Preparation and Characterisation of a Palladium–Copper Heterometallic Complex and its Catalytic Activity towards Oxidation of Alkenes

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Treatment of $PdCl_2(MeCN)_2$ and $CuCl_2$ with pyrrolidin-2-one **L** gives a novel Pd–Cu heterometallic complex having a polymeric structure of $[ClCu(\mathbf{L})_4(\mu\text{-}Cl)PdCl_2{\cdot}PdCl_2]_n$ which catalyses the oxidation of cyclohexene in $ClCH_2CH_2Cl$–MeOH.

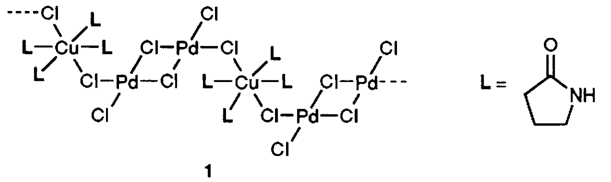
A combination of palladium(II) and copper salts effects a variety of oxidations of alkenes,[1] among which the Wacker oxidation of ethene to acetaldehyde in water is the most fundamental. In contrast to this well known process, we recently found that alk-1-enes are oxidised directly by molecular oxygen in anhydrous, aprotic solvents.[2] This finding reinforces our proposal[3] that a heterometallic species consisting of Pd and Cu is involved in these type of oxidations. However, the isolation and characterisation of such a complex has not been reported. We report here the preparation of a Pd–Cu heterometallic complex and its catalytic activity towards the oxidation of alkenes.

The reaction of $PdCl_2(MeCN)_2$ (520 mg, 2 mmol) and $CuCl_2$ (135 mg, 1 mmol) with excess amount of **L** (850 mg, 10 mmol) in CH_2Cl_2 (20 ml) under argon at room temperature gave a red-brown precipitate (795 mg) in 0.5 h. Recrystallisation of the crude complex from CH_2Cl_2–MeOH–ether (10 : 1 : 20) afforded dark brown crystals (**1**, 631 mg, 76%, mp 147–151 °C decomp) of $CuCl_2(\mathbf{L})_4(PdCl_2)_2$ [eqn (1)] which were suitable for X-ray analysis. **1** can also be obtained by using CuCl (Pd : Cu : L = 1 : 1 : 10) with O_2 in dimethoxyethane (DME) under the same conditions (88% yield based on Pd), since CuCl is oxidised to $CuCl_2$ by O_2 in aprotic solvents.

$$2\,PdCl_2(MeCN)_2 + CuCl_2 \xrightarrow[CH_2Cl_2]{\mathbf{L}} \underset{\mathbf{1}}{[CuCl_2(\mathbf{L})_4(PdCl_2)_2]_n} \qquad (1)$$

X-ray diffraction of **1** (Fig. 1)† revealed a polymeric structure which consisted of alternative units of $CuCl_2(\mathbf{L})_4$ and dimeric $PdCl_2$. The Cu and Pd units are linked by μ-Cl atoms. Since the Cu–Cl and Pd–Cl bond distances are normal [Cu–Cl(1), 2.823(1); Cl(1)–Pd(1), 2.271(1) Å; Cu–Cl(1)–Pd(1), 114.06(5)°], the complex is certainly heterometallic. The Cu atom is on a crystallographic centre of symmetry and is arranged in a tetragonal bipyramidal structure by two μ-Cl atoms and four amides **L**. The four amides coordinate to the Cu atom *via* their carbonyl groups, forming a square planar plane. The bond lengths between Cu and the amide oxygen atoms [Cu–O(1), 1.941(3) Å; Cu–O(2), 1.986(4) Å] are normal.[4] The adjacent amides are linked to each other through a N–H···O hydrogen bond [H(N1)–O(2), 2.08(6) Å; N(1)–O(2) = 2.815(5) Å; N(1)–H(N1)···O(2), 143(5)°],[4b] and the other N–H bond is linked with two Cl atoms *via* N–H···Cl hydrogen bonds [H(N2)···Cl(1), 2.76(6) Å; N(2)–H(N2)···Cl(1), 141(5)°, and H(N2)···Cl(2), 2.58(6) Å; N(2)–H(N2)···Cl(2), 143(5)°].[5] Among these are precedents for heterometallic complexes linked with μ-Cl atoms, such as Pd–Al,[6] Pd–Sn,[7] and Pt–Ag,[8] there is no unambiguous example of a Pd–Cu complex, though such complexes have been proposed to be involved in oxidations of alkenes.[3,9]

The polymeric complex **1** can be recrystallised from a solution of $ClCH_2CH_2Cl$–MeOH (10 : 1), in which the heterometallic structure of **1** is intact. Accordingly, the catalytic oxidation of alkenes with the complex **1** was examined in $ClCH_2CH_2Cl$–MeOH (10 : 1) under O_2. The oxidation of cyclohexene under the conditions shown in eqn. (2) (6 h, 50 °C) gave a mixture of cyclohexanone **2** and 2-cyclohexen-1-one **3** (80 : 20) in 1710% yield (based on Pd). For this oxidation, one may consider that the complex **1** decomposes into its components and acts as a catalyst. However, such a possibility is excluded by the following fact. Since complex **1** is composed of $PdCl_2$, $CuCl_2$, and **L** in a ratio of 2 : 1 : 4, a catalyst was prepared *in situ* by mixing these components in this ratio at 50 °C for 10 min. When cyclohexene was oxidised with this prepared catalyst a 360% yield of **2** and **3** (88 : 12) was formed in 6 h. Obviously, the catalytic efficiency of this catalyst is inferior to that of **1** itself. Therefore, it can be said that the oxidation shown in eqn. (2) is not effected by a simple combination of the components of **1**. Of course, no effective oxidation occurs using $PdCl_2$ catalyst alone (170%) or a



