VIP Switchable Catalyst

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Copper Catalyst Activation Driven by Photoinduced Electron Transfer: A Prototype Photolatent Click Catalyst**

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The development of catalysts with light-controlled activity is a challenging area of current research, with a strong potential for development.[1] Considering transition metal catalysts, the generation of a highly active catalytic species on demand by light irradiation of an inactive precatalyst presents several key benefits: 1) metal species that are stable for handling under ambient conditions; 2) switching on catalysis at a given time and place; 3) tuning the onset of the generated active catalyst by controlling the photoactivation process, which would be valuable for highly exothermic reactions conducted on a large scale. To date, most examples of photocontrolled transition metal catalysts are the so-called photocaged catalysts, which rely on the photodissociation or photodecomposition of ligands in coordinatively saturated metal complexes to generate vacant active sites.[1,2] Inoue and co-workers reported a rare example of a photoswitchable catalyst based on the use of a bulky photoisomerizable styryl pyridine ligand which, in its *Z* form, activates an aluminium porphyrin catalyst through efficient coordination to the metal center.[3] Photoinduced electron transfer to a metal cation might represent a valuable strategy to switch on the activity of metal-based catalysts that are inactive in their high-valent oxidized form, but active in their low-valent reduced form. This oxidation-state dependent activity is typically observed for the copper(I)-catalyzed alkyne-azide cycloaddition (CuAAC) click reaction,[4] a major reaction currently exploited in all fields of the chemical sciences.[5,6] Within the last ten years a large number of catalysts have been developed for this reaction.[7] Their common feature is that copper(I) has to be generated, the reaction proceeding first through the formation of a copper(I)-acetylide, followed by cycloaddition with a copper(I)-bound azide to generate a copper(II)-triazole, which is released by protonation. Among all the catalysts described so far, the only reported latent catalyst is the thermally activated [(NHC)CuCl] complex (NHC = N-heterocyclic carbene) developed by Nolan and co-workers.[8] This complex is inactive under ambient conditions at room temperature (DMSO is used as solvent) but only becomes active if the temperature is raised to 60 °C and water is added to the reaction mixture.

Chow and Buono-Core discovered that certain aromatic ketones, benzophenones in particular, could sensitize the photoreduction of transition-metal ML_2 complexes such as $[Cu(acac)_2]$ (acac = acetylacetonate),[9] $[Ni(acac)_2]$,[10] or $[Cu(Bp)_2]$ (Bp = dihydrobis(1-pyrazolyl)borate) in hydrogen-donating solvents.[11] Extensive studies of the sensitized photochemistry showed that the photoreduction involves quenching of the triplet aromatic ketone, most likely by a charge-transfer complex intermediate, which performs a monoelectronic oxidation of the ligand (L) to generate a ligand-centered radical that abstracts a H atom from the solvent (RCH_2OH). Overall the process generates the reduced complex ML, the protonated ligand L–H, and an α-hydroxy radical R·CHOH.

Herein, we report the synthesis, characterization, preliminary photochemical studies, and catalytic activity of the [Cu(*t*BuBz$_3$tren)ketoprofenate]ketoprofenate complex **1** (Figure 1). This species, which possesses a benzophenone-like chromophore, is the first example of a photolatent click catalyst.

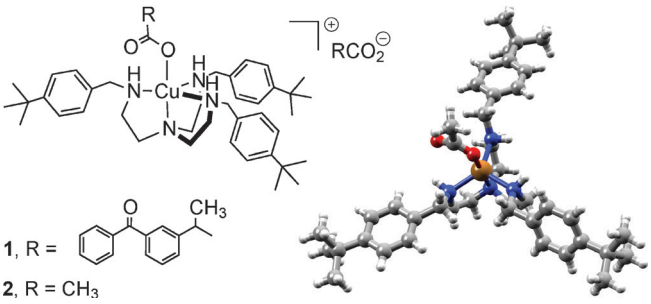

Figure 1. Structural formulas of complexes **1** and **2** (left) and molecular structure of the $[Cu(tBuBz_3tren)CH_3CO_2]^+$ cation (right).

Precatalyst **1** was designed to be easily prepared while possessing two key structural/functional features: 1) A tetradentate tren-derived ligand (tren = tris(2-aminoethyl)amine),

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which should favor the stabilization of the Cu^{I} reduced species, thus preventing the formation of colloidal Cu^{0}, which may occur during the photoreduction process. Moreover we,[12] and others,[13] have previously shown that the copper(I)-tren complexes are excellent click catalysts. 2) A ketoprofenate-ligating counter-anion as a photosensitizing group. Ketoprofen (2-(3-benzoylphenyl)-propionic acid) is a well-known, commercially available non-steroidal anti-inflammatory drug containing a benzophenone chromophore and a carboxylic acid group.

