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Dinuclear Copper Complexes Based on Parallel β-Diiminato Binding Sites and their Reactions with O_2: Evidence for a Cu−O−Cu Entity†

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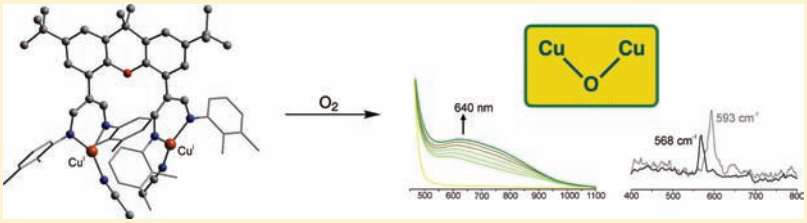
Supporting Information

ABSTRACT:



Investigations concerning the system β-diketiminato-Cu^I/O_2 have revealed valuable insights that may be discussed in terms of the behavior of mononuclear oxygenases containing copper. On the other hand nature also employs dinuclear Cu enzymes for the activation of O_2. With this background the ligand system $[^{Me_2C_6H_3}\mathbf{Xanthdim}]^{2-}$ containing two parallel β-diiminato binding sites linked by a xanthene backbone with 2,3-dimethylphenyl residues at the diiminato units was investigated with respect to its copper coordination chemistry. The diimine $[^{Me_2C_6H_3}\mathbf{Xanthdim}]H_2$ was treated with CuO*t*Bu in the presence of acetonitrile, PPh_3, and PMe_3 to yield the corresponding complexes $[^{Me_2C_6H_3}\mathbf{Xanthdim}](Cu(L))_2$ (L = CH_3CN, **1**, PPh_3, **2**, and PMe_3, **3**) that proved to be stable and were fully characterized. Single crystal X-ray diffraction analyses performed for the three complexes showed that considerable steric crowding within the binding pockets of **2** leads to a very long Cu−Cu distance while the structures of **1** and **3** are relaxed. Compounds **2** and **3** are relatively robust toward air, whereas **1** is very sensitive and quantitatively reacts with O_2 at room temperature (r.t.) within less than 2 min to give intractable compounds. At low temperatures the formation of a green intermediate was observed that was identified as a $Cu^{II}-O-Cu^{II}$ species spectroscopically and chemically. This finding is of relevance also in the context of the results obtained testing **1** as a catalyst for phenol oxidation using O_2: **1** efficiently catalyzes phenol coupling, while there was no evidence for any oxygenation reactions occurring.

INTRODUCTION

The β-diiminato ligand system is very versatile and has been shown to display a very rich coordination chemistry stabilizing high as well as low oxidation states.[1] This of course makes it also ideal as a ligand in transition metal complexes that activate small substrates, such as O_2, N_2, and CO_2, and recent years have revealed several impressive precedent cases.[2,3] Many of the corresponding systems have been shown to work via a mechanism where two metal centers cooperate in the activation process,[2] a principle that is also common in many metalloenzymes. This has recently stimulated a strong interest in the design of ligands containing two β-diiminato moieties in close proximity.[4] We have focused in particular on a ligand where two β-diiminato units are oriented parallel to each other, and recently we described the development of a corresponding ligand precursor, $[^{Me_2C_6H_3}\mathbf{Xanthdim}]H_2$ (Chart 1).[5] It has been successfully employed for the synthesis of zinc as well as of magnesium complexes, whose potential as epoxide/CO_2 copolymerization catalysts[6] has been investigated. Furthermore, corresponding iron(II) complexes were prepared to study their behavior in the presence of O_2.[7] It seemed only natural to extend this work also to copper chemistry: Both the discovery of various di- or polynuclear O_2-activating copper enzymes such as the particulate methane monooxygenase (pMMO)[8] as well as reports on the selective oxidation of methane to methanol at dinuclear copper sites embedded in zeolites,[9] stimulate research on dinuclear copper systems.

