

Short communication

Palladium–copper–DMF complexes involved in the oxidation of alkenes <sup>1</sup>

Takahiro Hosokawa <sup>a,\*</sup>, Toshihiro Nomura <sup>b</sup>, Shun-Ichi Murahashi <sup>b</sup>

<sup>a</sup> Department of Environmental Systems Engineering, Faculty of Engineering, Kochi University of Technology, Tosayamada, Kochi 782, Japan

<sup>b</sup> Department of Chemistry, Faculty of Engineering Science, Osaka University, Machikaneyama, Toyonaka, Osaka 560, Japan

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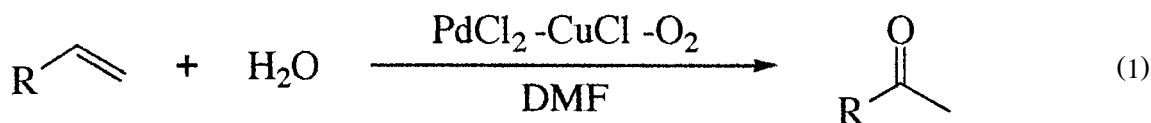
Abstract

Treatment of PdCl<sub>2</sub>(MeCN)<sub>2</sub> and CuCl with *N,N*-dimethylformamide (DMF) under O<sub>2</sub> gives polymeric complex [(PdCl<sub>2</sub>)<sub>2</sub>CuCl<sub>2</sub>(DMF)<sub>4</sub>]<sub>n</sub> (**1**) and Pd–Cu heterometallic complex **2** containing O atom derived from molecular oxygen. © 1998 Elsevier Science S.A.

**Keywords:** Palladium; Copper chloride; Molecular oxygen; DMF; Alkene

The ketonization of terminal alkenes with water by PdCl<sub>2</sub>–CuCl catalyst under O<sub>2</sub> is one of the representative metal-catalyzed oxidations, where *N,N*-dimethylformamide (DMF) is commonly used as the solvent (Eq. (1)) [1–7]. The role of this solvent is considered to lie in dissolving PdCl<sub>2</sub> and CuCl as well as the hydrophobic higher terminal alkene to a solution. However, there have been no reports referring to the participation of DMF as a ligand of the catalyst system. From

the reaction of PdCl<sub>2</sub> and CuCl with amides such as hexamethylphosphoramide or 2-pyrrolidinone under O<sub>2</sub>, we have recently succeeded in the isolation of Pd–Cu–amide complexes [8,9]. Our attention has thus directed towards the nature of the catalyst system shown in Eq. (1). Described herein is the isolation of a Pd–Cu–DMF complex from this system, which acts as the catalyst for the oxidation widely used in organic synthesis.



When PdCl<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub> and CuCl were allowed to react with DMF in ClCH<sub>2</sub>CH<sub>2</sub>Cl under O<sub>2</sub> at ambient temperature, a brown suspension turned to a deep brown solution. As the O<sub>2</sub> consumption proceeded, precipita-

tion of insoluble complex gradually occurred. After the O<sub>2</sub> uptake stopped, addition of ether followed by filtration afforded a brown complex **1** (mp 146–150°C (dec)) in 43% yield based on Pd. Recrystallization of **1** from dichloromethane–methanol–ether gave dark brown crystals of [(PdCl<sub>2</sub>)<sub>2</sub>CuCl<sub>2</sub>(DMF)<sub>4</sub>]<sub>n</sub> (**1**) which were suitable for X-ray analysis. Addition of ether to the filtrate mentioned above followed by standing at room temperature for 2 days gave another dark brown complex **2** (mp 135–138°C (dec)) which is considered to

\* Corresponding author.

<sup>1</sup> Dedicated to Professor Peter Maitlis on the occasion of his 65th birthday.

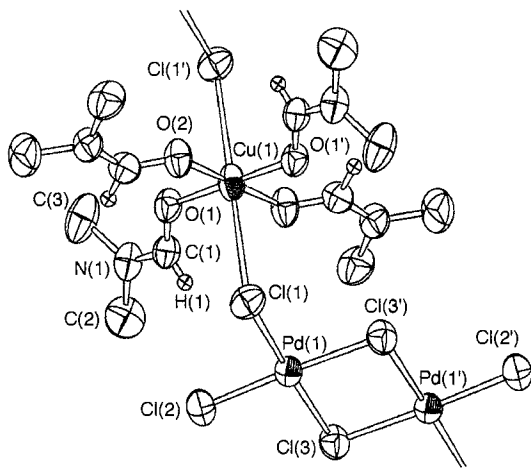
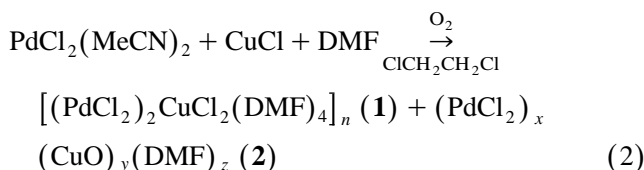


