–104.3(4)° and Pd–O–Pd equal to 107.5(4)–120.2(4)°, and the μ_4 -O atom is in a position (0.48 Å) slightly above the trigonal plane formed by three Pd centers.

Complex **2** crystallizes as a centrosymmetric polymer which consists of alternate units of CuCl₂(HMPA)₂ and dimeric PdCl₂. The ORTEP diagram of the monomeric part of **2** is shown in Figure 2.⁹ The Cu atom is held in a distorted bipyramidal structure by two O atoms of HMPA and four Cl ligands, and four corners of the square plane are occupied by two Cl and two O atoms. The other two Cl atoms are situated in the axial positions, and the bond distance between Cu and the axial Cl [Cu(1)–Cl(3), 2.799(4) Å; Cu(1)–Cl(5), 2.766(5) Å] is longer than that of other Cu–Cl bonds [Cu(1)–Cl(1), 2.349(4) Å; Cu(1)–Cl(4), 2.351(4) Å] in the square plane. The axial Cl and another Cl atom are also bonded to Pd in normal square planar arrangement, and all the bond lengths of Pd–Cl are normal.

Although various oxo metal complexes with the μ_4 -O atom have been documented,¹⁰ there are a few examples of tetrahedral μ_4 -O complexes of late transition metals. The only complex that O₂ is incorporated as a μ_4 -O atom is the homonuclear complex (NMP)₃Cu₄Cl₆O(H₂O)(NMP) prepared by the oxidation of CuCl with O₂ in *N*-methylpyrrolidin-2-one (NMP).¹¹ The heterometallic complex [Zn₄V₄O₄](O₂CPh)₆ bearing the μ_4 -O atom has been prepared by the reaction of [V₂Cl₃(THF)₆]₂[Zn₂Cl₆] and sodium benzoate;¹² however, this μ_4 -O atom is not derived from O₂, but it arises from benzoate anion. Thus, the complex **1** is regarded as the first example of a μ_4 -O atom being incorporated in the heterometallic complex from O₂.

The formation of heterometallic complexes **1** and **2** can be explained as follows. CuCl has been reported to react with O₂ in coordinating solvents (L) such as pyridine to give CuCl₂(L)_n

(7) X-ray crystallographic data were collected using the $\omega/2\theta$ technique on a RIGAKU AFC7R diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.71069$ Å) to maximum $2\theta = 55^\circ$ at room temperature. The structures were solved by direct methods using SAPI 91 for complex **1** and SHELXS-86 for complex **2** and refined by full-matrix least squares for observed unique reflections with $I > 3\sigma(I)$.

(8) Crystallographic data for complex **1** (Pd₆Cu₄Cl₁₂O₄(HMPA)₄): $m\bar{w} = 2098.94$, hexagonal, *R*-centered, space group *R3c* (No. 161), $a = b = 20.618(2)$ Å, $c = 27.923(2)$ Å, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$, $V = 10280(2)$ Å³, $Z = 6$, $D_{\text{calc}} = 2.07$ g cm⁻³. The structure was refined to $R = 5.1\%$ and $R_w = 3.7\%$ for 2855 reflections.

(9) Crystallographic data for complex **2** [(HMPA)₂CuCl₂(PdCl₂)₂]_n: $m\bar{w} = 847.47$, monoclinic, primitive, space group *P2₁/n* (No. 14), $a = 17.675(3)$ Å, $b = 9.932(6)$ Å, $c = 18.457(6)$ Å, $\alpha = \gamma = 90^\circ$, $\beta = 107.34(2)^\circ$, $V = 3092(1)$ Å³, $Z = 4$, $D_{\text{calc}} = 1.82$ g cm⁻³. The structure was refined to $R = 8.0\%$ and $R_w = 9.7\%$ for 3613 reflections.

