EurJIC
European Journal of Inorganic Chemistry

Research Article
doi.org/10.1002/ejic.202400570

Chemistry Europe
European Chemical Societies Publishing

www.eurjic.org

Stabilizing Copper(I) Complexes by Terminal Olefinic Side Arms and Studying Their Reactivity Towards Oxidation

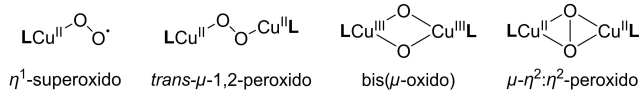
Alexander Granichny,[a] Christian Würtele,[a] and Siegfried Schindler*[a]

Many copper(I) complexes with aliphatic amine ligands have a strong tendency to disproportionate to copper(II) and elemental copper in solution at higher concentrations, making it difficult to isolate them and to study their reactivity. A series of copper(I) complexes with ligands based on tridentate N,N,N′,N″,N″-pentamethldiethylenetriamine (**Me$_5$dien**) were synthesized that included terminal olefinic and aromatic groups. It could be shown that the olefinic side arms stabilized some of the copper(I) complexes. Whether and how strongly the complexes were stabilized depended on the position and length of the olefinic sidearm. Additionally, the reactivity of the copper(I) complexes towards dioxygen was investigated.

Introduction

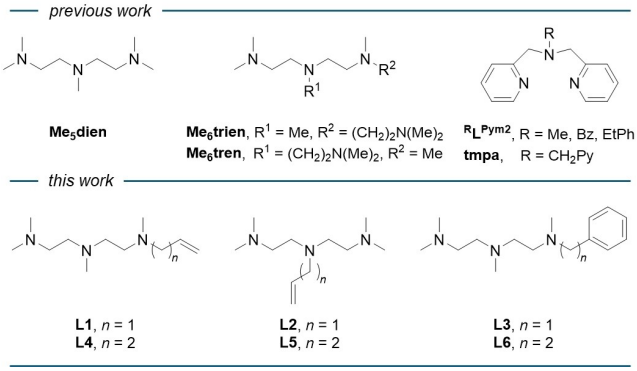
Selective oxygenation reactions are crucial in biological systems, synthesis, and the chemical industry.[1–5] While oxygenation reactions on an industrial scale usually use rare metal catalysts, apply toxic oxidants, and/or require high-pressure and high-temperature environments, enzymatic oxygenations occur in metal ions-containing catalytic pockets under ambient conditions using dioxygen from air. Biomimetic model complexes have been synthesized to study the underlying mechanisms in nature and find green and sustainable catalysts.[1–3] Especially copper(I) complexes are of particular interest because they can activate dioxygen, forming so-called "oxygen adduct complexes" (Scheme 1), which can oxygenate external substrates such as toluene to benzaldehyde.[6–8]

To observe these "oxygen adduct complexes", it is usually necessary to apply low-temperature stopped-flow techniques due to their short lifetime. The reactivity of a large number of copper(I) complexes towards dioxygen has been investigated and the results are summarized in several review articles.[1–4] However, it is important to point out that most of the time, it is not even possible to detect these reactive species spectroscopically despite the low temperatures. This happens when the consecutive reactions after the formation of the intermediates are much faster and thus do not allow their observation. For example, the copper complex [Cu(**Me$_6$trien**)]$^+$ (**Me$_6$trien** = N,N′-bis[2′(dimethylamino)ethyl]-N,N′-dimethyl-ethane-1,2-diamine, Scheme 2) reacts with dioxygen to the corresponding copper(II) complex without detection of an intermediate.[9] Unfortunately,



η^1-superoxido *trans*-μ-1,2-peroxido bis(μ-oxido) μ-η^2:η^2-peroxido

Scheme 1. Selection of "oxygen adduct complexes" (charges are omitted) formed by the reaction of copper(I) with dioxygen.[2]



Scheme 2. Ligands for copper(I) complexes discussed in here.[8–10,12,14,20,22–26]

many copper(I) complexes with aliphatic amine ligands have a strong tendency to disproportionate to copper(II) and elemental copper in solution at higher concentrations, making it difficult to isolate them and to study their reactivity.[10,11] However, if complex formation is faster than its reaction with dioxygen, it is possible to investigate this reaction by mixing an inert solution of a copper(I) salt with a dioxygen-saturated ligand solution using stopped-flow techniques.[12] An example is the copper(I) complex with the tridentate ligand N,N,N′,N″,N″-pentamethyldiethylenetriamine (**Me$_5$dien**, Scheme 2), which shows decomposition at higher concentrations.[12] For this system, the copper(I) salt, ligand, and dioxygen were rapidly mixed in a low-temperature stopped-flow setup, generating the copper(I) complex *in situ*, which then reacted with dioxygen. Applying this method, the formation of a bis(μ-oxido)dicopper(III) complex was spectroscopically observed.[12,13] A problem with this procedure is the introduction of acetonitrile derived from the copper(I) salts [Cu(MeCN)$_4$]$^+$. Acetonitrile is a strongly coordinat-

[a] *A. Granichny, C. Würtele, S. Schindler*
Institute of Inorganic and Analytical Chemistry, Justus Liebig University Giessen, Heinrich-Buff-Ring 17, Giessen 35392 Germany
E-mail: siegfried.schindler@anorg.chemie.uni-giessen.de

Supporting information for this article is available on the WWW under https://doi.org/10.1002/ejic.202400570

Research Article
doi.org/10.1002/ejic.202400570

ing ligand for copper(I), which leads to the stabilization of copper(I) complexes. However, it often leads to the suppression of the reaction with dioxygen.

Some copper(I) complexes are stabilized by sterically demanding anions.[6] The copper(I) complex with the tetradentate tripodal ligand tris(2-dimethylaminoethyl)amine (**Me$_6$tren**, Scheme 2), for example, has a strong tendency for disproportionation but can be stabilized to a large extent by applying tetraphenylborate as an anion.[6] Thus, the complex can be isolated as a colorless crystalline solid. However, kinetic studies were performed as described above by mixing an inert solution of a copper(I) salt with a dioxygen-saturated solution of **Me$_6$tren**.[10,14] At low temperatures, the so-formed copper(I) complex first reacts to a mononuclear η^1-superoxido copper(II) complex before forming a relatively stable *trans*-μ-1,2-peroxido dicopper(II) complex (Scheme 1). This contrasts the copper(I) complex with its isomer **Me$_6$trien** (described above), for which no intermediate could be spectroscopically detected.[9] It is interesting to note at this point that the copper(I) complex of the isomeric ligand **Me$_6$trien** can be obtained by a comproportionation reaction of the copper(II) complex with elemental copper, which was impossible with **Me$_6$tren**.[9,15] Furthermore, it is possible in some cases to achieve stabilization by synthesizing the corresponding copper(I) carbonyl complexes, for example [Cu(**tmpa**)(CO)]$^+$ (**tmpa** = tris(2-pyridylmethyl)-amine, Scheme 2).[16–18] However, here, the reaction with dioxygen was triggered by photodissociation, and it was determined that the photolabile carbonyl species in solution possessed a tridentate coordination mode to the copper(I) ion with one dangling arm of the tripodal ligand.[18]

Compared to using additional ligands like acetonitrile or carbon monoxide, which are prone to be non-removable and make the copper center sterically inaccessible to associative substitution by dioxygen,[16,18] aromatic ligands like benzene proved to be more hemilabile.[19] Itoh and co-workers showed that incorporating an ethylphenyl arm into $^{R}L^{Pym2}$ stabilizes the complex compared to its labile methyl or benzyl derivatives (Scheme 2). This is due to a d-π interaction of the copper(I) ion and the phenyl group of the ligand side arm forming a bis(μ-oxido)dicopper(III) complex upon oxygenation.[8,20–22] The absence of a binding mode in the benzyl derivative is due to the shorter linker, which shows that the position of the side arm and the linker length are important to stabilize the complex. Although the incorporation of aromatic groups binding the copper(I) ion is well established by now, the analogous use of olefinic units so far is underexplored. One example of a ligand containing an intramolecular olefinic arm is **L1** (Scheme 2) by Meyerstein and co-workers, whose copper(I) complex showed enhanced stability in aqueous solutions compared to complexes with ligands **Me$_5$dien** and **Me$_6$trien**.[23–25] This prompted us to reinvestigate the copper(I) complex with **L1** to explore its stability in solution and if the allyl function has any implication regarding the reactivity towards dioxygen. In addition, a series of related derivates was synthesized to study the above-mentioned influence of isomerism (**L2**), aromaticity (**L3**), and elongated linker length (**L4**–**L6**, Scheme 2).