Fig. 1. ORTEP drawing of a part of polymeric complex **1** with adopted atom numbering scheme. Hydrogen atoms on carbon atoms were omitted for clarity. Selected bond length (Å) and angles (°) with esds in parenthesis: Cu–Cl(1) 2.916(2), Pd(1)–Cl(1) 2.279(2), Pd(1)–Cl(2) 2.257(2), Pd(1)–Cl(3) 2.328(2), Pd(1)–Cl(3') 2.326(2), Cu–O(1) 1.934(4), Cu–O(2) 1.958(4); CuCl(1)–Pd(1) 116.96(6), Cl(1)–Pd(1)–Cl(2) 91.84(6), Cl(2)–Pd(1)–Cl(3) 90.58(6), Cl(3)–Pd(1)–Cl(3') 85.91(6), Cl(3')–Pd(1)–Cl(1) 91.69(6), O(1)–Cu–Cl(1) 93.9(1), O(2)–Cu–Cl(1) 93.7(1), O(1)–Cu–O(2) 91.7(2).

contain an O atom derived from O<sub>2</sub> (Eq. (2)) (vide infra).

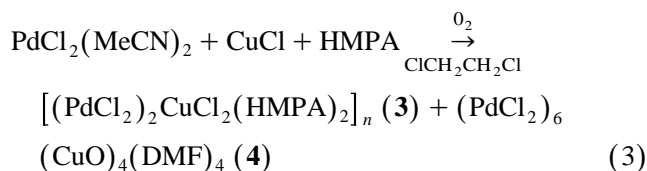


The ORTEP drawing of **1**<sup>2</sup> (Fig. 1) shows a polymeric structure which consists of alternative units of CuCl<sub>2</sub>(L)<sub>4</sub> (L = DMF) and dimeric PdCl<sub>2</sub>. The Cu and Pd units are linked by μ-Cl atoms, and this structural feature is fundamentally the same as that of [(PdCl<sub>2</sub>)<sub>2</sub>CuCl<sub>2</sub>(2-pyrrolidinone)<sub>4</sub>]<sub>n</sub> reported previously [9]. Although the bond distance of Cu(1)–Cl(1) [Cu(1)–Cl(1), 2.916(2)] is slightly longer than that of [(PdCl<sub>2</sub>)<sub>2</sub>CuCl<sub>2</sub>(2-pyrrolidinone)<sub>4</sub>]<sub>n</sub> [Cu–Cl(1), 2.823(1)], the distance is within the sum of van der Waals radius of Cu and Pd. In addition, the bond length of Cl(1)–Pd(1) is normal [Cl(1)–Pd(1), 2.279(2) Å; Cu–Cl(1)–Pd(1), 116.96(6)°]. Therefore, the complex **1** can be said to be bimetallic. The Cu atom is on a crystallographic center of symmetry and is arranged in tetragonal bipyramidal structure by two μ-Cl atoms and

four amides (L). The four amides coordinate to Cu atom via their carbonyl groups, forming a square plane. The bond lengths between Cu and the amide oxygen atoms [Cu(1)–O(1), 1.934(4) Å; Cu(1)–O(2), 1.958(4) Å] are normal [10,11].

As for complex **2**, no crystals suitable for X-ray analysis were obtained; however, the following observations indicate that the complex **2** is a Pd–Cu heterometallic complex bearing an O atom derived from O<sub>2</sub>. (i) The reaction of complex **2** with 1-decene under an inert atmosphere gives 2-decanone smoothly, and simple calculation shows that ~90% of the O atom contained in **2** is transferred into the alkene.<sup>3</sup> (ii) The IR spectrum of complex **2** shows a band at ~570 cm<sup>-1</sup> due to ν<sub>Cu–O</sub> absorption [12], and X-ray signals of Cu and Pd were detected by EDS (Energy Dispersive X-ray Spectroscopy).

