

Immobilization of a copper complex based on the tripodal ligand (2-aminoethyl)bis(2-pyridylmethyl)amine (uns-penp)

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Dedicated to the 60th birthday of Prof. Dr. Christoph Janiak

A new derivative of the ligand (2-aminoethyl)bis(2-pyridylmethyl)amine (uns-penp), capable for covalent immobilization on silica, was synthesized. Silica powder for column chromatography and mesoporous monoliths served as surface material. Functionalized silica was sufficiently characterized with reflectance UV/Vis and FTIR techniques. Copper(I) was successfully complexed with the immobilized ligand and exhibits reversible reactivity towards dioxygen at low temperatures. Suspending the oxygen species with toluene at low temperatures led to selective oxygenation to benzaldehyde, determined by GC-MS.

Copper(I) complexes with the ligands Me-PTS-uns-penp and Me-Prop-uns-penp were prepared and characterized to model the reaction behavior towards dioxygen in solution. Additionally, solid copper peroxido complexes with these ligands were obtained by precipitation with the sterically demanding anion tetraphenylborate. Furthermore, these complexes could be obtained in a reversible reaction by treating corresponding copper(I) complexes with dioxygen. With all oxygenated copper complexes catalytic oxidation of toluene was observed.

Introduction

Benzaldehyde is an industrially important chemical and thousands of tons are produced per year. It is used for a wide range of products such as dyes, drugs, cosmetics and foods.^[1] It has been first synthesized by Wöhler and Liebig and since then several ways of commercial fabrication have been established.^[2] The Gattermann-Koch synthesis, the chlorination of toluene with subsequent hydrolysis of the intermediate product and the direct oxygenation, catalyzed by transition metal oxides, are

currently the most common procedures^[3–5] However, these synthetic routes show some noticeable drawbacks: on the one hand, toxic reactants and catalysts are required and on the other hand, a range of side products due to overoxidation are formed. Furthermore, the huge consumption of energy and the necessary steps for product separation should be mentioned. Efforts to improve the industrial process have been reported, e.g. Gast et al. reported a catalyst-free method for direct oxygenation by treating toluene with dioxygen at high pressures and temperatures.^[6] However, again no selective oxygenation could be achieved. With regard to sustainable chemistry, it would be desirable to synthesize benzaldehyde directly without waste/side products by selective oxidation of toluene at room temperature using a catalyst and dioxygen/air as the sole oxidant. Several copper containing enzymes exist which are capable to selectively oxygenate organic substrates under mild conditions, for example dopamine- β -monooxygenase (D β M), peptidylglycine- α -hydroxylating monooxygenase (PHM) or tyrosinase.^[7] Modelling the reactivity of the copper enzymes with low molecular weight complexes therefore is a worthwhile approach to succeed in an optimized process for the synthesis of benzaldehyde. Different “dioxygen adduct” complexes as active species can form when a copper(I) compound is reacted with dioxygen. Some examples are shown in Figure 1.^[8]

Copper(I) complexes with the tetradentate ligand tris(2-methylpyridyl)amine (tmpa) as well as its derivatives (Figure 2) react with dioxygen to form a trans- μ -1,2-peroxido species (Figure 1b). The molecular structures for the two complexes [LCu(O₂)CuL]²⁺ (L=tmpa and Me₆tren, Figure 2) have been reported previously.^[7,8] While this binding motif has not been observed in nature so far (side-on, μ - η^2 : η^2 -peroxido, Figure 1e, is here preferred) it turned out that complexes of this type are

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Supporting information for this article is available on the WWW under <https://doi.org/10.1002/zaac.202100022>

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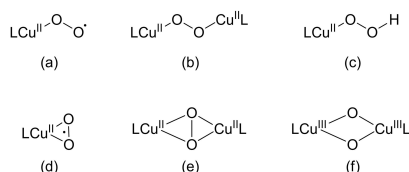


Figure 1. Examples of copper “dioxygen adduct” species: (a) *end-on* superoxido, (b) *trans-μ-1,2-peroxido*, (c) η^1 -hydroperoxido, (d) *side-on* superoxido, (e) μ - η^2 : η^2 -peroxido, (f) *bis(μ-oxido)*.

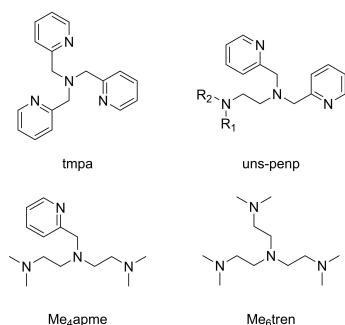


Figure 2. Tripodal ligand tmpa and derivatives: uns-penp ($R=R_2=H$), Me₄apme and Me₆tren.

capable to catalytically oxidize toluene selectively to benzaldehyde.^[9,10] Karlin and co-workers demonstrated that this reaction could be performed in solution at low temperatures with yields of up to 40%.^[10] The anion tetrakis (pentafluorophenyl)-borate was applied to achieve higher solubility to perform the reaction under homogeneous conditions. Around the same time, it was observed that it is possible to dramatically stabilize some of the *trans-μ-1,2-peroxido* copper complexes with (some) tripodal ligands in the solid state by using tetraphenylborate as an anion.^[9] These complexes were stable up to temperatures of +100 °C in the solid state and therefore seemed to be promising for heterogeneous catalytic oxidation of toluene. While this turned out to be correct, yields still remained rather low and did not exceed 20% for the copper/tmpa system that turned out to be most suitable for this application.

With regard to these findings, it was decided to immobilize tripodal copper complexes to optimize the catalytic system. As a sustainable carrier material, mesoporous silica was chosen that has been thoroughly investigated during the last years. It has been used to a large extent as grafting material and therefore has a number of advantages.^[11,12] Due to its wide application, various linking reagents are available on the market, suitable for a wide range of functionalization. Furthermore, it is resistant against organic solvents in contrast to organic surface materials such as polystyrene. Its thermal resistance and low costs are important features as well.^[13,14] Additionally, the generally high surface area is an advantage and the pore structure can be tailored towards the application.

The major goal would be to covalently graft an active complex onto a silica surface of a so-called silica monolith

(Figure 3). Its mesoporous structure in a network of macro pores are features of such a monolith for an application in a flow reactor. While the meso pores containing a large surface for a maximum of immobilization a regular network of macro pores is advantageous for the mass flow of the substrate through the monolith. This would allow the construction of a flow reactor in which the substrate and oxidant (dioxygen/air) would be combined in a solvent and passed through the monolith. As a consequence, the reaction would be clean (no fragments of catalyst decay) and only very few separation steps would be necessary. Moreover, after the oxygenation the complex could be easily reactivated by a reducing agent.

Results and Discussion

In general, there are two established immobilization/grafting processes to obtain functionalized silica: 1. The whole ligand gets incorporated into the silica framework in form of its metal complex. For this purpose, a mixture of the “linkable” complex with a tetraalkoxysilane is hydrolyzed in basic media, leading to a solid silica compound containing the active material. For example, Suspène et al. used a tren-based ligand system (Figure 4a) incorporated into a mesoporous silica framework. The immobilization thus allowed stabilization of a copper oxygen adduct compound that was reversibly formed.^[15] In a slightly different way a copper(II) tmpa complex has been incorporated into mesoporous silica-alumina (Al-MCM-41) and the obtained material had been used for catalytic hydroxylation of benzene to phenol using hydrogen peroxide as an oxidant.^[16]

2. Alternatively and more common is the approach to covalently graft the active materials onto an actual silica surface, usually silica gel. In addition, it is possible to precast the surface material into a suitable shape for further applications such as a monolith that could be used in a flow reactor (Figure 3). Two different synthetic routes can be applied to achieve this: a) first the linker will be attached to the silica surface and in a second step it will be reacted with the actual ligand prior to adding a metal salt to form the final active

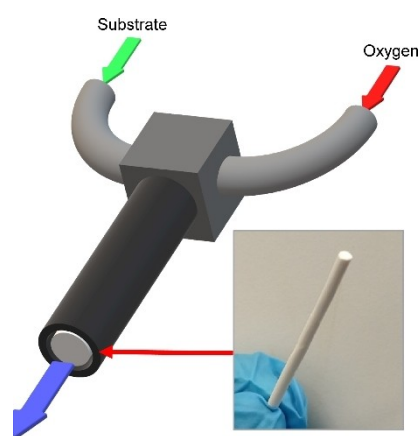


Figure 3. Functionalized silica monolith placed into a flow-reactor. Small picture at the right shows the silica monolith.

