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Aliphatic C−H Bond Oxidation of Toluene Using Copper Peroxo Complexes That Are Stable at Room Temperature

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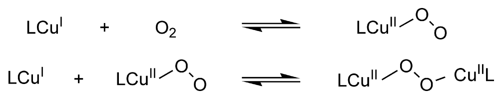
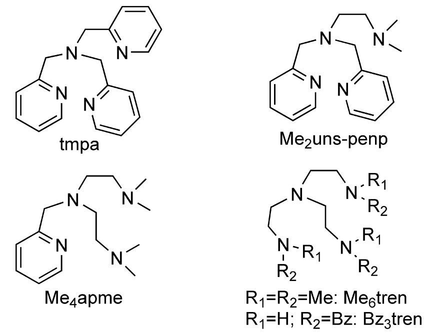
The interaction of copper(I) complexes with dioxygen has been studied intensively during the last 30 years with regard to the possible application of such compounds for the selective catalytic oxidation of organic substrates by air.[1−3] Monooxygenases that contain copper ions in their active sites [e.g., tyrosinase or α-hydroxylating monooxygenase (PHM)] perform selective hydroxylation reactions of organic substrates. Modeling the reactivity of these enzymes using low-molecular-weight copper complexes has attracted much attention. These studies have demonstrated that different copper "dioxygen adduct" complexes form during the interaction of the copper(I) compounds with dioxygen (Scheme 1, which shows only some of the possible reaction pathways). However, there are still open questions with regard to the nature of the active species in the oxidation process. The initially formed end-on "dioxygen adduct complex" in PHM has only recently been structurally characterized, and shortly afterward, some of us obtained the same structural unit in $[Cu(TMG_3tren)O_2]^+$ using tris(tetramethylguanidino)tren (TMG_3tren) as the supporting ligand.[4−6]

Scheme 1. Formation of End-On Superoxo and Peroxo Complexes



Such end-on superoxo complexes often cannot be isolated, as they show a strong tendency to react further to give the corresponding dinuclear peroxo complexes (Scheme 1). The end-on superoxo species (as well as other "dioxygen adduct" complexes) and the dinuclear copper peroxo complexes often must be handled at low temperature (ca. −80 °C).[7−9] Synthetic efforts, sometimes assisted by theoretical calculations, have shown that it is possible to obtain copper peroxo complexes that persist for some time at room temperature by using specially designed ligands.[10,11] The increased stability of the copper peroxo complexes was achieved by connecting mononuclear units to form a preorganized dinuclear system. In contrast, mononuclear copper complexes with the tetradentate tripodal ligands presented in Scheme 2 showed only the formation of thermally very labile dinuclear copper complexes such as $[Cu_2(tmpa)(O_2)](PF_6)_2$, the first crystallographically characterized copper peroxo complex.[7−9,12,13] However, these complexes can be stabilized further if the mononuclear complexes are connected by an appropriate bridge.[14,15]

Scheme 2. Tetradentate Tripodal Ligands



Previous findings by us[13] and others[15] demonstrated the importance of solvent effects on these oxidation reactions. Furthermore, recently we realized that the "right" choice of anion plays an important role. Using tetraphenylborate as the anion allowed a quite stable copper(I) complex with Me_6tren (Scheme 2) as the ligand to be obtained [the crystal structure and data for $[Cu(Me_6tren)]BPh_4$ (**1**) are reported in the Supporting Information (SI)]. This is in stark contrast to our previous findings on the ClO_4^- or PF_6^- salts of this complex, which were found to be extremely labile toward disproportionation.[13]

To our surprise, **1** in the solid state reacted immediately with air to form the extremely stable deep-blue peroxo complex $[Cu_2(Me_6tren)(O_2)](BPh_4)_2$ (**2**) (a movie showing this reaction is available). The molecular structure of **2** (Figure 1) is quite similar to those of the only other two known peroxo complexes of this type, $[Cu_2(tmpa)(O_2)](PF_6)_2$ and $[Cu_2(Bz_3tren)(O_2)](BPh_4)_2$.[12,16,17] However, the crystal packing is quite different within these

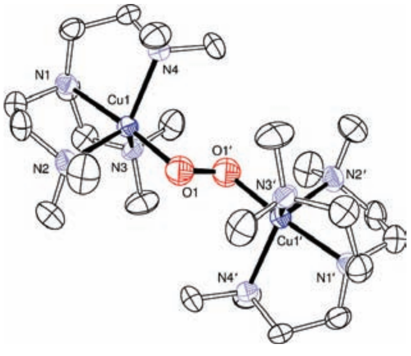


Figure 1. Molecular structure of $[Cu_2(Me_6tren)_2(O_2)]^{2+}$, shown as an ORTEP plot with thermal ellipsoids set at 50% probability.