The chemistry of *mononuclear* β-diketiminato copper complexes has been mainly investigated by Tolman et al., often with the aim of gaining insights into the binding and activation of O_2 in mononuclear copper enzymes, such as the neuroenzymes dopamine β-monooxygenase and peptidylglycine α-hydroxylating monooxygenase.[3,10,11] It has been found that Cu^I complexes

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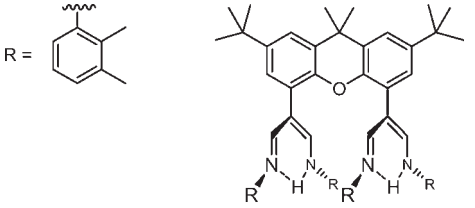
Chart 1



containing sufficiently bulky β-diketiminato ligands allow for the isolation and characterization of 1:1 adducts of O_2, while sterically less demanding ligands lead to dinuclear complexes with Cu(μ-O)$_2$Cu diamond core structures (Chart 2).[3] Moreover it was shown that within the 1:1 adducts the resulting superoxide/peroxide ligands can be further activated by the presence of an additional copper(I) center so that the β-diketiminato ligand gets oxidized to yield a Cu(II)-*o*-iminosemiquinone species.[12]

On this background we therefore set out exploring the capability of the novel ligand system [^{Me_2C_6H_3}**Xanthdim**]$^{2-}$ to form stable, *dinuclear* Cu^{I} complexes.

This appeared to be a challenging task, since Cu^{I} complexes are often unstable because of a marked intrinsic tendency to disproportionate to Cu^{II} and Cu metal, and this problem occurs all the more in dinuclear complexes. In case of success, an investigation seemed to be worthwhile not only concerning the cooperativity of the two Cu^{I} centers in a potential O_2 activation process but also to examine what kind of difference the parallel arrangement of the diiminato donor functions makes in comparison to the vis-à-vis orientation that is preferred if mononuclear complexes are employed (for instance a *cis* Cu−O−O−Cu unit could be imagined[13]).

EXPERIMENTAL SECTION

General Procedures. All manipulations were carried out in a glovebox, or else by means of Schlenk-type techniques involving the use of a dry argon atmosphere. The ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker DPX 300 NMR spectrometer (^{1}H 300.1 MHz, ^{13}C 75.5 MHz, ^{31}P 121.5 MHz) with CH_2Cl_2 or $CDCl_3$ as solvent at 20 °C. The ^{1}H NMR spectra were calibrated against the residual proton, the ^{13}C NMR spectra against natural abundance ^{13}C resonances of the deuterated solvents (CD_2Cl_2 δ_H 5.32 ppm and δ_C 53.5 ppm, $CDCl_3$ δ_H 7.26 ppm and δ_C 77.0 ppm, respectively), and the ^{31}P NMR spectra against H_3PO_4 as an external standard. Microanalyses were performed on a Leco CHNS-932 elemental analyzer. Infrared (IR) spectra were recorded using samples prepared as KBr pellets with a Shimadzu FTIR-8400S-spectrometer. UV/vis spectra were obtained at variable temperatures on an Agilent 8453 UV−visible Spectrophotometer equipped with a Unisoku USP-203-A cryostat. When necessary baseline drifting caused by minimal frosting of the cuvettes under low temperature conditions were corrected by subtracting an average value of a region with no absorbance (1080−1100 nm). Raman spectra at low temperature, controlled via a Bruker heating control unit, were acquired using a Bruker RAM II FT-Raman Module (1064-nm excitation; Nd:YAG laser) and a Horiba Jobin-Yvon LabRAM HR800 confocal Raman Spectrometer (647-nm excitation, Kr ion laser).