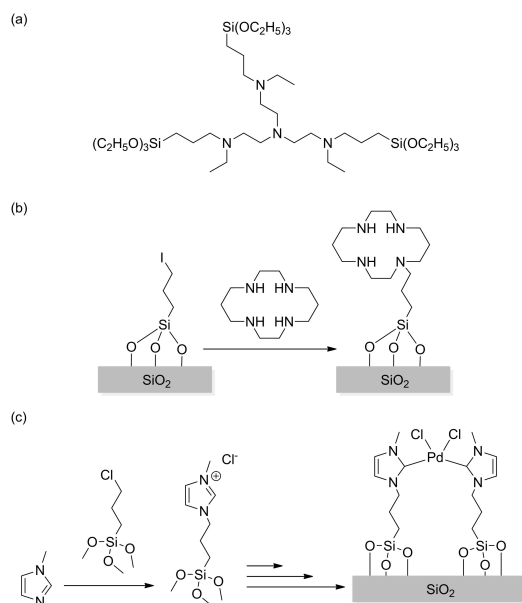
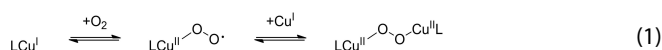


Figure 4. (a) tren derivative for incorporation into silica framework,^[15] (b) approach with pre-condensed linker on silica surface with subsequent attachment of a ligand,^[17] (c) approach with pre-combination of a linker with the ligand and subsequent condensation.^[18]

material. This has been accomplished e.g. for the attachment of the macrocyclic ligand cyclam (Figure 4b) to coordinate cobalt ions and further bonding to an enzyme.^[17] However, problems have been observed using this method with amines that can strongly bind to the surface of the silica and then are not available anymore for combination with the linker.^[19] For that reason it seems preferable to apply method b) attaching the linker with the ligand prior to grafting on the surface of the silica. For example, this method was applied for covalently grafting palladium complexes onto a silica surface to perform Heck reactions (Figure 4c).^[18]

Based on the previous results we chose (2-aminoethyl)bis(2-pyridylmethyl)amine (uns-penp, Figure 2, R=H) as a ligand for the combination with a suitable linker for the attachment at the terminal amine group. The ligand uns-penp has been first reported by Mandel et al. and has the advantage that it can be easily modified.^[20] A kinetic study has been performed in the past on the reaction of $[\text{Cu}(\text{Me}_2\text{-uns-penp})]^+$ (Me₂-uns-penp, Figure 2, R=Me) with dioxygen.^[21] Very similar to copper(I) complexes with tmpa or Me₆tren as ligands it reacts according to equation 1 ($\text{L}=\text{Me}_2\text{-uns-penp}$) in a first step to an *end-on* superoxido complex prior to its reaction with a second copper (I) unit to form a dinuclear *end-on* peroxido complex (Figure 1).



The hydrogen atoms of uns-penp need to be substituted by organic groups to obtain persistent peroxido complexes. If amine hydrogen atoms are present in the ligand system, hydrogen peroxide can be formed that would lead to quite

different reaction behaviour, usually involving radical pathways initiated by hydroperoxido complexes. Therefore, prior to modify uns-penp with silyl linker groups, one of the amine hydrogen atoms was substituted by a methyl group leading to Me-uns-penp (Figure 5).

Syntheses

The preparation of Me-uns-penp is a bit more of a challenge in contrast to the facile synthesis of uns-penp or Me₂-uns-penp. While a reductive alkylation reaction with formaldehyde allowed access to it, yields were very low and a large number of side products were obtained.^[22] A different synthetic approach based on selective protecting and deprotecting reactions of the fundamental methyl-ethylene diamine structure, followed by reductive alkylation performed according to the literature allowed to obtain Me-uns-penp in satisfying yields.^[23,24]

To enable Me-uns-penp for condensation and for covalent bonding on a silicon dioxide surface several silica linkers are commercially available that allow a large number of different possible reactions.^[25] Alkoxy silane linkers are commonly used for immobilisation on silica surfaces: on the one hand they can be managed quite well to obtain sufficient grafting quantities, on the other hand a lot of derivatives, suitable for a large number of different reactions are known and available.^[26] In here, application of a silane linker containing an alkyl group with a terminal halide suitable for amine attachment was chosen. As the most common silane linkers contain more than one alkoxy group at the silicon atom, there is the possibility of self-condensation between the linkers/ligands (frameworking) in the presence of moisture as shown in Figure 6.^[27] This effect can easily suppress a statistical distribution of the immobilized compounds on the surface of the solids and a distal grafting of the complexes would not be possible.^[19] The commercially available mono alkoxy linker (3-chloropropyl)dimethylmethoxy silane (CPDMS) was chosen as suitable starting material for immobilization. A comparison of both linker molecules is shown in Figure 6.

The substitution at the precursor ligand led to the product (2-methyl-(3-propyl)dimethyl-methoxysilane-aminoethyl)bis-(2-pyridylmethyl)amine (Me-PDMS-uns-penp, (Figure 5). However, this silane linker as well can undergo self-condensation. In

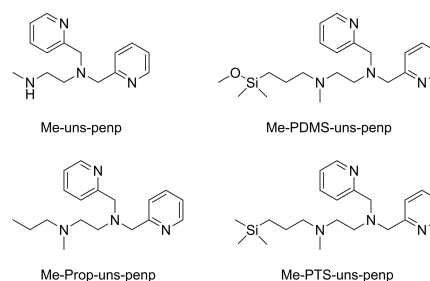


Figure 5. Precursor ligand Me-uns-penp and its derivatives for immobilization and solution experiments.

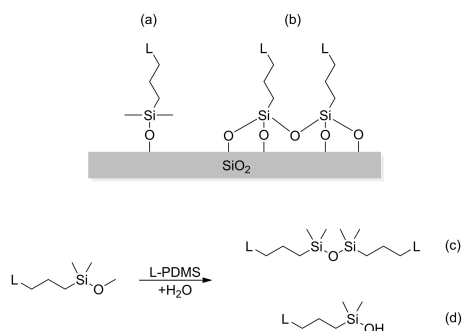


Figure 6. Top) Different grafting behaviour of the silane linker, L is the chosen ligand, (a) mono alkoxy silane linker units that are not capable of frameworking. It allows a roughly statistical distribution on a flat surface (b) frameworking of poly alkoxy silane linker units caused by self-condensation with subsequent immobilization. Bottom) Reaction of moisture with a mono alkoxy linker attached to a ligand (c) dimerization caused by self-condensation. (d) exchange of alkoxy anchor groups with hydroxyl groups.

contrast to its multi alkoxy silane derivatives, there is no prior frameworking but dimerization could still occur that would exclude the ability for grafting. (Figure 6c).^[27] Furthermore, the loss of the alkoxy group and a subsequent exchange with a hydroxyl group could be observed (Figure 6d).

Therefore, all chemicals were properly dried and all preparations were carried out under inert conditions in a glove box. As the terminal carbon-chlorine bond of the CPDMS linker does not feature a sufficient reactivity towards the secondary amine of the Me-uns-penp ligand, an exchange through a better leaving group through a Finkelstein reaction was necessary.^[28] The halide exchange as well as the linker attachment at the ligand were performed in a one-pot reaction in acetonitrile similar to reactions described previously.^[15,29] Controlling the reaction via ESI-MS, after linker addition was completed, revealed that besides the product mass peak, dimerization and hydroxyl exchange of the silane group had occurred (bottom of Figure 6). A separation via column chromatography or by distillation did not lead to a satisfying yield of pure product. However, the mixture could be purified by cleaving the dimeric silanol by adding one equivalent of sodium methoxide and an excess of dimethyl carbonate.^[30] Afterwards ESI-MS showed only the desired product mass. Even the hydroxy groups were converted under the basic conditions leading to the methoxy silane product. This step must be specifically highlighted as it represents the “bottle neck” reaction, which was fundamental for a pure product that precedes a reproducible grafting result and therefore to successfully apply it in catalysis. The overall synthetic procedure is presented in Figure 7.