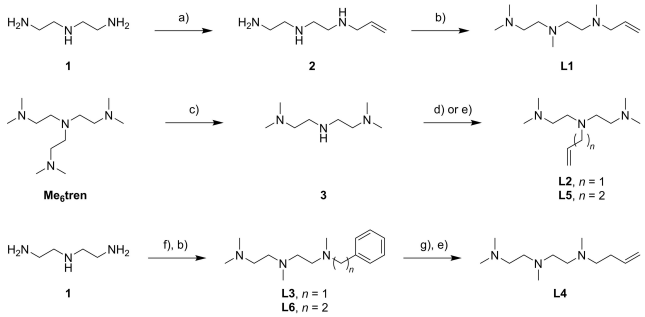
Results and Discussion

Synthesis of Ligands L1–L6

The ligands **L1**–**L6** were prepared according to Scheme 3. The synthesis of **L1** has been described in the literature by Meyerstein and co-workers and modified for this work.[23] In contrast to the literature, the reaction of diethylenetriamine (**1**) with allyl bromide did not yield pure monoalkylated (**2**). Instead, a mixture of mono- and dialkylated products was received and purified after subsequent Eschweiler-Clarke methylation to obtain **L1**. The synthesis of the symmetrical ligands **L2** and **L5** started with N,N,N′′,N′′-tetramethyldiethylenetriamine (**3**), which was synthesized from **Me$_6$tren** and *n*-BuLi according to a published procedure.[27] While deprotonation by sodium hydride and subsequent alkylation by allyl bromide was sufficient to obtain **L2** a different approach had to be chosen for **L5** due to the lower reactivity of 4-bromo-1-butene compared to allyl bromide. Hence, potassium iodide is added to exchange the bromide for iodide by a Finkelstein reaction to form a better-leaving group, which can alkylate **3** with potassium carbonate as a base to obtain **L5**. The aromatic ligands **L3** and **L6** were synthesized by reductive amination with benzaldehyde or phenylacetaldehyde and subsequent Eschweiler-Clarke methylation. The synthesis of **L4** starts from **L3** following a benzyl deprotection with palladium on charcoal and hydrogen and subsequent alkylation like for **L5** with potassium iodide, potassium carbonate, and 4-bromo-1-butene.

Synthesis, Characterization, and Dioxygen Reactivity of the Copper(I) Complexes with Ligands L1 and L4

Numerous efforts failed to obtain crystals of the copper(I) complexes with ligands **L1** and **L4** for structural characterization. Therefore, the complexes were characterized by elemental analysis (EA) and nuclear magnetic resonance (NMR) measurements. The synthesis of the copper(I) complex of **L1** was carried out by mixing [Cu(MeCN)$_4$]OTf and **L1** in acetonitrile before removing the solvent overnight *in vacuo*. While the synthesis of copper(I) complexes in acetonitrile can be a



Scheme 3. Synthesis of ligands **L1**–**L6**. a) allyl bromide, EtOH, RT; b) CH_2O, acetic acid, reflux; c) *n*-BuLi, *n*-pentane, 0 °C to RT, d) NaH, allyl bromide, THF, 0 °C to RT (**L2**); e) KI, K_2CO_3, 4-bromo-1-butene, THF, reflux (**L5**); f) $NaBH(OAc)_3$, benzaldehyde (**L3**) or phenylacetaldehyde (**L6**), DCM, RT; g) Pd/C, H_2, MeOH, RT.

Research Article
doi.org/10.1002/ejic.202400570

hindrance, *vide supra*, both EA and NMR spectra showed no presence of acetonitrile coordinating to the complex (Figure 1b). The colorless appearance, the absence of acetonitrile, and the high field shift of the olefinic protons of the copper(I) complex of **L1** compared to the ligand implies that the allylic side arm is coordinated to the copper ion and thus stabilizes it (Figure 1). The overall results show that the copper(I) complex is stabilized by the coordination of the allylic side arm in solid and organic solutions. The corresponding copper(II) complex could be structurally characterized, and, as expected, the allylic side arm is not coordinated with the copper(II) ion. The molecular structure of [Cu(**L1**)(H_2O)(OTf)](OTf) is shown in Figure 2, where the allylic side arm (double bond located between C(1) and C(2)) is pointing outwards away from the copper center. The copper(II) ion is coordinated in a distorted square pyramidal geometry (according to an analysis developed by Addison et al. with $\tau_5 = 0.3$)[28] by three N-donor atoms (N(1), N(2), N(3)) of **L1**, a water molecule (O(1)), and a triflate anion (O(2)).

Reacting a colorless solution of the copper(I) complex [Cu(**L1**)]OTf with dioxygen at −80 °C in acetone in a benchtop experiment first led to a bright yellow color, which then turned rapidly to green and finally to a blue-colored solution. Low-temperature stopped-flow UV-vis measurements revealed the fast formation of a bis(μ-oxido)dicopper(III) complex with an absorbance maximum at 406 nm (Figure 3), in line with previous investigations.[2,12,29] After a few seconds, decomposition of the "oxygen adduct" complex is observed. Extracting the oxygenated solution by basic workup and investigating it with GC-MS revealed that the ligand remains intact, and no intramolecular hydroxylation or demethylation occurred (Figure S34, S35). Furthermore, the reaction under pseudo-first-order conditions is independent of dioxygen concentration. The overall observations are similar to the reaction of [Cu(**Me$_5$dien**)(MeCN)]$^+$ with dioxygen.[12] However, for this complex, we had to perform the reaction *in situ* and could not avoid the presence of additional acetonitrile in the solution.

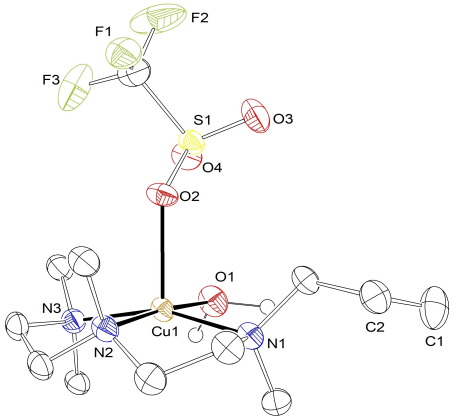


Figure 2. ORTEP Plot of the molecular structure of [Cu(**L1**)(H_2O)(OTf)](OTf). Non-binding anions and carbon-bound hydrogen atoms are omitted for clarity (except H_2O). Ellipsoids are drawn at 50% probability. Selected Bond Lengths (Å): Cu(1)–N(1): 2.088; Cu(1)–N(2): 2.028; Cu(1)–N(3): 2.087; Cu(1)–O(1): 2.014; Cu(1)–O(2): 2.259; C(1)–C(2): 1.318. Selected bond angles (°): N(1)–Cu(1)–N(2): 85.28; N(1)–Cu(1)–N(3): 158.99; N(2)–Cu(1)–N(3): 85.76; N(1)–Cu(1)–O(1): 94.37; N(1)–Cu(1)–O(2): 99.58; N(2)–Cu(1)–O(1): 174.69; N(2)–Cu(1)–O(2): 93.71; N(3)–Cu(1)–O(1): 92.82; N(3)–Cu(1)–O(2): 99.92; O(1)–Cu(1)–O(2): 91.57.