Materials. Solvents were purified, dried, degassed, and stored over molecular sieves prior to use. A mixture of $^{18}O_2$, $^{16}O^{18}O$, $^{16}O_2$ (1:2:1) was prepared by applying a discharge to a 1:1 mixture of $^{16}O_2$ and $^{18}O_2$ in a flask sealed with a Young tap (at 125 mbar) as evidenced by EI mass spectrometry. Subsequently, the flask was filled up with argon until a pressure of 1 bar was reached. The gas mixture (20−40 mL) was removed via a syringe and bubbled at −80 °C through the solution. Pure copper(I)-*tert*-butoxide, Cu*O*t*Bu*, was prepared according to the literature procedure.[14] [Na(thf)O(2,4-*t*Bu)C$_6$H$_3$], **A′**, was obtained by adding an excess of NaH to a solution of 2,4-di-*tert*-butylphenol, **A**, in tetrahydrofuran (thf). The resulting suspension was filtered after stirring for 4 h at r.t. Precipitation of the product was achieved by reducing the volume of the filtrate to a quarter under reduced pressure and adding a 3-fold excess of hexane. Filtration and drying in vacuo gave a white solid, **A′**, in 65% yield. Purity of **A′** was ensured by ^{1}H NMR spectroscopy. Compound **4**, [(N(2,6-Me$_2$C$_6$H$_3$)C(CH$_3$))$_2$CH]Cu(MeCN), is already known,[18] but was synthesized via an alternative route: After stirring a solution of β-diketimine [(N(2,6-Me$_2$C$_6$H$_3$)C(CH$_3$))$_2$CH]H and Cu*O*t*Bu* in a benzene/acetonitrile solvent mixture (2:1) for 18 h at r.t., all volatiles were removed. The product was extracted with hexane, and reduction of the volume caused the precipitation of a yellow solid. A filtration and subsequent drying in vacuo led to **4** in 38% yield. The NMR data and the chemical behavior of **4** are in agreement with those reported previously.[18]

[^{Me_2C_6H_3}Xanthdim](Cu(NCCH$_3$))$_2$, 1. Addition of 10 mL of benzene to a suspension of 400 mg (0.46 mmol) of [^{Me_2C_6H_3}**Xanthdim**]H$_2$ and 125 mg (0.92 mmol) of Cu*O*t*Bu* in 5 mL of acetoniltrile led to a clear yellow solution which was stirred for 18 h at r.t. The resulting cloudy solution was treated with 20 mL of acetonitrile. A yellow solid precipitated, which was filtered off after the reaction mixture had been stirred for further 4 h at r.t. Drying of the residue under vacuum yielded 348 mg (0.32 mmol, 70%) **1**.

^{1}H NMR (CD_2Cl_2, 297 K): δ 1.33 (s, 18H, C(C**H**$_3$)$_3$), 1.69 (s, 6H, C(C**H**$_3$)$_2$), 1.99 (s, 6H, C**H**$_3$CN), 2.19 (s, 12H, C**H**$_3$), 2.36 (s, 12H, C**H**$_3$), 6.73 (m, 8H, C**H**), 6.85 (ps-t, 4H, C**H**), 7.07 (d, ^{4}J(H, H) = 2.0 Hz, 2H, C**H**), 7.24 (d, ^{4}J(H, H) = 2.0 Hz, 2H, C**H**), 7.72 (s, 4H, NC**H**); ^{13}C NMR (CD_2Cl_2, 297 K): δ 2.6 (**C**H$_3$CN), 14.9 (**C**H$_3$), 20.5 (**C**H$_3$), 31.4 (C(**C**H$_3$)$_3$), 33.3 (C(**C**H$_3$)$_2$), 34.3 (**C**(CH$_3$)$_3$), 34.8 (**C**(CH$_3$)$_2$), 102.7 (**C**), 116.7 (**C**^{Ar}), 118.6 (**C**H^{Ar}), 119.5 (**C**H^{Ar}), 124.0 (**C**H^{Ar}), 124.1 (**C**H^{Ar}), 126.8 (**C**H^{Ar}), 128.4 (**C**^{Ar}), 129.2 (**C**^{Ar}), 131.3 (**C**^{Ar}), 136.8 (**C**^{Ar}), 144.3 (**C**^{Ar}), 145.9 (**C**^{Ar}), 154.5 (**C**^{Ar}), 158.9 (N**C**H); Anal. found: C 71.80, H 6.75, N: 8.13; Calcd for $C_{65}H_{74}N_6Cu_2O$: C 72.13, H 6.89, N 7.76%; IR (KBr, cm^{-1}): 3057 (w), 2867 (m), 2257 (w, C≡N), 1588 (s), 1573 (s), 1452 (vs), 1371 (m), 1323 (vs), 1244 (vs), 1219 (s), 1186 (w), 1165 (w), 1059 (m), 1017 (m), 985 (w), 877 (w), 857 (w), 808 (w), 782 (s), 748 (w), 726 (w), 682 (w), 654 (w).