Prior to immobilization of Me-PDMS-uns-penp a test reaction was performed if this modified uns-penp ligand system is still capable to support formation of copper “dioxxygen adduct” complexes that could become useful for catalytic oxidations. Due to the extreme sensitivity of Me-PDMS towards moisture two analogues of this ligand, Me-PTS-uns-penp and

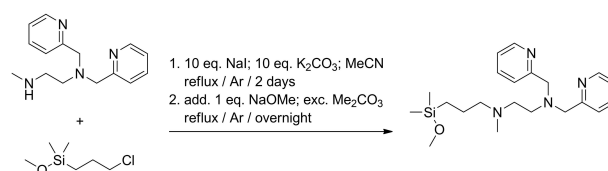


Figure 7. Synthesis of Me-PDMS-uns-penp ligand in a one-pot reaction: 1. linker attachment with prior halide exchange 2. side products were converted back into the desired species.

Me-Prop-uns-penp (Figure 5) were prepared. Copper(I) complexes from both ligands were synthesized and molecular structures of both complexes, [Cu(Me-PTS-uns-penp)]BPh₄ and [Cu(Me-Prop-uns-penp)]BPh₄ are presented in Figure 8 (Crystallographic data are reported in the Supporting Information).

It could be confirmed by low temperature stopped-flow measurements, that both copper(I) complexes reacted with dioxygen according to equation 1 described above. Time resolved spectra of the reaction of Cu(Me-PTS-uns-penp)]BPh₄ with dioxygen in acetone are presented in Figure 9 and is very

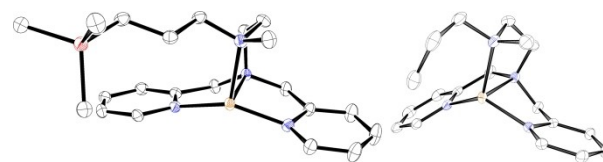


Figure 8. Molecular structures of the cations of [Cu(Me-PTS-uns-penp)]BPh₄ (left) and [Cu(Me-Prop-uns-penp)]BPh₄ (right). Ellipsoids set at 50% probability; the anions, H atoms, and solvent molecules are omitted for clarity. Carbon: black; nitrogen: blue; silicon: red; copper: brown.

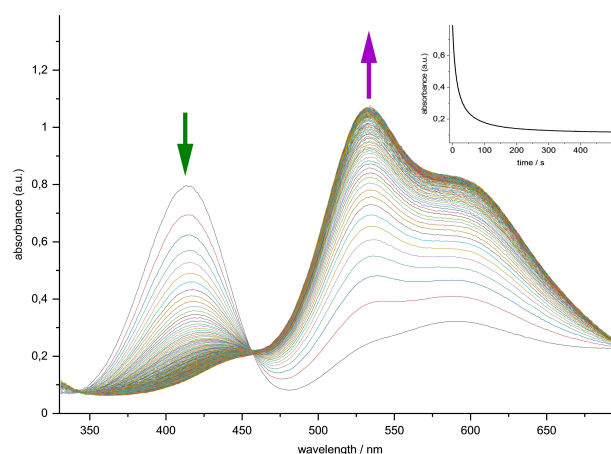


Figure 9. Time resolved spectra of the reaction of [Cu(Me-PTS-uns-penp)]BPh₄ with dioxygen in acetone at -81.0 °C ([complex] = 2.0×10^{-4} M, [O₂] = 4.4×10^{-3} M, total time: 250 s). At 414 nm the spectra shows the decreasing intensity of the superoxido intermediate. 535 nm shows the increasing intensity of the final peroxide complex. Time trace at the upper right shows decomposition of the superoxido species.

similar to the reaction of $[\text{Cu}(\text{Me-Prop-uns-penp})]\text{BPh}_4$ with dioxygen (reported in the Supporting Information). Furthermore, the reaction behavior is in excellent agreement with previous reports on other copper complexes with tripodal ligands.^[21,31–33] The decomposition of the copper superoxido complex can be followed by the decrease of the absorbance maxima at 414 nm (Figure 9, inset). The disappearance of this band and an increase of a band with a maximum at 532 nm is the formation of the consecutive reaction to the dinuclear copper peroxido complex (eq. 1).

While it is difficult to crystallize either an *end-on* superoxido or *end-on* peroxido intermediate complex (only a few examples have been reported in the literature)^[9,34–37] it is quite easy to obtain and crystallize related copper(II) chlorido complexes as a model compounds for these intermediates.^[38] Herein it was possible to crystallize $[\text{Cu}(\text{Me-Prop-uns-penp})\text{Cl}]\text{ClO}_4$ and its molecular structure is shown in Figure 10. Crystallographic data are reported in the Supporting Information.

In contrast to other structurally characterized copper(II) complexes with uns-penp derivatives as ligands the copper centre in $[\text{Cu}(\text{Me-Prop-uns-penp})\text{Cl}]\text{ClO}_4$ is not coordinated in a square pyramidal manner but in a trigonal bipyramidal geometry with a τ value of 0.83.^[39]

An essential intention of this work was to obtain an *end-on* superoxido copper complex by suppressing the consecutive formation of the dinuclear copper peroxido complex according to equation 1. This would allow a better modelling of the active site of dopamine- β -monooxygenase (D β M) and peptidylglycine- α -hydroxylating monooxygenase (PHM) and might result in a more active species with higher yields in catalytic toluene oxidation. While an *end-on* superoxido copper complex can be stabilized with a sterically more demanding ligand it furthermore should be possible to achieve this stabilization through distal immobilization of the mononuclear copper units on a silica surface.^[34,40] Therefore, the application of a trialkoxy silane linker was inapplicable due to its tendency towards frameworking.^[32] Ligands attached in such a pre-grafted framework may possess distances that would be too short to exclude formation of peroxido complexes.

This strategy has been applied successfully in the past for a mononuclear cobalt imine complex. Investigations with “model” complexes for the actual silyl-based units allowed in the process structural characterization of an *end-on* superoxido cobalt complex.^[41] Immobilization then proved the ability of this complex unit to catalytically oxidise *n*-alkanes.^[42]

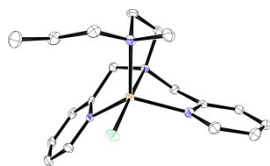


Figure 10. Molecular structure of the cation of $[\text{Cu}(\text{Me-Prop-uns-penp})\text{Cl}]\text{ClO}_4$. Ellipsoids set at 50 % probability; the anions, H atoms, and solvent molecules are omitted for clarity. Carbon: black; nitrogen: blue; silicon: red; copper: brown.

Immobilization

Common silica powder used in column chromatography (Kieselgel 60 M) was prepared for surface functionalization by refluxing it in concentrated hydrochloric acid for 24 hours and subsequent drying at 150 °C according to the literature.^[18,43] This procedure insured sufficient supply of silanol groups, which serve as anchor positions for ligand condensation. Besides, it removes potential impurities such as grease and side products of the fabrication process. Physisorption measurements with nitrogen of the activated silica gel determined a specific BET (Brunauer-Emmett-Teller) surface area of 348 m²/g (Table S1, Supporting Information). As described above, the spatially separated immobilization of the ligands should prevent the formation of dinuclear peroxido copper complexes. To manage the required distance, an immobilization of only one ligand molecule per 4 nm² was attempted. Geometrical basis of this surface concentration is the distance of 0.738 nm between the silicon atom of the propylene arm and the coordinating nitrogen atom, positioned between both methyl pyridyl residues, into a Cu(I) complex with the Me-PTS-uns-penp ligand. A schematic drawing is pictured in Figure 11.