The mechanism for the formation of the bis(μ-oxido)dicopper(III) complex can be assigned in the same way as reported previously.[12,20,30] According to Scheme 4, the forma-

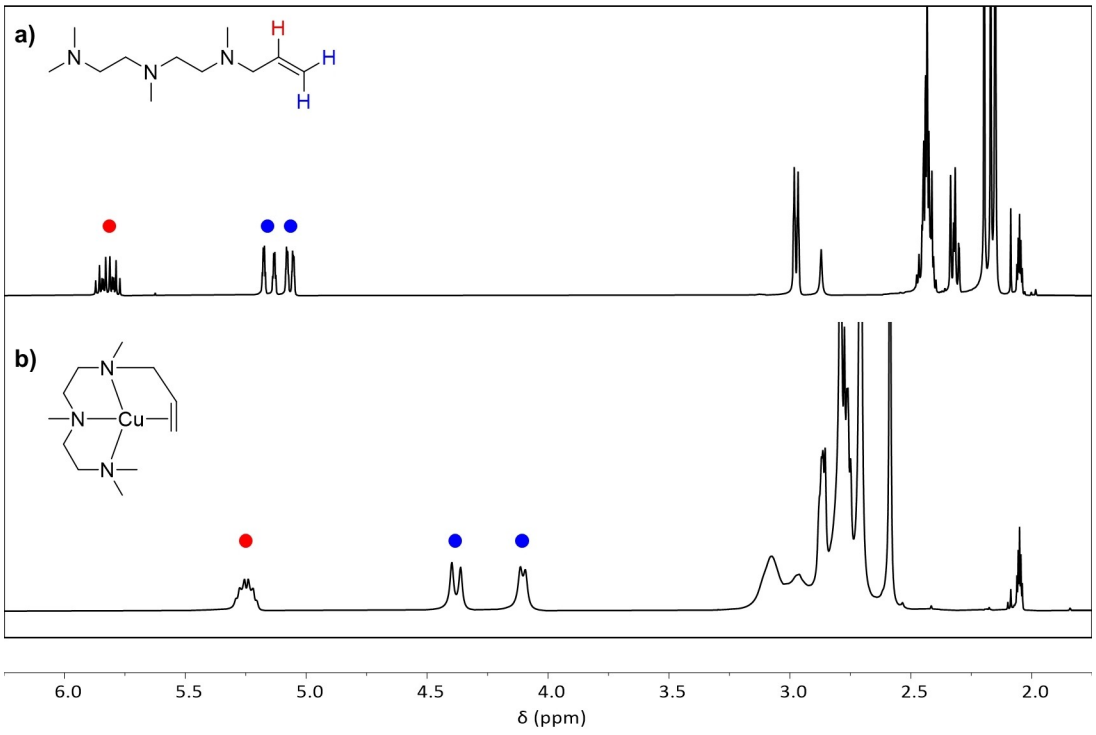


Figure 1. ^{1}H NMR spectra of (a) **L1**, (b) [Cu(**L1**)](OTf) measured in $(CD_3)_2CO$ at room temperature. Charges and anions are omitted for clarity.

Research Article
doi.org/10.1002/ejic.202400570

Chemistry Europe
European Chemical Societies Publishing

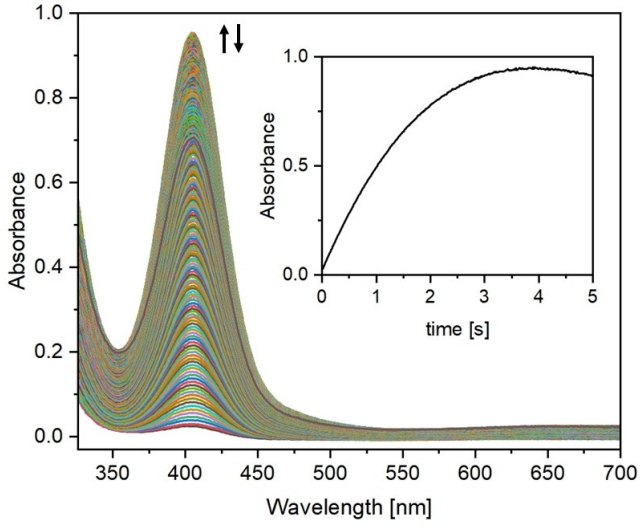
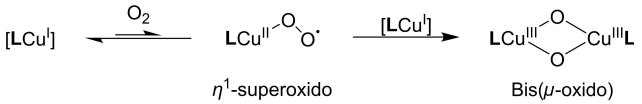


Figure 3. Time-resolved UV-vis spectra of the reaction of [Cu(**L1**)]OTf ($2.5 \cdot 10^{-4}$ mol L^{-1}) with dioxygen ($5.7 \cdot 10^{-3}$ mol L^{-1})[5] in acetone at −80 °C over a period of 5 s. The inset displays the time-dependent change in absorbance at 406 nm.



Scheme 4. Proposed mechanism for the formation of the bis(μ-oxido)dicopper(III) complex.

tion of an unstable η^1-superoxido complex in a rapid left-lying preequilibrium is proposed, followed by the reaction with another copper(I) complex to form the observed bis(μ-oxido)dicopper(III) complex.

Thus, we successfully stabilized this copper/dioxygen system by introducing an olefinic group. This conveys that incorporating the allyl sidearm into the ligand scaffold suppressed the disproportionation of the copper(I) complex in solid and solution and did not interfere with the activation of dioxygen. Considering the different reaction conditions, the bis(μ-oxido)dicopper(III) complex with the ligand **L1** lasts for a few seconds longer than with the ligand **Me$_5$dien** before decomposition under the same conditions (Figure S31). Additionally, we observed that the *in situ* reaction with **L1** did not work out. Here, the formation of the copper(I) complex is slower than the reaction of the complex with dioxygen, and only a very small part of the overall reaction could be spectroscopically detected.

Because chelate ring size plays an important role,[31] we investigated the copper(I) complex with ligand **L4**, which differs from **L1** by an elongated olefinic sidearm. As for the copper(I) complex with **L1**, the allylic protons were shifted to high field, and no acetonitrile was found to be coordinated (Figure S21, S22). The difference in linker length caused the copper(I) complex with **L4** as a ligand to become so stable that it did not react with dioxygen anymore (even at room temperature, Figure S32). This is a well-known phenomenon that larger chelate rings can stabilize copper(I) complexes to such an extent that they become less or even unreactive towards dioxygen.[31] Furthermore, it shows that an optimal linker length of the olefinic side arm is crucial for a ligand that can stabilize the copper(I) ion while still being reactive toward dioxygen.

Synthesis, Characterization, and Reactivity Towards Dioxygen of the Copper(I) Complexes with Ligands L2, L3, L5, and L6

After establishing that incorporating an allylic sidearm into the ligand scaffold of **Me$_5$dien** leads to a stable yet reactive copper(I) complex, and its elongated derivative led to an overstabilized and unreactive copper(I) complex; further insights were yet to be obtained. By comparing **L1** with its derivatives, the effect of isomerism (**L2**), aromaticity (**L3**), and elongated linker length (**L5**, **L6**) were studied (Scheme 2). The corresponding copper(I) complexes were synthesized and characterized, and the reactivity with dioxygen was tested. Unfortunately, again crystals of copper(I) as well as of copper(II) complexes with these ligands suitable for structural characterization could not be obtained. Disproportionation was observed for copper(I) complexes with ligands **L2** and **L3**.

The constitutional isomers **L2** and **L5** differ from **L1** and **L4** only by having the olefinic side arm attached to the central instead of the lateral amines. Analogous to the copper(I) complexes of **L1** and **L4** its isomeric complexes with **L2** and **L5** as ligands do not contain a coordinated acetonitrile according to elemental analysis and NMR spectra (Figure S17, S18). However, the copper(I) complex of **L2** showed disproportionation upon isolation, visible by a pale blue appearance (instead of being colorless) and broad signals in the ^{1}H-NMR spectrum (Figure S17). Nevertheless, reactions with the copper(I) complex of **L2** and dioxygen were conducted with stopped-flow measurements at −80 °C in acetone, revealing the formation of a small band at 409 nm resembling a bis(μ-oxido)dicopper(III) complex (Figure S33A), similar to the band appearing for **L1**. The measurements have been repeated under the same conditions with freshly generated copper(I) complex of **L2** in acetone, which showed a much higher absorbance at the same wavelength compared to the isolated complex (Figure S33B). The overall findings showed that the constitutional isomer **L2** cannot stabilize the copper(I) ion, likely due to the position of the allylic group, which is too rigid and not flexible enough to coordinate sufficiently.