The tBuBz$_3$tren ligand (Bz = benzyl) was prepared in 40% yield of isolated product through a reductive amination reaction (see the Supporting Information for details). The copper(II) complex [Cu(tBuBz$_3$tren)ketoprofenate]-ketoprofenate (**1**) was isolated as a blue powder in 90% yield by reacting the tBuBz$_3$tren ligand with $CuOTf_2$ (OTf = trifluoromethanesulfonate) and the sodium salt of ketoprofen in methanol. Complex **1** was characterized by UV–Vis and FT-IR spectroscopy, elemental analysis, and ESI-MS. In particular, the ESI-MS spectrum (given in the Supporting Information) shows a major peak (100%) at $m/z = 900.49$, which is assigned to the [Cu(tBuBz$_3$tren)ketoprofenate]$^+$ cation, suggesting that one ketoprofenate is bound to the copper(II) ion, as represented in Figure 1. This is further supported by single crystal X-ray diffraction studies of the structural analogue [Cu(tBuBz$_3$tren)CH_3CO_2](CH_3CO_2) (**2**),[23] which reveal a copper(II) ion in a distorted trigonal bipyramidal geometry with an acetate occupying the axial coordination site in a *syn* monodentate mode (Figure 1). As with complex **1**, the ESI-MS spectrum of **2** (given in the Supporting Information) shows an intense peak at $m/z =$ 706.42 (100%), which is attributed to the [Cu(t-BuBz$_3$tren)CH_3CO_2]$^+$ cation.

Complex **1** is fully soluble in most organic solvents, in particular alcohols such as MeOH, which seemed to be an appealing solvent for the photoreduction process.[9–11] Moreover, as MeOH is considered a green solvent,[14] it is a good solvent candidate for click reactions. The copper(II) to copper(I) photoreduction process was first evidenced by following the disappearance of the characteristic visible absorption band of **1**, which is centered at 828 nm and arises from a d–d transition. As shown in Figure 2, when a deoxygenated blue methanolic solution of **1** (1.9 mM) is irradiated at 365 nm, the complete disappearance of the 828 nm absorption band is observed within approximately 30 min and a limpid colorless solution, consistent with the formation of a cuprous [Cu(tBuBz$_3$tren)]$^+$ cationic species, is observed.

The quantum yield for this copper reduction process (Φ_{red}) in methanol was determined to be relatively high at 0.17, in comparison with a ferrioxylate salt actinometer irradiating at 365 nm. This assumes that the photoprocess is the only factor responsible for the changing absorption.[15]

Direct evidence for the clean formation of a cuprous [Cu(tBuBz$_3$tren)]$^+$ cationic species comes from ^{1}H NMR experiments. The ^{1}H NMR spectrum of **1** is characteristic of a paramagnetic complex ($S = {}^1/_2$), affording very broad peaks for the aromatic protons of the ketoprofenate anions and tren ligand (between 7.30 and 8.80 ppm), and the methyl protons of the *tert*-butyl groups (at 1.49 ppm), even if they are quite far from the copper(II) ion (Figure 3). Neither the methylenic

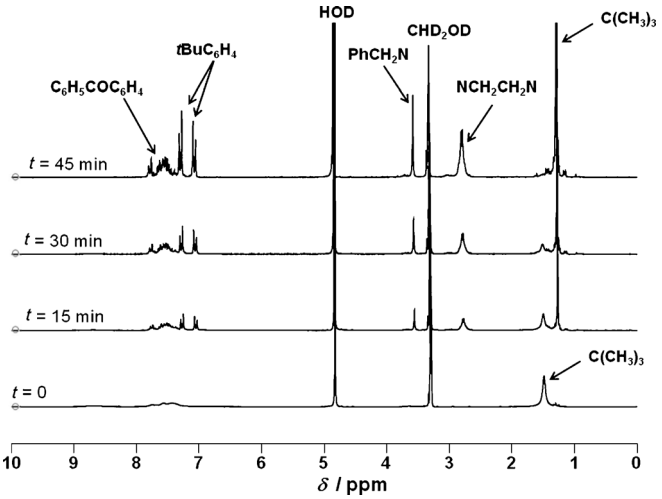

Figure 3. Evolution of the ^{1}H NMR spectrum of a CD_3OD solution of **1** (0.5 mL, 5 mM, deoxygenated by freeze-pump-thaw cycles, sealed tube) upon irradiation of the NMR tube at 365 nm.