A statistical distribution of the ligand at the surface was assumed by the applied concentration of the reaction suspension containing ligand and the surface material. In accordance with the Zhuravlev model, a number between 4.6 and 4.9 OH groups per nm² exists on silica.^[44] Therefore, an adequate amount of silanol groups is available for this assumption. Quantification of the resulting reaction solution via transmission UV/Vis spectroscopy shows that almost all molecules were successfully grafted on the silica surface (94 %, Figure S4, Supporting Information). However, applying twice the ligand concentration led to a grafting of only 83 % (Figure S4, Supporting Information). Despite the fact that more hydroxyl groups should be available the silica surface seems to be completely functionalized/saturated. One of the reasons for that effect may be the sterical hindrance of the ligand itself that

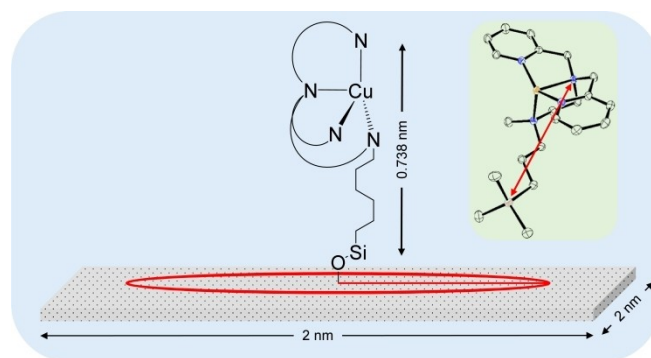


Figure 11. Schematic drawing of the immobilized copper(I) complex with the Me-PDMS-uns-penp ligand. The double-arrow illustrates the distance between the silicon anchor and the axial nitrogen atom. The red circle is an assumption of the rotational effect on the surface. The inset shows the molecular structure of the cation of $[\text{Cu}(\text{I})(\text{Me-PTS-uns-penp})]\text{BPh}_4$.

makes a further/additional consumption of the silanol groups through immobilization impossible. In addition, pores, which were blocked by an immobilized ligand at the entrance, cannot be accessed by ligand molecules anymore. Physisorption measurements of the functionalized material resulted in a reduction of the BET area with regard to the starting surface: Me-PDMS-uns-penp grafted an area of 47 m²/g, a loss of 14%. Applying twice the concentration as described above grafting of 72 m²/g (–21 %) was detected confirming the results of the UV/Vis quantification.

FTIR measurements using diffuse reflectance technique DRIFTS reveal an immobilization on the silica gel with the Me-PDMS-uns-penp ligand (Figure 12). Comparison with untreated silica shows a decrease in intensity of the silanol band (3734 cm^{–1}). Spectra with an enlarged area of interest are shown in the Supporting Information. Furthermore, the bands with low intensity between 2965 and 2907 cm^{–1} as well as between 1470 and 1430 cm^{–1} indicate the presence of an aliphatic group. The bands of the pyridyl groups with high wavenumbers cannot be seen due to the huge silanol absorption, however, the bands between 1600 and 1570 cm^{–1} are visible. Bands at 1245 cm^{–1} and 837 cm^{–1} are slightly visible. They indicate the Si–CH₃

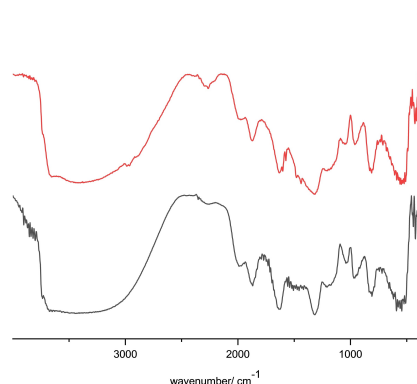


Figure 12. DRIFTS measurements of pure (black line, bottom) and functionalized (red line, top) silica gel. The band at 3734 cm^{–1} is missing for the functionalized sample what indicates a successful immobilization.

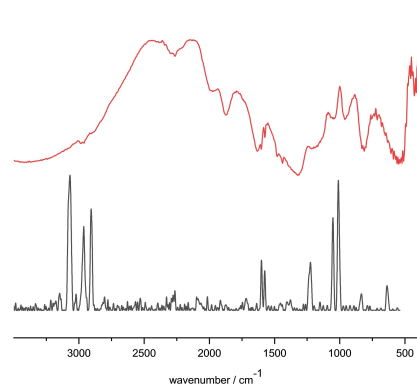


Figure 13. Comparison of DRIFTS spectra (red line, top) of functionalized silica gel with Raman spectra (black line, bottom).

groups, assigned to the presence of the ligand. The additional Raman spectra underline the successful covalent bonding (Figure 13). Some of the data obtained from the DRIFT spectra became clearer from the Raman measurements: the pyridyl band at 3068 cm^{–1} became much more visible and the band of the Si–CH₃ groups is more distinct as well (1245 cm^{–1}). The missing band of the Si–OCH₃ group at 1085 cm^{–1} is an indication of the covalent Si–O–Si bonding on the silica surface.^[45] Treatment of silica with the model ligand Me-PTS-uns-penp did not lead to comparable spectra, which proved the necessity of an anchor group to perform a successful immobilization.

A comparison of the surface investigation with the ATR spectra of the free model ligand Me-PTS-uns-penp is reported in the Supporting Information. Diffuse reflectance UV/Vis measurements showed two absorption maxima at 205 and 260 nm what is supposed to be a $n/\pi \rightarrow \pi^*$ transition of the pyridyl part of the ligand (Figure 14).^[46]

As described above monoliths based on mesoporous silica were applied as well to test for further applications in a flow reactor. Monoliths were synthesized by sol-gel procedures ("Nakanishi process") as described previously.^[47–49] In contrast to the procedure applied with silica powder described above the monoliths were not treated with concentrated HCl because these rough conditions could cause damage to the cylindrical shape. No further purification for the monoliths was performed to avoid deformation. The monoliths were dried at 150 °C overnight. They were obtained with a specific surface of 360 m²/g. Complexing experiments revealed that only the mantle of the monolith was functionalized due to the immobilization procedure: to functionalize its surface the monolith was placed into a special Schlenk tube with a double bottom to separate the stirring bar from the fragile structure (Figure S10, Supporting Information). UV/Vis quantification of the solution after the reaction showed almost complete ligand consumption (detailed spectra of the surface investigation are reported in the Supporting Information).

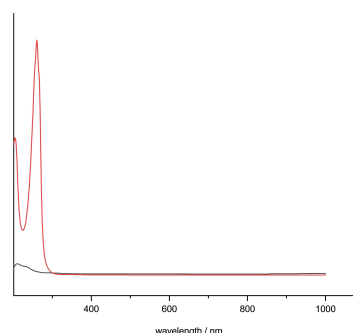


Figure 14. Diffuse reflectance UV/Vis measurements: Pure (black line) and functionalized silica (red line). Functionalized species shows a clear band at 205 and 260 nm caused by $\pi \rightarrow \pi^*$ transition of the pyridyl groups of the ligand.

Complexation

To determine the actual complexation ability of the grafted ligands and therefore a quantification of the desired catalytic properties, an excess of Cu(II) triflate was suspended into acetonitrile under inert conditions with a defined amount of functionalized silica gel. The silica powder apparently showed a change in colour from colourless to a light blue colour which is evidence of its complexation ability. However, a determination of the consumption of copper ions via UV/Vis measurements was not possible due to the low extinction coefficients in solution. Investigations with diffuse-reflectance UV/Vis revealed the ligand $\pi \rightarrow \pi^*$ transition as described above together with a shoulder at 288 nm and a broad maximum around 700 nm, typically for $d-d$ transitions of copper(II) ions (Figure 15).^[50] Longer exposition with the complexation solution (stirring for ca. one hour) led to a green powder. The green product showed an additional maximum at 421 nm. Most likely the copper complexes reacted with free OH-silyl groups to form copper silicate bonds (Cu–O–Si) after deprotonation. Exposure to air yielded again a blue coloured solid after a couple of days that is comparable in appearance with the blue coloured immobilized complex described above. Treating immobilized copper(II) triflate in acetonitrile with sodium methoxide what act as an analogue of the proposed Si–O species immediately led to a green powder. Washing the sample with acetonitrile caused a colour change to a blue colour as well, which is evidence for a ligand exchange at the fifth coordination position at the copper centre.