[^{Me_2C_6H_3}Xanthdim](Cu(PPh$_3$))$_2$, 2. After stirring a yellow solution of 300 mg (0.34 mmol) of [^{Me_2C_6H_3}**Xanthdim**]H$_2$, 94 mg (0.69 mmol) of Cu*O*t*Bu* and 180 mg (0.69 mmol) of PPh$_3$ in 3 mL of benzene for 19 h at r.t., it was concentrated to a volume of 1.5 mL. Addition of 10 mL of acetonitrile caused the formation of a yellow precipitate which was filtered off after stirring the suspension for additional 3 h. Separation of all volatile components under vacuum led to 394 mg (0.26 mmol, 75%) of **2**.

^{1}H NMR (CD_2Cl_2, 297 K): δ 1.32 (s, 18H, C(C**H**$_3$)$_3$), 1.68 (s, 6H, C(C**H**$_3$)$_2$), 1.88 (s, 12H, C**H**$_3$), 2.01 (s, 12H, C**H**$_3$), 6.70 −7.25 (m, br, 46H, C**H**), 7.92 (s, 4H, HC**N**); ^{13}C NMR (CD_2Cl_2, 297 K): δ 15.3 (C(**C**H$_3$)$_2$), 20.4 (**C**H$_3$), 31.4 (C(**C**H$_3$)$_3$), 34.2 (**C**(CH$_3$)$_2$), 34.3 (**C**H$_3$), 34.7 (**C**(CH$_3$)$_3$), 103.2 (**C**), 119.7 (**C**H^{Ar}), 121.8 (**C**H^{Ar}), 124.4 (**C**H^{Ar}), 125.1 (**C**H^{Ar}), 126.7 (**C**H^{Ar}), 128.3 (d, J(C, P) = 9.5 Hz, **C**H^{Ar}), 129.0 (J(C, P) = 10.1 Hz, **C**^{Ar}), 129.4 (**C**H^{Ar}), 131.0 (**C**^{Ar}), 132.7 (**C**^{Ar}), 133.3 (d, J(C, P) = 14.8 Hz, **C**H^{Ar}), 137.1 (**C**^{Ar}), 144.2 (**C**^{Ar}), 144.6 (**C**^{Ar}), 156.1 (**C**^{Ar}), 159.2 (N**C**H); ^{31}P NMR (CD_2Cl_2, 297 K): δ 3.52 (s); Anal. found: C 76.14, H 6.74, N: 3.41; Calcd for $C_{97}H_{98}N_4Cu_2OP_2$: C 76.40, H 6.48, N 3.67%; IR (KBr, cm^{-1}): 3054 (m), 2863 (m), 1588 (s), 1577 (s), 1459 (vs), 1437 (vs), 1364 (m), 1317

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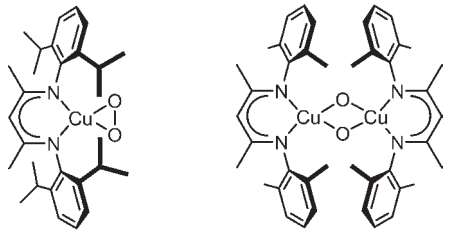
Chart 2



(vs), 1244 (m), 1217 (m), 1065 (m), 909 (w), 853 (w), 781 (m), 744 (m), 694 (s), 528 (s), 503 (m), 493 (m).