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complexes, which explains their different observed stabilities, as discussed below. The cation of **2** is completely shielded by eight BPh_4^- anions (Figure 2), and this encapsulation suppresses any further reactions, in contrast to the case for the accessible cation of $[Cu_2(tmpa)(O_2)](PF_6)_2$.

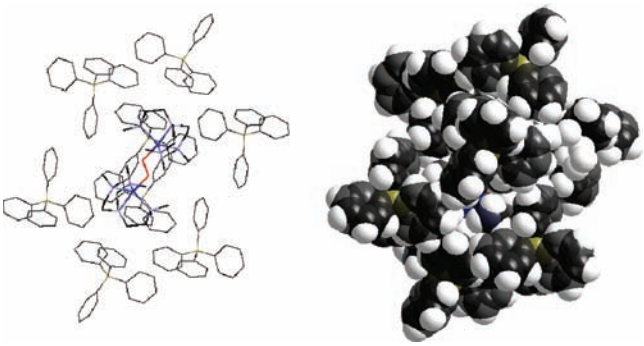


Figure 2. Anion shielding in 2.

Furthermore, a comparison of the crystal structures of complexes **1** and **2** shows that it is reasonably facile for the copper ions to rearrange during the reaction with dioxygen to form the peroxo complex, thus explaining the fast oxidation of **1** in the solid state.

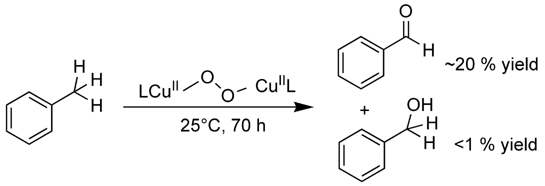
Copper peroxo complexes of the related ligands tmpa, Me_2uns-penp, and Me_4apme (Scheme 2) with tetraphenylborate as the anion can be prepared in a similar manner either by reaction of the precusor complexes with dioxygen in the solid state or by precipitation of the peroxo complexes from solution. All four peroxo complexes obtained can be stored open to air at room temperature (a picture of the four samples is presented in the SI) for a long time (we have not seen degradation of one-year-old samples of the copper peroxo complexes of the ligands Me_2uns-penp and tmpa prepared in our laboratory). Furthermore, it is even possible to heat these samples above 70 °C without any observable decomposition (see the SI).

In contrast to the above findings, it was not possible to stabilize the previously reported peroxo complex $[Cu_2(Bz_3tren)(O_2)](BPh_4)_2$[16,17] in the same manner. Examination of its crystal structure reveals that the sterically demanding benzyl groups do not shield/encapsulate the cationic unit in the same manner as observed in the tmpa, Me_2uns-penp, Me_4apme, and Me_6tren complexes.

While the solid peroxo complexes turned out to be extremely stable, they decomposed immediately when dissolved at room temperature in solvents such as acetone or propionitrile. However, when the solvents were precooled and the sample was cooled to −80 °C as well, solutions of the peroxo complexes were stable and showed UV−vis spectral features identical to those reported previously for these compounds.[1,7−9,16,18] Additionally, we measured resonance Raman spectra of all four solids and confirmed the data obtained previously for some of these compounds in solution or in the solid state (see the SI).[1,9,16,18]

We have demonstrated that peroxo complexes, which have been regarded previously as extremely labile at high temperatures, can be stabilized dramatically in the solid state by employing the correct conditions. Furthermore, the fast reaction of copper(I) complexes with air to form stable peroxo compounds in the solid state was unknown and thus might have application for dioxygen sensing in inert systems. Most interesting, however, is the fact that because of their increased stability, these compounds have a high potential for catalytic applications in selective oxidation reactions. To test this potential, we reacted the four peroxo complexes with technical-grade toluene at room temperature under air and observed the formation of benzaldehyde in yields of up to 20%, along with small amounts of benzyl alcohol (Scheme 3; for details of this reaction, see the SI).

Scheme 3. Oxidation of Toluene



Parallel to our investigations on these systems, excellent work by Karlin and co-workers on similar oxidation reactions using tmpa and derivatives as ligands (with yields of benzaldehyde up to 40%) has been described.[19] Furthermore, they have provided a detailed analysis of possible reaction mechanisms. However, during these studies, dry solvents and dioxygen were used, and reactions were performed in solution at −80 °C. Under our conditions, yields for the tmpa complex system were higher and allowed easier handling of the samples and reaction procedures. We believe that these reactions can be further optimized, and we are currently working on the inclusion of these complexes into solid phases such as mesoporous silica. With our new findings, we are now much closer to the possible application of copper complexes in heterogeneous catalytic oxidation reactions instead of just being limited to their usage in solution at low temperatures.

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Supporting Information Available: Experimental procedures and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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