Copper(I) complexes with triflate or hexafluorophosphate as anions were attached in the same way as the copper(II) salt leading to light yellow air sensitive powders similar to a previous report on the copper(I) complex with the ungrafted ligand Me₂uns-penp.^[9]

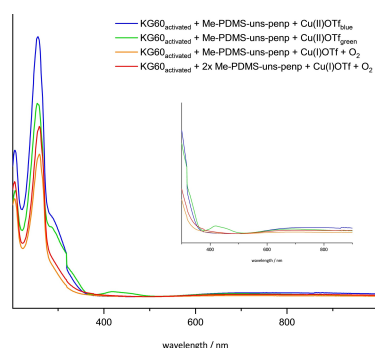


Figure 15. Comparison of copper complexes on functionalized silica: blue and green lines show the spectra of the blue and green coloured Cu(II)triflate complexes. The orange coloured spectrum shows the absorbance of the immobilized copper(I) triflate complex after its reaction with dioxygen. The red line shows the spectrum of the immobilized copper complex on a ligand-saturated silica surface.

Reactivity towards Oxygen

As described above, time resolved UV/Vis spectra obtained in solution for the oxygenation of the complexes [Cu(I)(Me-PTS-uns-penp)]BPh₄ and [Cu(I)(Me-Prop-uns-penp)]BPh₄ showed the formation of transient superoxido and peroxido complexes. Therefore, it was assumed that these reactions could take place in the solid state as well, similar to findings reported previously.^[9] The sterically demanding anion tetraphenylborate allowed precipitation of peroxido copper complexes from solution that turned out to be extremely stable.^[9] In comparison with these compounds the new complexes reported in here were much less stable in the solid state. Overnight, the characteristic blue/purple colour of the 1,2-peroxido species had faded and a grey coloured solid remained. Reflectance UV/Vis spectra revealed – as expected – the lack of the absorbance of a peroxide species (Figure-S11 + S12, Supporting Information). In contrast and as reported before, the complex with the symmetric substituted Me₂uns-penp as a ligand kept the blue colour quite persistently.^[9]

The blue coloured copper peroxido complexes could also be obtained by exposure of the corresponding solid copper(I) complexes towards dioxygen. However, treating the solid model compounds [Cu(I)(Me-PTS-uns-penp)]BPh₄ and [Cu(I)(Me-Prop-uns-penp)]BPh₄ with dioxygen turned the yellow coloured complexes into green coloured solids instead (Figure S13, Supporting Information). While the colour change indicated the formation of an *end-on* superoxido copper complex UV/Vis spectra did not really support this. Reflectance UV/Vis spectra showed a single maximum around 330 nm (Figure S14, Supporting Information) and not at around 410–440 nm where it would have been expected for a superoxido species.^[51,52] Keeping the complexes under an argon atmosphere the green colour changed back into a light yellow coloured solid within days. The colour change could be accelerated by moderate heat (~50 °C) under an argon flow within minutes (Figure S15, Supporting Information). The green colour however, could be reestablished by treating the complexes again with dioxygen, therefore demonstrating reversible reactivity. Further characterization of the green coloured solid has been unsuccessful so far. In contrast, the copper(I) complex with Me₂uns-penp as ligand exhibits two maxima at 318 nm and 540 nm after exposure to dioxygen (Figure S14, Supporting Information) clearly showing the formation of the blue/purple dinuclear peroxido complex [(Me₂uns-penp)Cu(O₂)Cu[(Me₂uns-penp)]²⁺.^[9]

Immobilized [Cu(uns-penp_{immob})](OTf) as well shows a strong sensitivity towards dioxygen: at room temperature the yellow powder immediately turned irreversibly into a light blue coloured solid, resembling the copper(II) product complex described above with the same spectroscopic features (Figure 15, orange and blue spectra). In contrast when the complex was reacted with dioxygen at –80 °C a dark green solid was formed. Flushing the reaction vessel with argon led back to the yellow coloured copper(I) complex. This process can be repeated for several times (Figure 16) until the compound is warmed under dioxygen that again led to the irreversible formation of the blue compound (Figure 15, orange spectre).

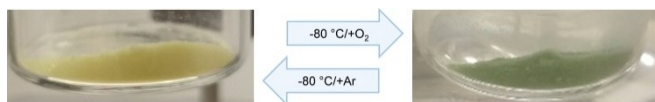


Figure 16. Reversible reaction of the immobilized copper(I) complex with dioxygen at low temperatures (-80°C).

Attempts to reactivate this compound, most likely a copper(II) species, by reducing it with ascorbate as described previously were not successful.^[53]

Due to the instability of the “oxygen adduct” complex at moderate temperatures no spectroscopic characterization could be obtained so far. Due to the green colour of the compound the formation of a *end-on* superoxido complex is proposed. Efforts to obtain the proposed superoxido species by addition of KO_2 (in combination with cryptand[2.2.2]) to an immobilized copper(II) complex, according to a procedure described by Bailey et al. failed.^[54]

The monolith was treated in the same way as the functionalized silica powder and showed the same reactivity towards dioxygen at low temperatures.

Catalysis

In general, all catalytic reactions were performed heterogeneously. For this purpose, the solid copper complex was suspended in a defined volume of toluene. In case of the model complexes, oxygen treated solid $[\text{Cu}(\text{Me-Prop-uns-penp})]\text{BPh}_4$ and $[\text{Cu}(\text{Me-PTS-uns-penp})]\text{BPh}_4$ were suspended with toluene and stirred at room temperature. Due to the sensitivity at moderate temperatures of the immobilized copper oxygen species, $[\text{Cu}(\text{uns-penp}_{\text{immob}})]^+$, it was treated with dioxygen at -80°C , covered with toluene and kept at this temperature for 120 h. Afterwards the toluene layer was separated by applying a PTFE syringe filter (pore size $20\ \mu\text{m}$). The products were determined by GC-MS technique. GC-MS data and a more detailed description of the procedure are reported in the Supporting Information. Table 1 shows the results and reaction conditions. Obviously, all compounds exhibit a catalytic activity towards the oxidation of toluene. The catalytic activity of the

“free” complexes $[\text{Cu}(\text{Me-Prop-uns-penp})]\text{BPh}_4$ and $[\text{Cu}(\text{Me-PTS-uns-penp})]\text{BPh}_4$ is in accordance with the results for $[\text{Cu}(\text{Me}_2\text{uns-penp})\text{O}]_2(\text{BPh}_4)_2$ (that reached a conversion to benzaldehyde of 15 %) reported previously by Würtele et al.^[8]

It should be pointed out however, that the proposed green coloured copper superoxido complexes $[(\text{Me-Prop-uns-penp})\text{Cu}(\text{O}_2)]\text{BPh}_4$ and $[(\text{Me-PTS-uns-penp})\text{Cu}(\text{O}_2)]\text{BPh}_4$ do not seem to be involved in the catalytic oxygenation process in contrast to our expectations. Deep blue solids, obviously the peroxido complexes $[\text{Cu}(\text{Me-Prop-uns-penp})\text{O}]_2(\text{BPh}_4)_2$ and $[\text{Cu}(\text{Me-PTS-uns-penp})\text{O}]_2(\text{BPh}_4)_2$ were formed once the corresponding copper(I) complexes were suspended in toluene under dioxygen. This effect was not observed if the treatment with toluene was carried out under an argon atmosphere. Under these conditions the green compound turned back into the yellow coloured copper(I) complex instead and no oxygenation reactions could be detected.

Processing the catalytic reaction with preformed $[\text{Cu}(\text{Me-Prop-uns-penp})\text{O}]_2(\text{BPh}_4)_2$ and $[\text{Cu}(\text{Me-PTS-uns-penp})\text{O}]_2(\text{BPh}_4)_2$ led to similar conversion of 18 % and 14 %, respectively (Table 1). However, here as well no oxygenation of toluene was observed under an argon atmosphere, clearly indicating the necessity of the presence of dioxygen.