Furthermore, the copper(I) complex with the elongated ligand **L5** confirms this. The copper(I) complex is stable in solution and upon isolation. It reacts in benchtop experiments at −80 °C in acetone to a bright, yellow-colored solution before decomposing to a green-colored solution. However, no "oxygen adduct" species was detectable by stopped-flow measurements under the same conditions. Only the formation of the corresponding copper(II) complex is observed by a slow buildup of a shoulder at 359 nm and a broad band at 656 nm over the period of one hour (Figure 4). By comparing the spectra with its corresponding copper(II) complex, it is reasonable that the

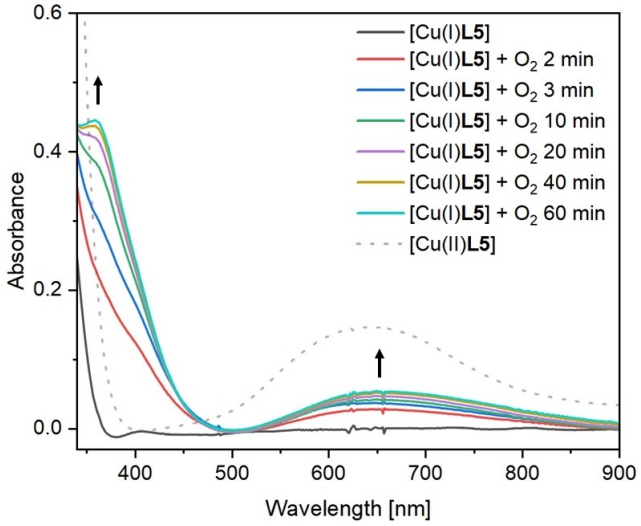


Figure 4. UV-vis spectra of the reaction of [Cu(**L5**)]OTf ($5.0 \cdot 10^{-4}$ mol L^{-1}) with dioxygen gas in acetone at −80 °C over a period of 60 min compared with its corresponding copper(II) complex [Cu(**L5**)$(MeCN)_2$]$(OTf)_2$ ($5.0 \cdot 10^{-4}$ mol L^{-1}).

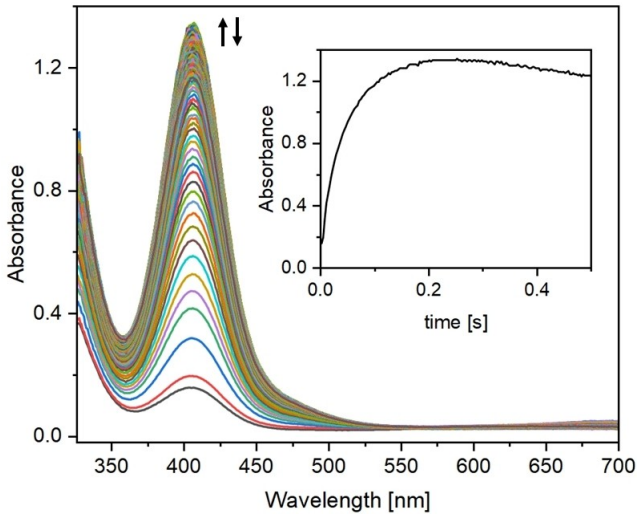


Figure 5. Time-resolved UV-vis spectra of the reaction of [Cu(**L3**)(MeCN)]OTf ($2.5 \cdot 10^{-4}$ mol L^{-1}) with dioxygen ($5.7 \cdot 10^{-3}$ mol L^{-1})[5] in acetone at −80 °C over a period of 0.5 s. The inset displays the time dependent change in absorbance at 406 nm.

broad band shows the formation of copper(II) while the shoulder is likely decomposed ligand.

Following the work by Itoh and co-workers[8] with the ligand $^{R}L^{Pym2}$, aromatic groups were introduced in our ligand system instead of aliphatic olefinic groups, leading to ligands **L3** and **L6**. The synthesis of the copper(I) complex with **L3** as a ligand resulted in a green-colored oil, which turned out to be the mono acetonitrile copper(I) complex through EA and NMR spectra (Figure S19, S20). No shifts in the aromatic region were detected by comparing the ^{1}H and ^{13}C-NMR of **L3** and its corresponding copper(I) complex (Figure S29a, S29b, S30a, S30b). This means that the benzylic side arm is not attached to the copper(I) ion, explaining the reason for the coordinated acetonitrile and, therefore, closely resembles $^{Bz}L^{Pym2}$.[8] The color of the isolated copper(I) complex and a broad band in the 500–700 nm range in the UV-vis spectrum indicated disproportionation, similar to the copper(I) complex with **L2** as a ligand. Stopped-flow measurements with the copper(I) complex of **L3** were conducted at –80 °C in acetone, revealing the formation of a band at 406 nm, indicating a bis(μ-oxido)dicopper(III) complex (Figure 5). While the reactivity of the copper(I) complex with dioxygen is analogous to the copper(I) complexes with **L1** and **L2**, the oxygen adduct starts decaying a magnitude faster. This is likely due to the missing coordination of the benzylic sidearm, which is why the complex is mainly stabilized by the coordinated acetonitrile, making the complex more labile and reactive. Measurements at different dioxygen concentrations under the same conditions showed that the reaction rate was independent of dioxygen concentration. These results are in line with the reactivity of the copper(I) complex of **L1**, and the same mechanism can be proposed (Scheme 4). **L3** compares well with $^{Bz}L^{Pym2}$ because the linker of the additional benzylic side arm is not long enough to bind to the copper(I) center, and therefore the isolated complex coordinated acetonitrile and decomposed partially.[8,20] However, the direct comparison with **L1**, which has the same methyl linker, can coordinate the copper(I) ion, showing that it is likely the rigid nature of the aromatic group that hinders coordination.

The copper(I) complex with **L6** showed no sign of disproportionation, and coordination of acetonitrile was not observed. While the ^{1}H-NMR seemed to suggest that the ethylphenyl side arm was not attached to the copper(I) ion (Figure S29c, S29d), the ^{13}C-NMR clearly showed that two carbon signals of the phenyl group are significantly shifted and broadened (in comparison with the ligand), confirming that the ethylphenyl side arm is coordinated to the copper(I) ion (Figure S30c, S30d). By elongating the linker length from **L3** to **L6**, the phenylic side arm becomes more flexible, coordinates with the copper ion, and stabilizes the complex. In stopped-flow experiments with the copper(I) complex of **L6** the formation of an absorption band at 409 nm again showed the formation of a bis(μ-oxido)dicopper(III) complex (Figure 6). The spectra, as well as the lifetime of the dioxygen adduct complex with **L6** as a ligand, resembles the one with **L1** more than with **L3**, likely because the increased linker length now allows the phenylic side arm to coordinate the copper(I) ion and therefore reacts slower than the corresponding complex with coordinated acetonitrile. This is very similar to the above-discussed results by Itoh and co-workers and their finding that the ligand system $^{R}L^{Pym2}$ with a benzyl side arm is not stable, while its derivative with an ethylphenyl derivative is.[20] Here, the authors could support their findings with molecular structures of the corresponding copper complexes.

Conclusions

In this work, we established with derivatives of **Me$_5$dien** that adding terminal olefinic side arms into a ligands scaffold can

Research Article
doi.org/10.1002/ejic.202400570

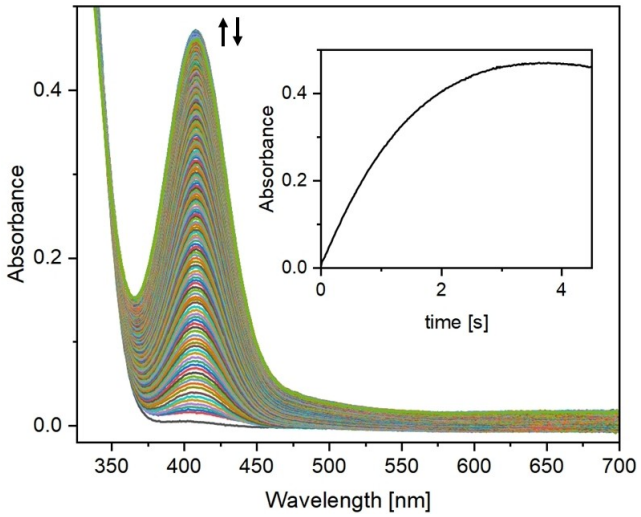


Figure 6. Time-resolved UV-vis spectra of the reaction of [Cu(**L6**)]OTf ($2.5 \cdot 10^{-4}$ mol L^{-1}) with dioxygen ($5.7 \cdot 10^{-3}$ mol L^{-1})[5] in acetone at −80 °C for 4.5 s. The inset displays the time-dependent change in absorbance at 409 nm.