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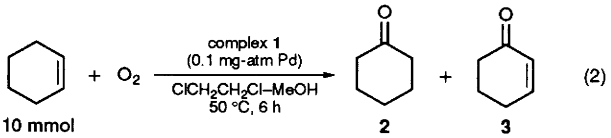

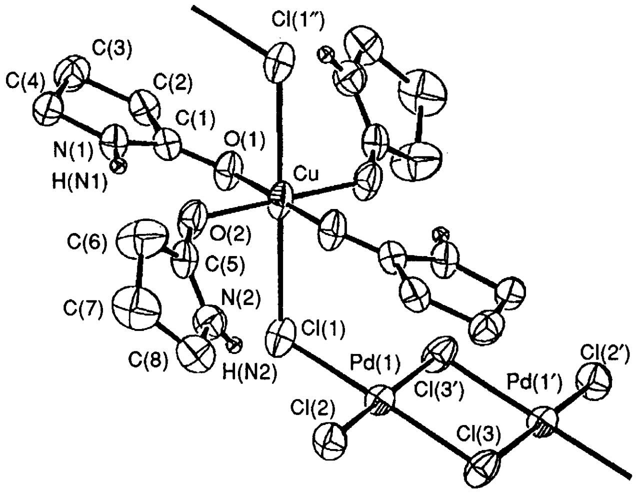

Fig. 1 ORTEP drawing of a part of polymeric complex **1** with adopted atom numbering scheme. Hydrogen atoms on carbon atoms were omitted for clarity. Selected bond length (Å) and angles (°) with esds in parentheses: Cu–Cl(1) 2.823(1), Pd(1)–Cl(1) 2.271(1), Pd(1)–Cl(2) 2.264(1), Pd(1)–Cl(3) 2.329(1), Pd(1)–Cl(3′) 2.331(1), Cu–O(1) 1.943(1), Cu–O(2) 1.986(4), H(N1)···O(2) 2.08(6), H(N2)···Cl(1) 2.76(6), H(N2)···Cl(2) 2.58(6); Cu–Cl(1)–Pd(1) 114.06(5), Cl(1)–Pd(1)–Cl(2) 90.89(5), Cl(2)–Pd(1)–Cl(3) 90.93(5), Cl(3)–Pd(1)–Cl(3′) 86.52(5), Cl(3′)–Pd(1)–Cl(1) 91.80(5), O(1)–Cu–Cl(1) 88.50(11), O(2)–Cu–Cl(1) 90.70(11), O(1)–Cu–O(2) 93.44(15), N(1)–H(N1)···O(2) 143(5), N(2)–H(N2)···Cl(1) 141(5), N(2)–H(N2)···Cl(2) 143(5).

combination with the amide **L** (2 equiv. to Pd) (70%). Under the reaction conditions shown in eqn. (2), the polymeric structure of **1** is possibly cleaved by coordination of the alkene to a $PdCl_2$ unit to form a Pd–Cu–Pd heterometallic complex which acts as a real catalyst. In general, the Pd^{II}-catalysed ketonisation of cyclohexene does not proceed effectively in the conventional manner.[10] The present result is not unexceptional; however, it provides the first example that oxidations of this type are brought about by a Pd–Cu heterometallic catalyst.

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Footnote

† *Crystal Data* for **1**: $C_{16}H_{28}N_4O_4Pd_2CuCl_6$, $M_r = 829.49$, dark brown crystal (0.2 × 0.2 × 0.4 mm), monoclinic, space group $P2_1/c$ (No. 14), $a = 10.8184(19)$, $b = 13.3823(16)$, $c = 10.4782(20)$ Å, $\beta = 115.780(14)°$, $U = 1365.99(43)$ Å^3 (by least-squares refinement on diffractometer angles for 25 centred reflections using graphite monochromated Mo-Kα radiation, $\lambda = 0.71069$ Å), $Z = 2$, $D_c = 2.02$ g cm^{-3}, $\mu = 26.9$ cm^{-1}, $F(000) = 814$. Automated Four-Circle Diffractometer (Rigaku C4), ω-2θ mode with $\Delta\omega = 1.40 + 0.35 \tan\theta$, ω-scan speed = 4°·min^{-1}, $T = 295$ K, 6496 reflections measured ($1.5 \leq \theta \leq 35$, $\pm h, k, l$), 6009 unique [merging $R = 0.039$ after empirical absorption correction (max., min. transmission factors = 1.22, 0.99)], giving 4285 with $F_o > 3\sigma(F_o)$. The structure was partly solved by using the SHELXS 86 and the remaining non-hydrogen atoms were located in succeeding difference Fourier synthesis. Refinement was started by the block diagonal least-squares and finally by the full matrix least-squares method; final R and R_w values are 0.047, 0.068, $S = 1.26$, $(\Delta\rho)$max, min = +0.90, −0.80 eÅ^{-3} near Pd atom on a final difference map. All non-hydrogen atoms were refined with anisotropic thermal parameters. Amide hydrogen atoms were located on a difference Fourier map and refined isotropically. Other hydrogen atoms were included in the calculation with the isotropic temperature parameter B_{Hi} (= B_{eq} of respective carrier atom) on calculated positions (C–H = 0.98 Å) riding on their carrier atoms. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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