Conversion was also achieved with the immobilized species $[\text{Cu}(\text{uns-penp}_{\text{immob}})]^+$, however, yields were rather low. The silica approach delivers a slightly higher conversion to benzaldehyde by comparison with the monolith (Table 1). The reason for this could be the nearby positioning of the ligands on the surface of the monolith that can lead to peroxide formation/deactivation. Even though there is no huge influence of the anions detected with regard to the conversion it turned out that the immobilized oxygenated complex with PF_6^- as an anion was much more stable towards decomposition. Even at moderate temperatures, the green colour of the oxygenated complex with this anion can be observed for a short time while the complex with triflate already decomposed immediately.

Conclusions and Outlook

We succeeded with the immobilization of a copper complex system that is known to oxygenate toluene selectively to benzaldehyde, however in only moderate yields. Superoxido

Table 1. Results of the catalytic reaction of free and immobilized copper oxygen complexes into toluene.

Catalyst ^[a]	Duration	Temperature	Conversion ^[b]
$[\text{Cu}(\text{uns-penp}_{\text{immob}})]_{\text{silica}}\text{OTf}$	120 h	-80°C	3 %
$[\text{Cu}(\text{uns-penp}_{\text{immob}})]_{\text{silica}}\text{PF}_6$	120 h	-80°C	5 %
$[\text{Cu}(\text{uns-penp}_{\text{immob}})]_{\text{monolith}}\text{OTf}$	120 h	-80°C	1 %
$[\text{Cu}(\text{Me-Prop-uns-penp})]\text{BPh}_4$ ^[c]	70 h	r.t.	21 %
$[\text{Cu}(\text{Me-PTS-uns-penp})]\text{BPh}_4$ ^[c]	70 h	r.t.	18 %
$[\text{Cu}(\text{Me-Prop-uns-penp})]\text{BPh}_4$ ^[d]	70 h	r.t.	18 %
$[\text{Cu}(\text{Me-PTS-uns-penp})]\text{BPh}_4$ ^[d]	70 h	r.t.	14 %

[a] Active oxygenated species were prepared according to the description in the experimental section [b] conversion to benzaldehyde [c] the oxygen species were formed by exposure of the corresponding solid copper(I) complexes with dioxygen [d] copper peroxido adducts were obtained by precipitation at low temperatures.

and peroxido copper complexes have been assigned previously as active catalytic species. Unfortunately, the intention to model the active site of the peptidylglycine- α -hydroxylating monooxygenase (PHM), an *end-on* copper superoxido species, through immobilization was not really successful. While we observed green solids when reacting corresponding copper(I) complexes with dioxygen, indicating the formation of such species, it was not possible to obtain analytical data to support this, mainly due to the lability of these complexes. Furthermore, it was observed that oxygenation reactions still seemed to be mainly caused by the blue/purple dinuclear copper peroxido complexes instead. The expectation that an immobilized copper superoxido complex might result in a more active species with higher yields in catalytic toluene oxidation therefore were not fulfilled. However, it is quite important that it could be shown that the immobilized complexes are capable to bind dioxygen reversible at low temperature and that they are still able to selectively oxidize toluene to benzaldehyde, despite the low yields. A big advantage here lies in the fact that GC-MS measurements showed a pure product solution without any detectable side products. This is in contrast to the applied solid model complexes for the immobilized species where different side products were observed (e.g. products of the decomposition of the anion BPh_4^-). Despite the problems and the low yields encountered, in principle we were successful to demonstrate that the approach to immobilize active copper complexes in silica have their potential for future applications in catalytic oxygenation reactions. Optimization of the catalytic system is still necessary (probably tridentate ligands might be better than the tripodal ligands applied herein) and most likely a system should be developed that allows the immobilization of neutral copper(I) complexes to avoid problems with anions.

Experimental Section

Materials and Methods

All chemicals were purchased from commercial suppliers. Extra dry solvents were refluxed under argon over drying agents prior to transfer into the glove box. All reaction vessels were dried under vacuum with a hot air gun. NaI and K_2CO_3 were dried in vacuum at 250°C and stored under argon. $[\text{Cu}(\text{MeCN})_4]^+$ salts were synthesized according to the literature.^[24] Storage and preparation of air sensitive compounds were carried out in an argon glove box (MBraun, Garching, Germany; water and dioxygen <0.1 ppm). NMR measurements were performed with a Bruker Avance II 400 MHz (AV II 400) and Bruker Avance III HD 400 MHz (AV III 400). Solid UV/Vis spectra were recorded using a Perkin Elmer Lambda 750 UV/Vis-NIR spectrometer using a Harrick praying mantis. All shown spectra were converted applying the Kubelka–Munk equation. FTIR measurements were performed using a Bruker Alpha spectrometer equipped with either a DRIFT or an ATR module. Raman spectroscopy was executed on a SENTERRA dispersive Raman microscope (Bruker optics) equipped with a Nd:YAG laser ($\lambda_{\text{exc}} = 532$ nm). For determination of the specific surface for silica gel and monoliths, the Brunauer–Emmett–Teller method (BET) was used. A Hi-Tech SF-615X2 low-temperature stopped-flow unit equipped with a diode array spectrophotometer (Hi-Tech, Salisbury, UK) was used for kinetic measurements in solution. A two-syringe setup was used. A

detailed description has been reported previously.^[21] UV/Vis spectra in solution were obtained with an Agilent 8453 spectrometer. GC-MS measurements were performed using an Agilent Technologies 5977B with a 7820 A GC system. Crystallographic structure determination is described in the Supporting Information.

Syntheses

***N,N*-Boc-methylethylenediamine:** The protected precursor was synthesized according to the literature.^[23] *N*-methylethylenediamine (2.00 g, 27.7 mmol) was dissolved in 50 mL dichloromethane. The solution was cooled to 0°C in an ice bath and a solution of ethyl trifluoroacetate (3.83 g, 27.7 mmol) in 50 mL dichloromethane was added dropwise over a period of 40 minutes under argon. After the addition was complete, the resulting mixture was stirred for another 60 minutes at room temperature. Finally, the solvent was removed under vacuum. The colourless oil obtained, soon turned into a white solid. The product was dissolved in another 100 mL of dichloromethane. Di-*tert*-butyldicarbonate (5.89 g, 27.7 mmol) in 10 mL dichloromethane was added to the product solution at 0°C under argon. The reaction mixture was stirred for 90 minutes at room temperature and quenched with 30 mL of a saturated sodium hydrogen carbonate solution and 30 mL of ethyl acetate subsequently. The aqueous phase was extracted three times with ethyl acetate. The combined organic layer was washed with brine, dried over MgSO_4 , filtrated and concentrated with a rotary evaporator. The resulting oil slowly turned into a white solid. The product was placed into a vessel with 75 mL methanol and 25 mL of a 2–3 mol/L sodium hydroxide solution and stirred at room temperature for two hours. Methanol was removed and the aqueous layer was extracted three times with ethyl acetate. The combined organic layer was washed with brine, dried over magnesium sulphate, filtrated and the solvent was removed in vacuum. The crude product was obtained as a pale yellow oil (3.74 g, 21.5 mmol, 79%) and was used without further purification. $^1\text{H-NMR}$ (400 MHz, CDCl_3 , 24°C , δ [ppm]): 3.31 (br, 2 H, NH_2), 2.88 (s, 5 H, NCH_2/CH_2), 2.63 (s, 2 H, CH_2), 1.46 (s, 9 H, $\text{C}(\text{CH}_3)_3$). **ESI-MS** (m/z): $[\text{M} + \text{H}]^+$: 175.15; $[\text{M} + \text{Na}]^+$: 197.13; $[2\text{M} + \text{H}]^+$: 349.28; $[2\text{M} + \text{Na}]^+$: 371.47;