stabilize the corresponding copper(I) complexes upon isolation and in solution in contrast to the non-derivatized ligand. Whether and how strongly the complexes are stabilized highly depends on the position and length of the olefinic sidearm. Generally, sterically hindered positions require a longer linker to bind the copper(I) ion than sterically less hindered positions. However, linkers that are too lengthy over-stabilize the copper(I) complexes, which then become unsusceptible to further reactions with dioxygen. This is not unusual as copper(I) complexes can be pretty stable towards oxidation due to donor atoms and/or the size of the chelate ring or the anion.[31] Furthermore, oxidation of a copper(I) to a copper(II) complex is much more common than observing an intermediate in this process due to the kinetics of this reaction.[32] In addition, we showed that olefinic side arms need shorter linkers to sufficiently bind the copper(I) ions compared to phenylic side arms at the same position, which is probably due to the higher flexibility. Furthermore, the dioxygen activation of the copper(I) complexes was tested. The best result was obtained with the ligand **L1** (reported previously by the Meyerstein group), whose position and length of the allylic side arm allow it to bind the copper(I) ion strongly enough to stabilize it while binding weakly enough to react with dioxygen. According to the mechanism shown in Scheme 4, which had been assigned previously,[20,30] first a η^1-superoxido copper(II) complex forms before reacting to the observed bis(μ-oxido)dicopper(III) complex, confirming that the olefinic side arm does not affect the intermediate formed as it is the same as for **Me_5dien**. The difficulty in spectroscopically observing the η^1-superoxido complex as an intermediate was demonstrated by DFT calculations on related systems.[33] Only recently, England and coworkers obtained and characterized an η^1-superoxido copper(II) complex by using a sterically encumbered tridentate ligand.[34]

All in all, our work demonstrates that incorporating olefinic side arms into a ligand scaffold is a non-invasive way to study the oxygen adduct formation of labile copper(I) complexes. To further elaborate on this methodology, ligands can be equipped with olefinic side arms that form unstable copper(I) complexes to study their dioxygen activation in the future.

Experimental Section

Materials and Methods: Air-sensitive copper(I) complexes were synthesized under inert conditions in a glove box (MBraun, Germany) filled with argon 5.0. Solvents and reagents were used as purchased from common suppliers unless stated otherwise. **Me_6tren**, **3**, and [Cu(MeCN)$_4$]OTf were prepared according to the literature and stored in the glove box.[27,35] Solvents used to synthesize copper complexes were bought as anhydrous solvents under nitrogen atmosphere, distilled under argon, and stored in the glove box. NMR measurements were performed using a Bruker Avance II 400 MHz, Bruker Avance III 400 MHz HD, Bruker Avance III 600 MHz HD, and Bruker Avance Neo 700 MHz spectrometer. The ^{1}H- and ^{13}C-NMR spectra were calibrated using the residual proton and carbon signals of acetone ($\delta = 2.05$ and $\delta = 29.8$).[36] ESI-MS (HRMS) was measured using a Bruker Daltonica micrOTOF. Elemental analysis was carried out using a Thermo FlashEA-1112 series CHN-analysator. GC-MS measurements were carried out using an Agilent Technologies 5977B mass detector with a 7820 A GC system. UV-vis measurements were carried out using an Agilent 8453 spectrometer. Stopped-Flow UV-vis measurements were performed on a commercial HI-TECH SF61SX2 stopped-flow unit (TgK Scientific, Bratford-on-Avon, UK). The data were processed using Kinetic Studio version 5.02 Beta. The procedure for kinetic measurements was described in detail in previous work.[37] Details of X-Ray crystal structure determination are reported in the Supporting Information. Deposition Number 2376264 (for [Cu(**L1**)(MeCN)](OTf)$_2$) contains the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

Preparation of L1: A modified version of the synthesis reported in the literature[23] was used to obtain **L1**. Allyl bromide (7.0 g, 5.0 mL, 0.058 mol) in 20 mL of dry ethanol was added dropwise to a solution of diethylenetriamine (17.9 g, 18.7 mL, 0.175 mol) in 50 mL dry ethanol over the course of 3 h at 0 °C. Then 5 g KOH was added to the reaction mixture, and the colorless precipitate obtained was removed by filtration. The solvent was removed under reduced pressure. The excess amine was removed from the reaction mixture by distillation with a Vigreux column at 91 °C and 15 mbar, while the crude intermediate product was collected above 92 °C (4.80 g). The latter was dissolved in 20 mL acetic acid at 0 °C, then 30 mL formaldehyde (30 wt%) was added. The reaction mixture was refluxed overnight. After cooling to room temperature, the reaction mixture was made basic with aq. NaOH and extracted three times with 50 mL DCM. The combined organic phases were dried over Na_2SO_4, and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (DCM, MeOH 10 : 1 + 1 % NEt_3) and a colorless oil (1.39 g, 6.99 mmol, 12 %, $R_f = 0.2$) was received. ^{1}H NMR (400 MHz, acetone-d_6): δ [ppm] = 5.87–5.77 (m, 1H, C*H*=CH$_2$), 5.19–5.12 (m, 1H, CH=C*H*$_2$), 5.09–5.04 (m, 1H, CH=C*H*$_2$), 2.99–2.95 (m, 2H, C*H*$_2$–CH=CH$_2$), 2.48–2.39 (m, 6H), 2.34–2.29 (m, 2H), 2.20 (s, 3H, N–(C*H*$_3$)), 2.17 (s, 3H, N–(C*H*$_3$)), 2.15 (s, 6H, N–(C*H*$_3$)$_2$); ^{13}C NMR (101 MHz, acetone-d_6): δ [ppm] = 137.5, 116.9, 61.9, 58.6, 57.1, 57.0, 56.1, 46.1, 43.3, 42.8; HRMS (ESI): m/z calcd. for $C_{11}H_{25}N_3$: 200.2121 $[M+H]^+$; found: $m/z = 200.2120$.

Preparation of L2: To a suspension of NaH (0.573 g, 23,3 mmol) in 100 mL dry THF N,N,N′′,N′′-tetramethldiethylenetriamine (**3**) (3.38 g,

21,2 mmol) was added dropwise over the course of 5 min at 0 °C. After stirring the reaction for 1 h at 0 °C allyl bromide (2.82 g, 2.02 mL, 23.3 mol) was added dropwise over the course of 10 min, and the reaction mixture was allowed to warm to room temperature, at which it was stirred for 19 h. Then 14 mL of deionized water were added, and the reaction was stirred for 10 min before the solvent was removed under reduced pressure. The residue was taken up in 70 mL NaOH (1 mol L^{-1}) and extracted three times with 135 mL DCM. The combined organic phases were dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (DCM, MeOH 10:1 + 2% NEt_3) and a colorless oil (0.328 g, 1.64 mmol, 8%, R_f = 0.34) was received. ^{1}H NMR (400 MHz, acetone-d_6): δ [ppm] = 5.89–5.78 (m, 1H, C*H*=CH_2), 5.20–5.14 (m, 1H, CH=C*H*$_2$), 5.09–5.04 (m, 1H, CH=C*H*$_2$), 3.12 (dt, J = 6.3, 1.4 Hz, 2H, C*H*$_2$–CH=CH_2), 2.57–2.52 (m, 4H), 2.35–2.30 (m, 4H), 2.15 (s, 12H, N−(C*H*$_3$)$_4$); ^{13}C NMR (101 MHz, acetone-d_6): δ [ppm] = 137.7, 116.7, 58.8, 53.2, 46.2; HRMS (ESI): m/z calcd. for $C_{11}H_{25}N_3$: 200.2121 $[M+H]^+$; found m/z = 200.2123.