The formation of complex **1** is viewed as the following sequence. (i) CuCl reacts with O<sub>2</sub> to form Cl–Cu–O–O–Cu–Cl which disproportionates to CuCl<sub>2</sub>(L)<sub>n</sub> (L = DMF) and a copper oxo species formally represented by [Cu = O] [13–16]. (ii) CuCl<sub>2</sub>(L)<sub>n</sub> (n = 4) combines with two PdCl<sub>2</sub> to afford one unit of the complex **1** (Eq. (2)). In the reaction with HMPA, the disproportionation mentioned here is also presumed to take place, affording [(PdCl<sub>2</sub>)<sub>2</sub>CuCl<sub>2</sub>(HMPA)<sub>2</sub>]<sub>n</sub> (**3**) and μ<sub>4</sub>-oxo complex (PdCl<sub>2</sub>)<sub>6</sub>(CuO)<sub>4</sub>(HMPA)<sub>4</sub> (**4**) as shown in Eq. (3). The μ<sub>4</sub>-oxo complex **4** is formed by assembly of 4 [L–Cu = O] (L = HMPA) and 6 PdCl<sub>2</sub>. In the reaction with DMF, similar assembly could result in the formation of (PdCl<sub>2</sub>)<sub>x</sub>(CuO)<sub>y</sub>(DMF)<sub>z</sub> (**2**) as shown in Eq. (2).<sup>4</sup>



In order to examine whether the heterometallic complex obtained acts as a catalyst for the oxidation shown

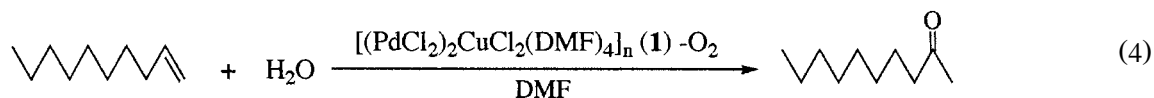
<sup>2</sup> Crystallographic Data for **1**: C<sub>12</sub>H<sub>28</sub>N<sub>4</sub>O<sub>4</sub>Pd<sub>2</sub>CuCl<sub>6</sub>, mw = 781.44, dark brown crystal (0.3 × 0.3 × 0.3 mm), monoclinic, space group C2/c (No. 15), a = 20.095(5), b = 9.182(4), c = 16.647(3) Å, β = 116.81(1)°, V = 2741(1) Å<sup>3</sup>, Z = 4, D<sub>calc</sub> = 1.89 g cm<sup>-3</sup>. The structure was refined to R = 3.8% and R<sub>w</sub> = 3.5% for 2528 reflections.

<sup>3</sup> The O<sub>2</sub> uptake in the reaction of Eq. (2) is dependent on the amount of DMF used. When DMF is used in more than 10-fold excess per CuCl (Pd/Cu = 1), the O<sub>2</sub> uptake becomes nearly constant. For example, ~2.6 ml (~0.1 mmol) of O<sub>2</sub> was consumed per 0.5 mmol of CuCl under the conditions using PdCl<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub> (0.5 mmol), CuCl (0.5 mmol), and DMF (10 mmol) in ClCH<sub>2</sub>CH<sub>2</sub>Cl (5 ml) at 35°C under O<sub>2</sub> for 2 h. This reaction gave 0.065 g of complex **2** and 0.084 g of complex **1**. When the complex **2** (0.065 g) obtained was reacted with 1-decene (1 mmol, 0.19 ml) under argon atmosphere (2 h, ClCH<sub>2</sub>CH<sub>2</sub>Cl–DMF), 0.18 mmol of 2-decanone was formed (glc analysis with n-tridecane as internal standard). If O<sub>2</sub> molecules absorbed (~0.1 mmol) in Eq. (2) are all incorporated into 0.065 g of **2**, the O atom transfer from **2** to the alkene can be calculated to be ~90%.

<sup>4</sup> Purification of complex **2** is difficult because of its insolubility into various solvents. From several elemental analyses of **2**, its composition appears to be around x = 4, y = 5, and z = 6.

in Eq. (1), 1-decene (1 mmol) was allowed to react with water in DMF (1 ml) in the presence of complex **1** (0.1 mmol) and O<sub>2</sub> (balloon) at 50°C for 2 h (Eq. (4)). Although the rate of reaction was dependent on the amount of water used, the complex **1** was found to catalyse the reaction. Thus, in the presence of 0.2 mmol of water under the conditions mentioned above, 2-decanone was formed in 200% yield based on Pd. When

the amount of water was increased to 5 mmol, the yield of 2-decanone was 720%. Combined with the isolation of Pd–Cu heterometallic complexes, this result strongly suggests that the oxidation of alkenes with water by a PdCl<sub>2</sub>–CuCl–O<sub>2</sub> system in DMF (Eq. (1)) may be catalysed by a Pd–Cu–DMF heterometallic complex such as **1**, as an alternative to the well-documented redox–catalysis of palladium and copper [8].



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