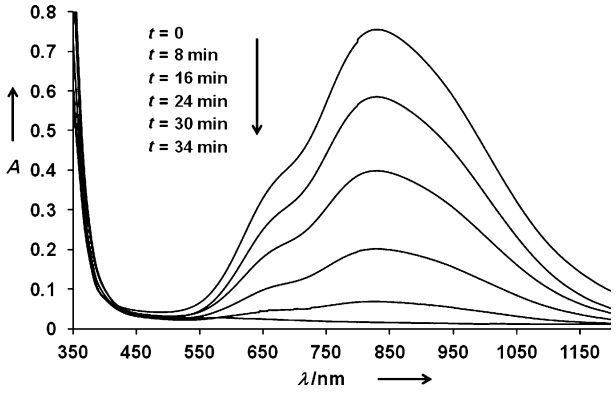

Figure 2. Evolution of the visible absorption spectrum of a MeOH solution of **1** (3 mL, 1.85 mM, deoxygenated by freeze-pump-thaw cycles, sealed cell) upon irradiation at 365 nm.

protons of the benzylic positions and the tren scaffold, nor the aliphatic protons of the ketoprofenate ions are observed. Upon irradiation of the NMR tube, a fast and dramatic change in the spectrum is observed, with the complete disappearance of the broad resonances of **1** within ca. 45 min while, concomitantly, sharp resonances assigned to the diamagnetic ($S = 0$) cuprous [Cu(tBuBz$_3$tren)]$^+$ cation appear. In particular, all of the proton resonances of the tBuBz$_3$tren ligand of the cuprous cation can be clearly identified at 7.28 and 7.06 ppm for the phenyl rings, and at 3.56, 2.78, and 1.27 ppm for the benzylic CH_2, CH_2N, and tBu groups, respectively. The complicated resonance pattern observed for the aromatic protons of ketoprofen is ascribed to the coexistence, after reduction, of several types of ketoprofen species: one ketoprofenate interacting with the copper(I) cation, and one equivalent of ketoprofen (acid form) with respect to copper released during the reduction

process (see the photochemical study below and the proposed mechanism).

To gain insight into the photoreduction mechanism, preliminary transient absorption studies were performed in degassed MeOH solution. On irradiating **1** at 355 nm, a positive transient absorption band is observed in the visible region at 530 nm (Supporting Information, Figure S4), which is characteristic of the triplet ketoprofen, the formation of which is a key primary step in the photoinduced sequence of events.[16,17] Although a similar signature is noted for the ketoprofen alone (acid form), it is clear that the decay kinetics are very different (Supporting Information, Figure S5). The kinetics of the deexcitation of the ketoprofen (acid form) exhibit a typical, relatively slow decay ($\tau = 370$ ns) of the visible transient absorption band,[16,17] which normally involves reaction with methanol, a rather efficient hydrogen donor.[17] For complex **1**, the decay of the absorption band has a time constant of 9.4 ns. Thus, the long decay time constant is dramatically reduced in the presence of the copper complex. As in previous reports by Chow, Buono-Core, and co-workers on the related benzophenone-sensitized photoreduction of $[Ni(acac)_2]$, $[Cu(acac)_2]$, or $[Cu(Bp)_2]$ complexes,[9–11] the observed triplet decay in **1** is thus much faster ($k = 1.0 \times 10^8\ s^{-1}$) than the triplet decay measured in MeOH for the acid form of ketoprofen ($k = 2.7 \times 10^6\ s^{-1}$), which shows the intervention of a fast additional quenching pathway for this excited state in the presence of the copper complex. From these results, and by analogy with previous studies, a tentative mechanism for the reduction process is proposed, according to equations 1–4. Irradiation of **1** produces the ketoprofen (ket) triplet [Eq. (1)] which can be quenched by electron

$$[\text{trenCu(II)ket}]^+ \xrightarrow{h\nu} [\text{trenCu(II)ket*}]^+ \quad (1)$$