Preparation of L3: To a solution of diethylenetriamine (1.00 g, 1.04 mL, 9.69 mmol) and benzaldehyde (1.03 g, 0.99 mL, 9.69 mmol) in 30 mL DCM sodium triacetoxyborohydride (3.02 g, 14.5 mmol) was added. After stirring the reaction for 3 h at RT, the reaction was quenched with water, was made basic with aq. NaOH and extracted three times with 30 mL DCM. The combined organic phases were dried over Na_2SO_4, and the solvent was removed under reduced pressure. Without further purification the crude product was dissolved in 4 mL acetic acid at 0 °C and then 4.5 mL formaldehyde (30 wt%) were added. The reaction mixture was refluxed overnight. After cooling to room temperature, the reaction mixture was made basic with aq. NaOH and extracted three times with 30 mL DCM. The combined organic phases were dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (DCM, MeOH 50:1 to 10:1 + 1% NEt_3) and a colorless oil (0.378 g, 1.51 mmol, 15%, R_f = 0.25) was received. ^{1}H NMR (400 MHz, acetone-d_6): δ [ppm] = 7.35–7.27 (m, 4H, Ph), 7.24–7.19 (m, 1H, Ph), 3.50 (s, 2H, C*H*$_2$–Ph), 2.54–2.46 (m, 4H), 2.46–2.41 (m, 2H), 2.34–2.30 (m, 2H), 2.19 (s, 3H, N–(C*H*$_3$)), 2.17 (s, 3H, N–(C*H*$_3$)), 2.14 (s, 6H, N–(C*H*$_3$)$_2$); ^{13}C NMR (101 MHz, acetone-d_6): δ [ppm] = 140.7, 129.6, 128.9, 127.6, 63.3, 58.6, 57.1, 57.0, 56.3, 46.1, 43.3, 42.9; HRMS (ESI): m/z calcd. for $C_{15}H_{27}N_3$: 250.2278 $[M+H]^+$; found m/z = 250.2278.

Preparation of L4: To a solution of **L3** (2.21 g, 8.88 mmol) in 200 mL MeOH palladium on carbon (10 wt.%) (0.94 g, 0.89 mmol) was added. The reaction mixture was stirred at room temperature under a hydrogen atmosphere at atmospheric pressure (balloon) for 13 h. The suspension was filtered, and the solvent was removed under reduced pressure to receive the crude intermediate product (0.766 g) as a yellow oil. Without further purification, the crude product and 4-bromo-1-butene (0.71 g, 0.54 mL, 5.29 mmol) were dissolved in 50 mL THF, and KI (0.884 g, 5.29 mmol) and K_2CO_3 (1.33 g, 9.62 mmol) were added. the reaction mixture was refluxed for 40 Then 10 mL deionized water were added, and the reaction was stirred for 10 min before the THF was removed under reduced pressure. The residue was taken up in 20 mL aq. KOH and extracted four times with 40 mL DCM. The combined organic phases were dried over Na_2SO_4, and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (DCM, MeOH 10:1 + 1% NEt_3) and a colorless oil (0.155 g, 0.728 mmol, 8%, R_f = 0.21) was received. ^{1}H NMR (400 MHz, acetone-d_6): δ [ppm] = 5.88–5.77 (m, 1H, C*H*=CH_2), 5.07–5.00 (m, 1H, CH=C*H*$_2$), 4.96–4.91 (m, 1H, CH=C*H*$_2$), 2.46–2.38 (m, 8H), 2.35–2.31 (m, 2H), 2.23–2.17 (m, 8H), 2.16 (s, 6H, N–(C*H*$_3$)$_2$); ^{13}C NMR (101 MHz, acetone-d_6): δ [ppm] = 138.1, 115.5, 58.6, 58.4, 57.1, 57.0, 56.6, 46.1, 43.3, 42.7, 32.7; HRMS (ESI): m/z calcd. for $C_{12}H_{27}N_3$: 214.2278 $[M+H]^+$; found m/z = 214.2279.

Preparation of L5: To a suspension of KI (1.06 g, 6.39 mmol) and K_2CO_3 (1.60 g, 11.6 mmol) in 50 mL THF, **3** (0.925 g, 1.00 mL, 5.81 mmol) and 4-bromo-1-butene (0.86 g, 0.65 mL, 6.39 mmol) were added and the reaction mixture was kept under reflux for 26 Then 10 mL deionized water were added, and the reaction was stirred for 10 min before the THF was removed under reduced pressure. The residue was taken up in 20 mL aq. KOH and extracted four times with 40 mL DCM. The combined organic phases were dried over Na_2SO_4, and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (DCM, MeOH 10:1 + 1% NEt_3), and a colorless oil (0.219 g, 1.03 mmol, 18%, R_f = 0.21) was received. ^{1}H NMR (400 MHz, acetone-d_6): δ [ppm] = 5.89–5.77 (m, 1H, C*H*=CH_2), 5.06–5.00 (m, 1H, CH=C*H*$_2$), 4.96–4.91 (m, 1H, CH=C*H*$_2$), 2.58–2.50 (m, 6H), 2.35–2.29 (m, 4H), 2.22–2.17 (m, 2H), 2.16 (s, 12H, N–(C*H*$_3$)$_4$); ^{13}C NMR (101 MHz, acetone-d_6): δ [ppm] = 138.2, 115.5, 58.9, 55.4, 53.6, 46.2, 32.8; HRMS (ESI): m/z calcd. for $C_{12}H_{27}N_3$: 214.2278 $[M+H]^+$; found m/z = 214.2280.

Preparation of L6: To a solution of diethylenetriamine (1.14 g, 1.19 mL, 11.1 mmol) and phenylacetaldehyde (1.34 g, 1.30 mL, 11.1 mmol) in 30 mL DCM sodium triacetoxyborohydride (3.53 g, 16.7 mmol) was added. After stirring the reaction for 6 h at RT the reaction was quenched with water, was made basic with aq. NaOH, and extracted three times with 30 mL DCM. The combined organic phases were dried over Na_2SO_4 and the solvent was removed under reduced pressure. Without further purification the crude product was dissolved in 5 mL acetic acid at 0 °C and then 5.5 mL formaldehyde (37 wt%) were added. The reaction mixture was refluxed overnight. After cooling to room temperature, the reaction mixture was made basic with aq. NaOH and extracted three times with 30 mL DCM. The combined organic phases were dried over Na_2SO_4, and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (DCM, MeOH 20:1 + 1% NEt_3), and an orange oil (0.309 g, 1.17 mmol, 11%, R_f = 0.26) was received. ^{1}H NMR (400 MHz, acetone-d_6): δ [ppm] = 7.29–7.21 (m, 4H, Ph), 7.19–7.13 (m, 1H, Ph), 2.77–2.72 (m, 2H, C*H*$_2$–Ph), 2.62–2.57 (m, 2H, C*H*$_2$–C*H*$_2$–Ph), 2.52–2.47 (m, 2H), 2.47–2.41 (m, 4H), 2.35–2.30 (m, 2H), 2.27 (s, 3H, N–(C*H*$_3$)), 2.20 (s, 3H, N–(C*H*$_3$)), 2.15 (s, 6H, N–(C*H*$_3$)$_2$); ^{13}C NMR (101 MHz, acetone-d_6): δ [ppm] = 141.9, 129.6, 129.0, 126.6, 60.8, 58.6, 57.2, 57.1, 56.5, 46.2, 43.3, 42.9, 34.5; HRMS (ESI): m/z calcd. for $C_{16}H_{29}N_3$: 264.2434 $[M+H]^+$; found m/z = 264.2435.

General procedure for the synthesis of copper(I) complexes: In an argon-filled glovebox, the ligand and copper salt were each dissolved in dry acetonitrile. Then, the copper solution was added dropwise under vigorous stirring to the ligand solution at room temperature. The reaction mixture was stirred for 30 min, and subsequently, the solvent was removed under reduced pressure to obtain the complex without further purification.