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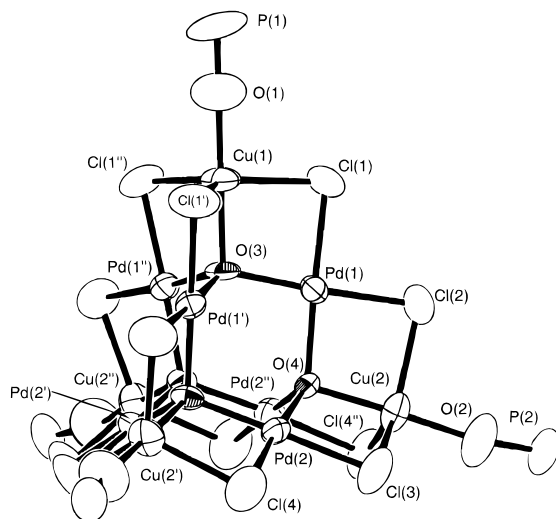
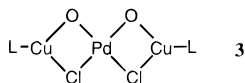


Figure 1. ORTEP drawing of complex **1** with adopted numbering scheme. Prime- and nonprime-numbered atoms are related by a three-fold symmetrical operation. Dimethylamino groups on P atoms are omitted for clarity. Selected bond lengths and angles: Cu(1)–O(1) 1.87(3) Å, Cu(1)–O(3) 1.93(1) Å, Pd(1)–O(3) 2.028(4) Å, Pd(1)–Cl(1) 2.280(4) Å, Cu(1)–Cl(1) 2.350(4) Å, Cu(2)–O(4) 1.962(8) Å, Pd(1)–O(4) 2.039(7) Å, Cu(2)–Cl(2) 2.342(5) Å, Pd(1)–Cl(2) 2.279(4) Å, Pd(2)–O(4) 2.010(8) Å, Cu(2)–O(4) 1.962(8) Å, Pd(2)–Cl(3) 2.286(4) Å, Cu(2)–Cl(3) 2.307(5) Å, Cu(2)–O(2) 1.86(1) Å; O(1)–Cu(1)–O(3) 180.0(0)°, O(1)–Cu(1)–Cl(1) 94.4(1)°, Cu(1)–O(3)–Pd(1) 103.8(4)°, Pd(1)–O(3)–Pd(1') 114.5(3)°, Cu(1)–Cl(1)–Pd(1) 84.6(2)°, Cl(1)–Pd(1)–O(3) 85.4(4)°, O(3)–Pd(1)–O(4) 97.0(4)°, O(4)–Pd(1)–Cl(2) 86.1(2)°, Pd(1)–O(4)–Cu(2) 102.4(3)°, Pd(1)–O(4)–Pd(2) 120.2(4)°, Pd(1)–O(4)–Pd(2'') 107.5(4)°, Cu(2)–Cl(3)–Pd(2) 85.7(1)°, O(4)–Pd(2)–O(4') 97.5(4)°, O(4')–Pd(2)–Cl(4) 86.6(2)°, Cl(4)–Pd(2)–Cl(3) 90.9(2)°, O(2)–Cu(2)–O(4) 176.4(5)°, O(2)–Cu(2)–Cl(2) 96.2(4)°, O(2)–Cu(2)–Cl(3) 90.9(4)°, O(2)–Cu(2)–Cl(4'') 96.9(4)°.

and μ -peroxocopper species L–Cu–O–O–Cu–L.^{13–15} The polymeric complex **2** is thus formed by a linear combination of CuCl₂L₂ (L = HMPA) formed in situ with PdCl₂. The μ -peroxocopper species (L–Cu–O–O–Cu–L) formed concurrently reacts with PdCl₂ to give the cluster unit **3** in the complex