transfer from copper(II), see below, leading to a formal $[\text{trenCu}^{\text{III}}\text{ket}^{\bullet-}]^+$ intermediate, followed by a one-electron oxidation of the ligand to generate $[\text{tren}^{\bullet+}\text{Cu}^{\text{II}}\text{ket}^{\bullet-}]^+$ [Eq. (2)]. The resulting ligand-centered radical may then

$$[\text{trenCu(II)ket*}]^+ \xrightarrow[2)\ e^-]{1)\ e^-} [\text{tren}^{\bullet+}\text{Cu(II)ket}^{\bullet-}]^+ \quad (2)$$

abstract an H atom from the H-donating MeOH solvent [Eq. (3)]. A back electron transfer affords the copper(I)

$$[\text{tren}^{\bullet+}\text{Cu(II)ket}^{\bullet-}]^+ + CH_3OH \longrightarrow [\text{trenCu(II)ket}^{\bullet-}] + {}^{\bullet}CH_2OH + H^+ \quad (3)$$

species and regenerates the ketoprofenate counteranion [Eq. (4)]. It is noteworthy that the photoinduced reduction

$$[\text{trenCu(II)ket}^{\bullet-}] \xrightarrow{e^-} [\text{trenCu(I)ket}] \quad (4)$$

does not occur in **2** (where acetate replaces the ketoprofen), which shows the fundamental photostability of the inorganic moiety when irradiating at 365 nm. Moreover, when the methanol solvent is replaced by dichloromethane, which is a poor H-donating solvent, the reduction process is much less efficient as ca. 75% of **1** is reduced after 3 h irradiation (Supporting Information, Figure S1). This is in agreement with a radical process, which necessitates H-atom abstraction [Eq. (3)].

The driving force and hence the feasibility for the initial photoinduced electron transfer [PET; Eq. (2)] can be estimated by considering the difference in potential for oxidation of the ligated Cu^{II} center and the potential for reduction of the excited ketoprofen moiety.[18] The reduction of ketoprofen at −1.36 V (V vs. SCE; SCE = saturated calomel electrode) and the triplet energy of related benzophenones at 3.0 eV have previously been determined.[19,20] Cyclic voltammetry was performed in both methanol and in acetonitrile (wherein the reversibility of the redox processes at the copper center was improved, thus allowing half-wave potential determination, see Figure S6 in the Supporting Information). A fully reversible wave attributed to the Cu^I/Cu^{II} couple (−0.34 V vs. SCE) as well as a quasi-reversible wave corresponding to Cu^{II}/Cu^{III} (+1.29 V vs. SCE) were observed. The tren-like ligand clearly plays an important role in facilitating these two one-electron oxidation processes. The thermodynamic driving force (ΔG^0) for the PET process from Cu^{II} to the ketoprofen triplet is ca. −0.35 eV, showing it to be exothermic and favorable. Further studies will be conducted to confirm the proposed mechanism, in particular the intermediacy of a ligand-centered radical, as unambiguously evidenced for the photoreduction of $[Cu(acac)_2]$ and $[Ni(acac)_2]$.[9,10]

The latent behavior and click reactivity of **1** was probed with the reaction between the unprotected sugar β-D-galactopyranosyl azide (**3**) and propargyl alcohol (**4**), both of which are soluble in methanol. Figure 4 shows the conversion profiles of click reactions run at room temperature in deoxygenated CD_3OD (Ar purged) with 0.5 mol% **1** (reactions followed by ^1H NMR spectroscopy, see Figure S2 in the Supporting Information). It is noteworthy that under ambient conditions **1** exhibits no residual background activity (Figure 4, ●), a crucial parameter when considering effective photoswitchable catalysts. Irradiating the NMR tube at

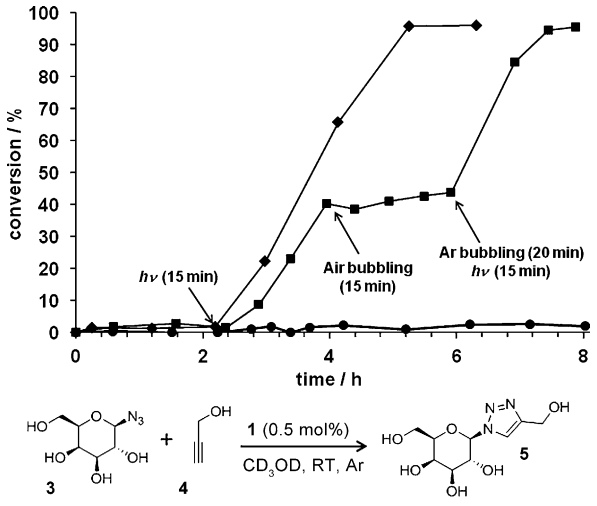

Figure 4. Reaction profiles of CD_3OD solutions (0.33 M, 0.75 mL) of **3** and **4** with **1** (0.5 mol%) followed by ^1H NMR spectroscopy and applying external stimuli.