[Cu(L1)]OTf: Following the general procedure **L1** (100 mg, 0.502 mmol) and [Cu(MeCN)$_4$]OTf (180 mg, 0.478 mmol) in 6 mL dry acetonitrile were used to obtain the corresponding complex as a colorless solid (194 mg, 0.472 mmol, 99%). ^{1}H NMR (400 MHz, acetone-d_6): δ [ppm] = 5.31–5.18 (m, 1H, C*H* = CH_2), 4.38 (d, J = 14.5 Hz, 1H CH=C*H*$_2$), 4.10 (d, J = 7.9 Hz, 1H, CH=C*H*$_2$), 3.18–2.72 (m, 14H), 2.71 (s, 6H, N–(C*H*$_3$)$_2$), 2.59 (s, 3H, N–(C*H*$_3$)); ^{13}C NMR (101 MHz, acetone-d_6): δ [ppm] = 122.40 (q, J = 322.4 Hz, OTf), 100.9, 79.7, 59.6, 59.2, 58.9, 55.7, 55.2, 48.4, 46.0, 45.8; Elemental analysis calcd. (%) for $C_{12}H_{25}CuF_3N_3O_3S$: C 34.99, H 6.12, N 10.20; found: C 35.28, H 6.06, N 10.02.

[Cu(L2)]OTf: Following the general procedure **L2** (100 mg, 0.502 mmol) and [Cu(MeCN)$_4$]OTf (180 mg, 0.478 mmol) in 6 mL dry acetonitrile were used to obtain the corresponding complex as a pale blue solid (199 mg, 0.472 mmol, 97%). ^{1}H NMR (400 MHz,

acetone-d_6): δ [ppm] = 5.22 (s, 1H, C*H*=CH$_2$), 4.78 (s, 1H, CH=C*H*$_2$), 4.62 (s, 1H, CH=C*H*$_2$), 3.84 (s, 2H, C*H*$_2$–CH=CH$_2$), 3.48–2.46 (m, 20H); ^{13}C NMR (101 MHz, acetone-d_6): δ [ppm] = 122.1 (q, J = 321.4 Hz, OTf), 96.5, 88.2, 59.7, 58.8, 48.8; Elemental analysis calcd. (%) for $C_{12}H_{25}CuF_3N_3O_3S$: C 34.99, H 6.12, N 10.20; found: C 35.22, H 5.98, N 10.27.

[Cu(L3)(MeCN)]OTf: Following the general procedure **L3** (125.3 mg, 0.502 mmol) and [Cu(MeCN)$_4$]OTf (180 mg, 0.478 mmol) in 6 mL dry acetonitrile were used to obtain the corresponding complex as a green oil (248 mg, 0.472 mmol, 98%). ^{1}H NMR (400 MHz, acetone-d_6): δ [ppm] = 7.58–7.54 (m, 2H, Ph), 7.45–7.34 (m, 3H, Ph), 3.87 (s, 2H, C*H*$_2$–Ph), 2.90–2.64 (m, 8H), 2.63 (s, 3H, N–(C*H*$_3$)), 2.59 (s, 6H, N–(C*H*$_3$)$_2$), 2.34 (s, 3H, N–(C*H*$_3$)), 2.24 (s, 3H, MeCN); ^{13}C NMR (101 MHz, acetone-d_6): δ [ppm] = 136.2, 131.3, 129.1, 128.9, 122.5 (q, J = 322.3 Hz, OTf), 117.3 (MeCN), 65.2, 59.8, 57.7, 55.2, 55.0, 48.9, 46.4, 43.3, 1.9 (MeCN); Elemental analysis calcd. (%) for $C_{18}H_{30}CuF_3N_4O_3S$: C 42.98, H 6.01, N 11.14; found: C 43.12, H 5.48, N 11.62.

[Cu(L4)]OTf: Following the general procedure **L4** (53 mg, 0.25 mmol) and [Cu(MeCN)$_4$]OTf (90 mg, 0.24 mmol) in 3 mL dry acetonitrile were used to obtain the corresponding complex as a colorless solid (98 mg, 0.23 mmol, 96%). ^{1}H NMR (700 MHz, acetone-d_6): δ [ppm] = 5.02–4.94 (m, 1H, C*H*=CH$_2$), 4.36 (d, J = 15.3 Hz, 1H, CH=C*H*$_2$), 4.27 (d, J = 8.9 Hz, 1H, CH=C*H*$_2$), 3.05–2.79 (m, 6H), 2.77 (s, 3H, N–(C*H*$_3$)), 2.75–2.67 (m, 6H), 2.64 (s, 3H, N–(C*H*$_3$)), 2.62 (s, 3H, N–(C*H*$_3$)), 2.53–2.47 (m, 1H), 2.32–2.27 (m, 1H), 2.04–1.99 (m, 1H); ^{13}C NMR (176 MHz, acetone-d_6): δ [ppm] = 102.6, 82.5, 59.6, 55.9, 55.6, 55.0, 54.2, 50.6, 48.0, 46.8, 45.0, 31.8; Elemental analysis calcd. (%) for $C_{13}H_{27}CuF_3N_3O_3S$: C 36.66, H 6.39, N 9.86; found: C 36.52, H 6.48, N 9.60.

[Cu(L5)]OTf: Following the general procedure **L5** (53 mg, 0.25 mmol) and [Cu(MeCN)$_4$]OTf (90 mg, 0.24 mmol) in 3 mL dry acetonitrile were used to obtain the corresponding complex as a colorless solid (99 mg, 0.23 mmol, 98%).^{1}H NMR (700 MHz, acetone-d_6): δ [ppm] = 5.57–5.49 (m, 1H, C*H*=CH$_2$), 4.61–4.56 (m, 1H, CH=C*H*$_2$), 4.56–4.53 (m, 1H, CH=C*H*$_2$), 3.09–3.06 (m, 2H), 2.98–2.87 (m, 4H), 2.82–2.69 (m, 4H), 2.66 (s, 12H, (N–(C*H*$_3$)$_2$)$_2$), 2.28 (q, J = 6.3 Hz, 2H); ^{13}C NMR (176 MHz, acetone-d_6): δ [ppm] = 114.3, 88.9, 60.8, 55.9, 51.6, 49.4, 34.8; Elemental analysis calcd. (%) for $C_{13}H_{27}CuF_3N_3O_3S$: C 36.66, H 6.39, N 9.86; found: C 36.68, H 6.41, N 9.97.

[Cu(L6)]OTf: Following the general procedure **L6** (66 mg, 0.25 mmol) and [Cu(MeCN)$_4$]OTf (90 mg, 0.24 mmol) in 3 mL dry acetonitrile were used to obtain the corresponding complex as a colorless solid (113 mg, 0.238 mmol, 99%). ^{1}H NMR (600 MHz, acetone-d_6): δ [ppm] = δ 7.51 (t, J = 7.5 Hz, 2H, Ph), 7.37–7.30 (m, 3H, Ph), 3.18–2.86 (m, 4H, (C*H*$_2$)$_2$=Ph), 2.83–2.08 (m, 20H); ^{13}C NMR (151 MHz, acetone-d_6): δ [ppm] = 129.1, 127.2, 122.8 (broad), 122.5 (q, J = 322.3 Hz, OTf), 117.6 (broad), 59.48, 57.1, 54.9, 54.6, 54.5, 49.2 (broad), 48.5 (broad), 46.0, 45.5, 33.1; Elemental analysis calcd. (%) for $C_{17}H_{29}CuF_3N_3O_3S$: C 42.89, H 6.14, N 8.83; found: C 43.53, H 6.20, N 8.75.

[Cu(L1)(MeCN)](OTf)$_2$: Following the general procedure **L1** (50 mg, 0.25 mmol) and Cu(OTf)$_2$ (91 mg, 0.25 mmol) in 1 mL dry acetonitrile were used to obtain the corresponding complex as a blue solid (160 mg, 0.25 mmol, 99%). Elemental analysis calcd. (%) for $C_{15}H_{28}CuF_6N_4O_6S_2$: C 29.92, H 4.69, N 9.31; found: C 29.72, H 4.72, N 9.19. Slow evaporation of a complex solution in methanol resulted in blue crystals suitable for X-ray structural characterization.

Oxygenation Reaction of [Cu(L1)]OTf: To investigate whether the ligand **L1** is still intact after oxidation of the corresponding copper(I) complex with dioxygen, the copper was extracted, and the organic residue was analyzed. For that, [Cu(L1)]OTf (40 mg, 0.097 mmol) was dissolved in 10 mL acetone, and dioxygen was bubbled through the solution for 5 min at −80 °C. After the solution warmed up to room temperature 20 mL aq. ammonia was added and the solution was extracted three times with 20 mL DCM. The combined organic phases were dried over Na_2SO_4, and the solvent was removed under reduced pressure. The organic residue was analyzed using GC-MS.