1. Assembling of two units of **3** and four PdCl₂ leads to **1**.

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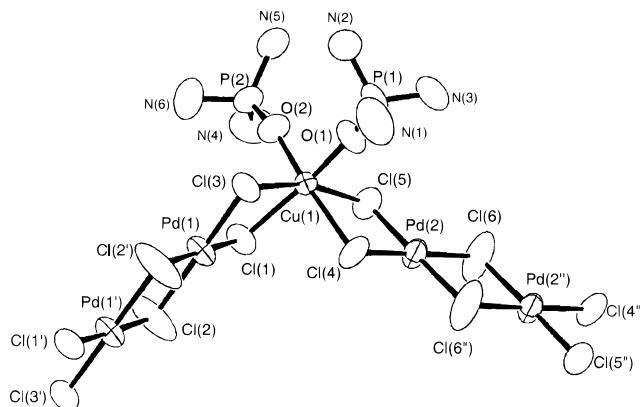
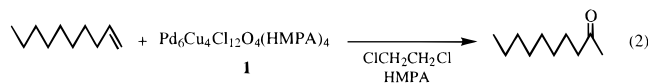


Figure 2. ORTEP presentation of a part of complex **2** with adopted numbering scheme. Prime- and nonprime-numbered atoms are related by a symmetrical operation. Methyl groups on N atoms are omitted for clarity. Selected bonds and angles: Cu(1)–O(1) 1.90(1) Å, Cu(1)–O(2) 1.91(1) Å, Cu(1)–Cl(1) 2.349(4) Å, Cu(1)–Cl(3) 2.799(4) Å, Cu(1)–Cl(4) 2.351(4) Å, Cu(1)–Cl(5) 2.766(5) Å, Pd(1)–Cl(1) 2.275(4) Å, Pd(1)–Cl(2) 2.322(5) Å, Pd(1)–Cl(2') 2.294(5) Å, Pd(1)–Cl(3) 2.258(4) Å, Pd(2)–Cl(4) 2.276(4) Å, Pd(2)–Cl(5) 2.263(4) Å, Pd(2)–Cl(6) 2.299(5) Å, Pd(2)–Cl(6'') 2.321(5) Å; O(1)–Cu(1)–O(2) 90.9(5)°, Cl(1)–Cu(1)–Cl(3) 77.7(1)°, Cl(4)–Cu(1)–Cl(5) 77.9(2)°, Cu(1)–Cl(1)–Pd(1) 100.6(2)°, Cu(1)–Cl(3)–Pd(1) 88.7(1)°, Cl(1)–Pd(1)–Cl(2) 90.8(2)°, Cl(2)–Pd(1)–Cl(2') 86.7(2)°, Cl(2')–Pd(1)–Cl(3) 91.0(2)°, Cl(3)–Pd(1)–Cl(1) 91.5(2)°, Cl(4)–Pd(2)–Cl(5) 90.8(2)°, Cl(5)–Pd(2)–Cl(6) 91.1(2)°, Cl(6)–Pd(2)–Cl(6'') 87.0(2)°, Cl(6'')–Pd(2)–Cl(4) 91.1(2)°.

The μ_4 -O atom of complex **1** is easily and stoichiometrically transferred into 1-alkenes. Thus, under an inert atmosphere such as argon, 1-decene (1 mmol) reacts with a suspension of **1** (0.1 mmol per O atom contained in **1**) in ClCH₂CH₂Cl (1 mL) and HMPA (2 mmol) at 50 °C to give 2-decanone in >99% yield (based on the O atom contained in **1**, 4 h) (eq 2). Under an O₂ atmosphere, the reaction proceeds catalytically to give 2-decanone in 360% (based on Pd, 4 h).



Combined with the above result, the present isolation of Pd–Cu heterometallic complex **1** indicates that in the oxidation of 1-alkenes by using PdCl₂ catalyst along with CuCl and HMPA under O₂, a Pd–Cu heterometallic catalyst containing oxygen atom is formed by the action of O₂, which agrees with our previous proposal.^{3,4}

Supporting Information Available: Tables of crystallographic data including atomic positional and thermal parameters for complexes **1** and **2** (9 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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