(2-methylaminoethyl)bis(2-pyridylmethyl)amine (Me-uns-penp): Reductive alkylation was performed similar to published procedures.^[24] *N,N*-Boc-methylethylenediamine was dissolved in 60 mL dichloroethane, 2-pyridinecarboxaldehyde (4.82 g, 45.1 mmol) and sodium triacetoxyborohydride (13.63 g, 64.4 mmol) were added. The solution was stirred overnight under argon. Afterwards the reaction suspension was quenched with 60 mL of 2 mol/L NaOH solution and extracted three times with dichloromethane. The organic layers were combined, washed with brine, dried over MgSO_4 , filtrated and the solvent was removed in vacuum. The obtained brown oil was treated with 100 mL of half concentrated hydrochloric acid. The brown solution was refluxed overnight. NaOH solution (6 mol/L) was slowly added up to a pH of 14 while cooling in an ice bath. The resulting solution was extracted three times with dichloromethane, washed with brine, dried over MgSO_4 , filtrated and the solvent was removed in vacuum. Kugelrohr distillation led to a pure product which was stored in the glove box (3.11 g, 56%). Overall yield 45% (respectively 2.00 g *N*-methylethylenediamine). $^1\text{H-NMR}$ (400 MHz, CDCl_3 , 24°C , δ [ppm]): 8.53 (d, 2 H, py-H), 7.65 (td, 2 H, py-H); 7.48 (d, 2 H, py-H), 7.14 (t, 2 H, py-H), 3.85 (s, 4 H, py- CH_2), 2.75 (t, 2 H, $\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{py})_2$), 2.67 (t, 2 H, $\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{py})_2$), 2.31 (s, 2 H, NCH_3). $^{13}\text{C-NMR}$ (101 MHz, CDCl_3 , 24°C , δ [ppm]): 159.6, 149.0, 136.4, 122.9, 121.9, 64.4, 60.8, 53.9, 49.4, 36.3. **ESI-MS** (m/z): $[\text{M} + \text{H}]^+$: 257.18; $[\text{M} + \text{Na}]^+$: 279.16

(2-methyl-(3-propyl)dimethyl-methoxysilane-aminoethyl)bis(2-pyridylmethyl)amine (Me-PDMS-uns-penp): Alkylation of an amine via $\text{S}_{\text{N}}2$ reaction and halide exchange into acetonitrile has been

reported previously.^[15,29] The preparation was carried out in an argon box: Me-uns-penp (0.85 g, 3.32 mmol) was dissolved in 40 mL of acetonitrile and transferred into a 100 mL-two-neck Schlenk flask. NaI (5.00 g, 33.4 mmol) and K₂CO₃ (5.00 g, 36.2 mmol) were added. When the Schlenk Flask was removed from the argon box it immediately was covered with aluminium foil. While applying an argon counter flow (3-chloropropyl)dimethylmethoxysilane (650 µL, 0.69 g, 4.14 mmol) was added via an Eppendorf pipet. The reaction mixture was refluxed under argon at 90 °C for two days. The reaction progress was controlled by sampling the mixture above the free neck of the flask for ESI-MS measurements. After there was no further mass of the precursor ligand detected, dimethyl carbonate (0.5 mL, 0.47 g, 5.19 mmol) and sodium methoxide (0.18 g, 3.33 mmol) dissolved in 3.5 mL of dry methanol were added under argon to transform the side products into the desired product.^[30] The reaction was continued overnight. Afterwards the solvent was removed by transferring it into a cold trap. The resulting solid was treated with dry pentane under argon. The suspension was separated via an equipped pre-dried Schlenk frit, end-capped with a flask suitable for Kugelrohr distillation. After transferring the pentane into a cold trap, the crude product was purified via Kugelrohr distillation and then stored in an argon box (0.66 g, 51 %). ¹H-NMR (400 MHz, CDCl₃, 24 °C, δ [ppm]): 8.48 (d, 2 H, py-H), 7.60 (td, 2 H, py-H); 7.51 (d, 2 H, py-H), 7.09 (t, 2 H, py-H), 3.83 (s, 4 H, py-CH₂), 3.36 (s, 3 H, SiOCH₃), 2.67 (t, 2 H, NCH₂CH₂N(CH₂py)₂), 2.52 (t, 2 H, NCH₂CH₂N(CH₂py)₂), 2.24 (t, 2 H, NCH₂CH₂CH₂Si), 2.12 (s, 3 H, NCH₃), 1.41 (m, 2 H, NCH₂CH₂CH₂Si), 0.48 (t, 2 H, NCH₂CH₂CH₂Si), 0.04 (s, 6 H, Si(CH₃)₂) ¹³C-NMR (101 MHz, CDCl₃, 24 °C, δ [ppm]): 160.0, 149.1, 136.4, 122.9, 121.9, 61.6, 61.0, 55.8, 52.3, 50.4, 42.6, 21.0, 13.5, -2.6 ESI-MS (m/z): [M+H]⁺: 387.26; [M+Na]⁺: 409.24 IR (ATR, ν̃ [cm⁻¹]): 3052 (w), 3009 (w) 2933 (m), 2827 (m), 1589 (s), 1570 (m), 1427 (m), 1433 (s), 1362 (m), 1305 (w), 1250 (s), 1188 (m), 1146 (m), 1085 (vs), 1047 (s), 1015 (m), 994 (m), 981 (m), 882 (m), 836 (vs), 757 (vs), 729 (s), 634 (w), 615 (m), 470 (w), 404 (s)

(2-methyl-(3-propyl)trimethylsilane-aminoethyl)bis(2-pyridylmethyl)-amine (Me-PTS-uns-penp): Me-uns-penp (0.75 g, 2.9 mmol) was dissolved in 30 mL acetonitrile, mixed with K₂CO₃ (4.9 g, 35.5 mmol) and (3-chloropropyl)trimethylsilane (0.55 mL, 0.49 g, 3.2 mmol) and covered with aluminium foil. The suspension was heated to reflux for two days under argon. The solvent was removed by rotary evaporation and the residue was treated with diethyl ether and filtered. The obtained solution was concentrated and the crude product was purified via Kugelrohr distillation (0.65 g; 60%). The product was stored in absence of oxygen and moisture in an argon box. ¹H-NMR (400 MHz, CDCl₃, 24 °C, δ [ppm]): 8.50 (d, 2 H, py-H), 7.62 (td, 2 H, py-H); 7.52 (d, 2 H, py-H), 7.11 (t, 2 H, py-H), 3.84 (s, 4 H, py-CH₂), 2.68 (t, 2 H, NCH₂CH₂N(CH₂py)₂), 2.53 (t, 2 H, NCH₂CH₂N(CH₂py)₂), 2.24 (t, 2 H, NCH₂CH₂CH₂Si), 2.13 (s, 3 H, NCH₃), 1.37 (m, 2 H, NCH₂CH₂CH₂Si), 0.37 (t, 2 H, NCH₂CH₂CH₂Si), -0.07 (s, 9 H, Si(CH₃)₃) ¹³C-NMR (101 MHz, CDCl₃, 26 °C, δ [ppm]): 160.1, 149.2, 136.5, 123.0, 122.0, 62.0, 61.1, 55.84, 55.7, 52.4, 42.8, 21.9, 14.4, -1.5 ESI-MS (m/z): [M+H]⁺: 371.26 IR (ATR, ν̃ [cm⁻¹]): 3051 (w), 3009 (w) 2950 (m), 2795 (m), 1589 (s), 1570 (m), 1472 (s), 1433 (s), 1362 (m), 1303 (m), 1247 (s), 1172 (m), 1146 (m), 1121 (m), 1047 (m), 1016 (m), 994 (m), 982 (m), 835 (vs), 775 (vs), 691 (m), 634 (w), 613 (m), 513 (w), 472 (w), 404 (w)

(2-methyl-propyl-aminoethyl)bis(2-pyridylmethyl)amine (Me-Prop-uns-penp): Me-uns-penp (1.00 g, 3.9 mmol) was mixed with *n*-iodopropane (0.7 g, 4.1 mmol) and K₂CO₃ (2.5 g, 18.1 mmol) in 20 mL of acetonitrile. The mixture was stirred under argon at 50 °C for two days. The solvent was removed by rotary evaporation and the residue was dissolved in diethyl ether and filtered. Removing the solvent *in vacuo* and purification via Kugelrohr distillation yielded the product as a yellow oil (0.65 g, 56%). The product was stored in the absence of oxygen and moisture in an argon box. ¹H-