Acknowledgements

We gratefully acknowledge the Justus Liebig University Gießen and the German Research Foundation (Deutsche Forschungsgemeinschaft; SS, SCHI 377/20-1) for financial support. Project DEAL enabled and organized open-access funding. Open Access funding enabled and organized by Projekt DEAL.

Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: Bioinorganic chemistry · Copper · Dioxygen activation · Olefines · Stabilization

[1] E. A. Lewis, W. B. Tolman, *Chem. Rev.* **2004**, *104*, 1047.
[2] L. M. Mirica, X. Ottenwaelder, T. D. P. Stack, *Chem. Rev.* **2004**, *104*, 1013.
[3] C. E. Elwell, N. L. Gagnon, B. D. Neisen, D. Dhar, A. D. Spaeth, G. M. Yee, W. B. Tolman, *Chem. Rev.* **2017**, *117*, 2059.
[4] D. A. Quist, D. E. Diaz, J. J. Liu, K. D. Karlin, *J. Biol. Inorg. Chem.* **2017**, *22*, 253.
[5] H. Sterckx, B. Morel, B. U. W. Maes, *Angew. Chem. Int. Ed.* **2019**, *58*, 7946.
[6] C. Würtele, O. Sander, V. Lutz, T. Waitz, F. Tuczek, S. Schindler, *J. Am. Chem. Soc.* **2009**, *131*, 7544.
[7] C. Noß, R. Göttlich, S. Schindler, *Chem. Eur. J.* **2023**, *29*, e202301142.
[8] H. R. Lucas, L. Li, A. A. N. Sarjeant, M. A. Vance, E. I. Solomon, K. D. Karlin, *J. Am. Chem. Soc.* **2009**, *131*, 3230.
[9] M. Becker, F. W. Heinemann, F. Knoch, W. Donaubauer, G. Liehr, S. Schindler, G. Golub, H. Cohen, D. Meyerstein, *Eur. J. Inorg. Chem.* **2000**, *2000*, 719.
[10] M. Becker, F. W. Heinemann, S. Schindler, *Chem. Eur. J.* **1999**, *5*, 3124.
[11] J. Becker, Y. Y. Zhyhadlo, E. D. Butova, A. A. Fokin, P. R. Schreiner, M. Förster, M. C. Holthausen, P. Specht, S. Schindler, *Chem. Eur. J.* **2018**, *24*, 15543.
[12] J. Astner, M. Weitzer, S. P. Foxon, S. Schindler, F. W. Heinemann, J. Mukherjee, R. Gupta, V. Mahadevan, R. Mukherjee, *Inorg. Chim. Acta* **2008**, *361*, 279.
[13] S. Schindler, *Eur. J. Inorg. Chem.* **2000**, *2000*, 2311.
[14] M. Weitzer, S. Schindler, G. Brehm, S. Schneider, E. Hörmann, B. Jung, S. Kaderli, A. D. Zuberbühler, *Inorg. Chem.* **2003**, *42*, 1800.
[15] a) G. Golub, H. Cohen, D. Meyerstein, *J. Chem. Soc. Chem. Commun.* **1992**, *5* 397; b) G. Golub, H. Cohen, P. Paoletti, A. Bencini, D. Meyerstein, *J. Chem. Soc. Dalton Trans.* **1996**, *10*, 2055.
[16] M. Pasquali, C. Floriani, G. Venturi, A. Gaetani-Manfredotti, A. Chiesi-Villa, *J. Am. Chem. Soc.* **1982**, *104*, 4092.
[17] D. V. Scaltrito, H. C. Fry, B. M. Showalter, D. W. Thompson, H. C. Liang, C. X. Zhang, R. M. Kretzer, E. Kim, J. P. Toscano, K. D. Karlin, et al., *Inorg. Chem.* **2001**, *40*, 4514.

[18] H. C. Fry, H. R. Lucas, A. A. N. Sarjeant, K. D. Karlin, G. J. Meyer, *Inorg. Chem.* **2008**, *47*, 241.
[19] G. J. Karahalis, A. Thangavel, B. Chica, J. Bacsa, R. B. Dyer, C. C. Scarborough, *Inorg. Chem.* **2016**, *55*, 1102.
[20] T. Osako, Y. Ueno, Y. Tachi, S. Itoh, *Inorg. Chem.* **2003**, *42*, 8087.
[21] T. Osako, Y. Tachi, M. Doe, M. Shiro, K. Ohkubo, S. Fukuzumi, S. Itoh, *Chem. Eur. J.* **2004**, *10*, 237.
[22] X. Zhong, C. J. Bouchey, E. Kabir, W. B. Tolman, *J. Inorg. Biochem.* **2021**, *222*, 111498.
[23] N. Navon, G. Golub, H. Cohen, P. Paoletti, B. Valtancoli, A. Bencini, D. Meyerstein, *Inorg. Chem.* **1999**, *38*, 3484.
[24] N. Navon, H. Cohen, P. Paoletti, B. Valtancoli, A. Bencini, D. Meyerstein, *Ind. Eng. Chem. Res.* **2000**, *39*, 3536.
[25] N. Navon, A. Burg, H. Cohen, R. van Eldik, D. Meyerstein, *Eur. J. Inorg. Chem.* **2002**, *2002*, 423.
[26] M. J. Scott, R. H. Holm, *J. Am. Chem. Soc.* **1994**, *116*, 11357.
[27] H. Luitjes, M. Schakel, G. W. Klumpp, *Synth. Commun.* **1994**, *24*, 2257.
[28] A. W. Addison, T. N. Rao, J. Reedijk, J. van Rijn, G. C. Verschoor, *J. Chem. Soc. Dalton Trans.* **1984**, *7*, 1349.
[29] S. Mahapatra, J. A. Halfen, E. C. Wilkinson, G. Pan, X. Wang, V. G. Young, C. J. Cramer, L. Que, W. B. Tolman, *J. Am. Chem. Soc.* **1996**, *118*, 11555.
[30] H.-C. Liang, C. X. Zhang, M. J. Henson, R. D. Sommer, K. R. Hatwell, S. Kaderli, A. D. Zuberbühler, A. L. Rheingold, E. I. Solomon, K. D. Karlin, *J. Am. Chem. Soc.* **2002**, *124*, 4170.
[31] M. Schatz, M. Becker, F. Thaler, F. Hampel, S. Schindler, R. R. Jacobson, Z. Tyeklár, N. N. Murthy, P. Ghosh, Q. Chen, et al., *Inorg. Chem.* **2001**, *40*, 2312.
[32] M. Becker, S. Schindler, R. van Eldik, *Inorg. Chem.* **1994**, *33*, 5370.
[33] A. Hoffmann, M. Wern, T. Hoppe, M. Witte, R. Haase, P. Liebhäuser, J. Glatthaar, S. Herres-Pawlis, S. Schindler, *Eur. J. Inorg. Chem.* **2016**, *2016*, 4744.
[34] S. Debnath, S. Laxmi, O. McCubbin Stepanic, S. Y. Quek, M. van Gastel, S. DeBeer, T. Krämer, J. England, *J. Am. Chem. Soc.* **2024**, *146*, 23704.
[35] a) D. F. Shriver, *Inorganic Syntheses*, Wiley, New York **1979**; b) G. J. P. Britovsek, J. England, A. J. P. White, *Inorg. Chem.* **2005**, *44*, 8125.
[36] G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw, K. I. Goldberg, *Organometallics* **2010**, *29*, 2176.
[37] M. Weitzer, M. Schatz, F. Hampel, F. W. Heinemann, S. Schindler, *J. Chem. Soc. Dalton Trans.* **2002**, 686.
[38] L. Krause, R. Herbst-Irmer, G. M. Sheldrick, D. Stalke, *J. Appl. Crystallogr.* **2015**, *48*, 3.
[39] G. M. Sheldrick, *Acta Crystallogr. Sect. A: Found. Adv.* **2015**, *71*, 3.
[40] G. M. Sheldrick, *Acta Crystallogr. Sect. C: Struct. Chem.* **2015**, *71*, 3.

Manuscript received: September 2, 2024
Revised manuscript received: September 28, 2024
Accepted manuscript online: October 4, 2024
Version of record online: November 7, 2024