365 nm for 15 min, for example, after a latency period of 2 h, switches the catalysis on (Figure 4, ◆). The resulting copper(I) catalyst is highly reactive, affording an almost quantitative formation of the triazole **5** in ca. 3 h.

Once started, the reaction can be stopped completely at any time by simply bubbling air through the reaction mixture, because of the almost instantaneous oxidation of the catalyst by molecular oxygen (Figure 4, ■). Indeed, when exposed to air the solution immediately turned green, indicating that the photogenerated copper(I) complex is readily reoxidized by oxygen. Interestingly, the inhibition process is fully reversible. Bubbling Ar through the reaction mixture followed by 15 min irradiation restores the catalytic activity, with a reaction rate similar to that observed before oxygen inhibition (Figure 4). For comparison, conversions of 10–25 % were determined by ^{1}H NMR spectroscopy after 3 h reaction time using 0.5 mol % of $CuSO_4$/sodium ascorbate,[4a] $CuPPh_3CN$,[21] or CuOAc[22] in solvents that provided the best activity for these catalysts in our hands: D_2O for $CuSO_4$ and $CuPPh_3CN$, and CD_3OD for CuOAc (24 h reaction profiles are given in the Figure S3 of the Supporting Information).

Finally, click reactions were conducted for a range of alkynes with aromatic, aliphatic, electron-withdrawing, or bulky substituents (round-bottom flask, 20 min Ar bubbling, 30 min of irradiation). The catalyst loading was 0.5 mol %, except for the ethyl propiolate (1 mol %). The reactions were stopped at > 95 % conversions (determined by ^{1}H NMR) at the times indicated in Figure 5. The pure triazoles **5**–**12** were

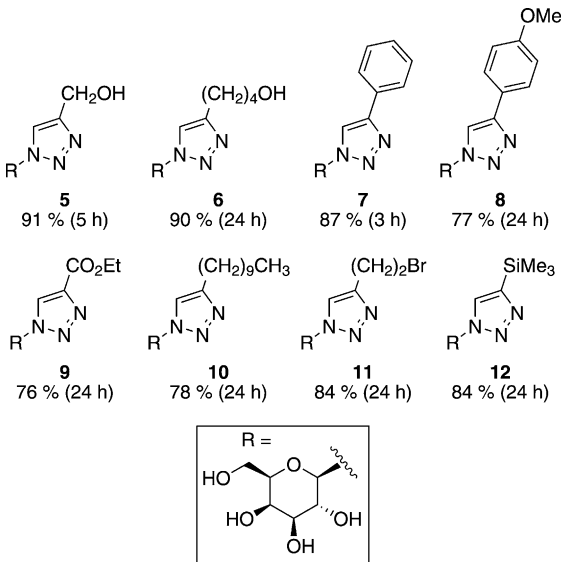

Figure 5. Structures and reaction yields for the triazoles **5**–**12**. Reaction times are shown in parentheses.

isolated in 76–91 % yield without chromatography by simple precipitation upon addition of either diethyl ether or toluene.

In conclusion, by exploiting the benzophenone-derived ketoprophenate counteranion, it is possible to efficiently photoreduce the copper(II) ion of air-stable complex **1** to generate a highly reactive copper(I)-tren click catalyst on demand. From a practical perspective, such photolatent catalysts should prove very useful. Indeed, copper(I)-polyamino/imino complexes possessing accessible coordination sites are well-known to be extremely reactive towards oxygen, thus complicating the preparation, handling, and storage of such compounds. Moreover, when conducting highly exothermic reactions, which is the case with CuAAC, particularly on large scale and/or in high concentration, the use of a catalytic system that can be switched on upon irradiation and switched off by simply introducing air into the reaction medium, should be very attractive. The fact that the onset of the active species can be finely controlled depending on the irradiation time is an additional interesting feature for such applications. Finally, we believe that the reported photoinduced reduction process could be extended, not only to other important copper(I)-catalyzed reactions, but also to other transition-metal-catalyzed processes. Studies along these lines are currently in progress.

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[23] CCDC 867283 (**2**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