NMR (400 MHz, CDCl₃, 23 °C, δ [ppm]): 8.49 (d, 2 H, py-H), 7.61 (td, 2 H, py-H); 7.52 (d, 2 H, py-H), 7.10 (t, 2 H, py-H), 3.83 (s, 4 H, py-CH₂), 2.67 (t, 2 H, NCH₂CH₂N(CH₂py)₂), 2.52 (t, 2 H, NCH₂CH₂N(CH₂py)₂), 2.21 (t, 2 H, NCH₂CH₂CH₃), 2.14 (s, 3 H, NCH₃), 1.40 (m, 2 H, NCH₂CH₂CH₃), 0.80 (t, 2 H, NCH₂CH₂CH₃) ¹³C-NMR (101 MHz, CDCl₃, 24 °C, δ [ppm]): 160.0, 149.1, 136.4, 122.9, 122.0, 61.0, 60.24, 55.7, 52.26, 42.7, 20.5, 12.0 ESI-MS (m/z): [M+H]⁺: 299.22 IR (ATR, ν̃ [cm⁻¹]): 3063 (w), 3009 (w), 2958 (m), 2933 (m), 2873 (m), 2801 (m), 1676 (w), 1589 (s), 1570 (s), 1472 (s), 1433 (s), 1362 (m), 1305 (m), 1249 (m), 1216 (m), 1147 (m), 1122 (m), 1083 (m), 1047 (s), 994 (s), 892 (m), 842 (m), 755 (vs), 613 (s), 516 (m), 468 (m)

Me-uns-penp_{immob}(silica gel): Silica gel for column chromatography (Kieselgel 60 M, Macherey-Nagel, Germany) was prepared by refluxing it in concentrated hydrochloric acid for 24 h followed by washing it with demineralized water for neutralisation.^[43] Me-PDMS-uns-penp (56 mg, 0.14 mmol) was dissolved in dry toluene, suspended with 1.00 g of prepared silica gel and stirred for at least 30 minutes. The condensation on the silica surface was performed at 130 °C under argon for 24 h.^[55] Additionally, the functionalized powder was filtered with a glass frit pore 4, washed with toluene, ethanol and diethyl ether. The material was transferred into an argon box, suspended in 10 mL of acetonitrile and 0.5 mL trimethylamine and stirred for ten minutes. The powder was washed again with acetonitrile, diethyl ether and dried in vacuum. The final functionalized silica gel was kept under argon in a glove box. IR (DRIFTS, ν̃ [cm⁻¹]): 2963, 2910, 1601, 1575, 1482, 1439, Raman (raman shift, ν̃ [cm⁻¹]): 3069 (s), 2962 (s), 2906 (s), 1661 (m), 1575 (m), 1224 (m), 1053 (s), 1010 (s), 833 (w), 636 (w), 486 (w) UV/Vis (diffuse reflectance, λ [nm]): 205, 260

Me-uns-penp_{immob}(monolith): A silica monolith (108 mg), pre-dried at 150 °C, was placed in a Schlenk reactor (Figure S10, Supporting Information) and covered with 60 mL of dry toluene with Me-PDMS-uns-penp (8.0 mg, 0.03 mmol). The reactor was heated to reflux for 24 h under argon.^[55] The monolith was placed into a petri dish and first covered with toluene, then with ethanol and finally with diethyl ether for 15 minutes each. Further preparation took place in an argon box. The monolith was treated with 1.0 mL trimethylamine in 20 mL acetonitrile for ten minutes. Afterwards the monolith was treated again with first acetonitrile and finally with diethyl ether each for 10 minutes. The monolith was dried in vacuum and stored in a glove box. IR (DRIFTS, ν̃ [cm⁻¹]): 2961, 1601, 1573, 1480, 1439 Raman (raman shift, ν̃ [cm⁻¹]): 3079 (w), 3069 (w), 2964 (w), 2909 (w), 1228 (w), 1052 (w), 1009 (vw), UV/Vis (diffuse reflectance, λ [nm]): 205, 260

[Cu(Me-uns-penp_{immob}(silica gel))](SO₃CF₃)₂: 200 mg of Me-uns-penp_{immob} were suspended in a solution of 100 mg copper(II) trifluoromethanesulfonate in 10 mL acetonitrile and stirred for one hour. Blue powder can be obtained by interrupting the reaction after ten minutes. The green product obtained after approximately one hour of complexation reaction. Both products were washed properly with acetonitrile and diethyl ether. After drying in vacuum, products were stored under argon. UV/Vis (diffuse reflectance, λ [nm]): 205, 260, 288, (421 for the green product)

[Cu(Me-uns-penp_{immob}(silica gel))]X (X: SO₃CF₃⁻, PF₆⁻): 50 mg of [Cu(MeCN)₄]X was dissolved in dry acetonitrile under inert conditions. 100 mg functionalized silica were suspended in the copper solution. After one hour the yellow solid was removed from the suspension, washed several times with acetonitrile and diethyl ether and dried in vacuum. The silica appears as a yellow solid and was stored under argon. UV/Vis (diffuse reflectance, λ [nm]): 205, 260, 288

[Cu(Me-uns-penp_{immob}(monolith))]SO₃CF₃: The functionalized monolith was placed into a petri dish and covered with a solution

of 50 mg $[\text{Cu}(\text{MeCN})_4] \text{SO}_3\text{CF}_3$ dissolved in 20 mL acetonitrile. After ten minutes, the monolith was kept in acetonitrile and diethyl ether, each time for ten minutes, to remove the remaining copper salt. After drying in vacuum the monolith had turned into a yellow colour. UV/Vis (diffuse reflectance, λ [nm]): 205, 260, 288

$\text{Cu}(\text{I})$ and $\text{Cu}(\text{II})$ complexes with the derivatives of uns-penp described below were prepared under argon similar to published procedures for related complexes.^[9,24]

[Cu(Me-PTS-uns-penp)]BPh₄: A solution of $[\text{Cu}(\text{MeCN})_4]\text{PF}_6$ (0.19 g, 0.51 mmol) in 2 mL acetone was added dropwise with stirring to a solution of Me-PTS-uns-penp (0.20 g, 0.54 mmol) in 0.5 mL acetone. Additionally, sodium tetraphenylborate (0.19 g, 0.56 mmol) was added to the yellow coloured complex solution. The final solid was obtained by adding the solution into approximately 40 mL of pentane. The yellow compound was filtered off, washed with diethyl ether and dried in vacuum. Single crystals for X-ray diffraction were obtained by diffusion of diethyl ether.

[Cu(Me-Prop-uns-penp)]BPh₄: A solution of $[\text{Cu}(\text{MeCN})_4]\text{PF}_6$ (0.24 g, 0.64 mmol) in 2 mL acetone was added dropwise to a stirred solution of Me-Prop-uns-penp (0.20 g, 0.67 mmol) in 0.5 mL acetone. Additionally sodium tetraphenylborate (0.24 g, 0.70 mmol) was added to the yellow coloured complex solution. The final solid was obtained by adding the solution into approximately 40 mL of diethyl ether. The yellow compound was filtered off, washed with diethyl ether and dried in vacuum. Single crystals for X-ray diffraction were obtained by ether diffusion.

[Cu(Me-Prop-uns-penp)Cl]ClO₄: Me-Prop-uns-penp (50 mg, 0.16 mmol) was dissolved into 4 mL of methanol. $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (14 mg, 0.08 mmol) and of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (31 mg, 0.08 mmol) were added. After brief stirring suitable crystals for X-ray analysis could be obtained by slow evaporation of the solvent.

Supporting Information (see footnote on the first page of this article): Additional information about time resolved stopped flow measurements, calibration values via UV/Vis measurement, BET values, spectra of surface investigations, schematic drawing of the monolith reactor, additional results of oxygen treatment, GC-MS and crystallographic data.

Acknowledgements

Financial support is gratefully acknowledged by the Deutsche Forschungsgemeinschaft (DFG SPP1740, SCHI 377/13-2). Open access funding enabled and organized by Projekt DEAL.

Keywords: immobilization • monolith • copper complex • tripodal ligands • superoxido complex

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Manuscript received: January 16, 2021

Revised manuscript received: February 17, 2021

Accepted manuscript online: February 17, 2021