[^{Me_2C_6H_3}Xanthdim](Cu(PMe$_3$))$_2$, 3. A yellow solution of 300 mg (0.34 mmol) of [^{Me_2C_6H_3}**Xanthdim**]H_2 and 94 mg (0.69 mmol) of CuO*t*Bu in 5 mL of benzene was rapidly cooled to −30 °C. On top of the resulting frozen mixture approximately 0.5 mL (369 mg, 4.73 mmol) of PMe_3 were condensed. Slowly warming to r.t. led to an orange solution, which was stirred for 17 h. After the removal of all volatiles the remaining orange crude product was redissolved in 2 mL of benzene followed by an addition of 10 mL of acetonitrile. The resulting yellow suspension was stirred for further 16 h at r.t. Filtration and drying of the residue under vacuum gave 264 mg of (0.23 mmol, 67%) **3** as a yellow solid.

^{1}H NMR (CD_2Cl_2, 297 K): δ 0.81 (d, ^2J(H, P) = 6.3 Hz), 18H, P−C**H**$_3$), 1.33 (s, 18H, C(C**H**$_3$)$_3$), 1.68 (s, 6H, C(C**H**$_3$)$_2$), 2.22 (s, 12H, C**H**$_3$), 2.33 (s, 12H, C**H**$_3$), 6.75−6.91 (m, 12H, C**H**), 7.07 (d, ^4J(H, H) = 2.1 Hz, 2H, C**H**), 7.21 (d, ^4J(H, H) = 2.4 Hz, 2H, C**H**), 7.82 (d, J(H, P) = 2.1 Hz, 4H, NC**H**); ^{13}C NMR (CD_2Cl_2, 297 K): δ 15.2 (d, ^1J(C, P) = 22.6 Hz, **C**H$_3$), 15.2 (d, J(C, P) = 3.1 Hz, **C**H$_3$), 20.5 (**C**H$_3$), 31.4 (C(**C**H$_3$)$_3$), 34.0 (C(**C**H$_3$)$_2$), 34.2 (**C**(CH$_3$)$_3$), 34.7 (**C**(CH$_3$)$_2$), 103.1 (d, J(C, P) = 1.4 Hz, (**C**)), 119.6 (**C**H^{Ar}), 120.8 (**C**H^{Ar}), 124.0 (**C**H^{Ar}), 125.9 (**C**H^{Ar}), 126.7 (**C**H^{Ar}), 128.3 (**C**^{Ar}), 129.0 (**C**^{Ar}), 131.1 (**C**^{Ar}), 136.6 (**C**^{Ar}), 144.2 (**C**^{Ar}), 145.0 (**C**^{Ar}), 156.3 (**C**^{Ar}), 158.2 (NC**H**^{Ar}); ^{31}P NMR (CD_2Cl_2, 297 K): δ −47.72 (s); Anal. found: C 70.06, H 7.33, N: 4.81; Calcd for $C_{67}H_{86}N_4Cu_2OP_2$: C 69.83, H 7.52, N 4.86%; IR (KBr, cm^{-1}): 3058 (w), 2901 (m), 2865 (m), 1588 (s), 1577 (s), 1459 (vs), 1445 (vs), 1380 (m), 1362 (vs), 1322 (s), 1284 (m), 1273 (m), 1246 (m), 1219 (s), 1187 (w), 1063 (m), 986 (w), 958 (m), 856 (w), 780 (m), 721 (m), 671 (w).

Catalytic Oxidative Coupling of 2,4-Di-*tert*-butylphenol A in Presence of 1 to 3,3′,5,5′-Tetra-*tert*-butyl 2,2′-biphenol B. Under strictly anaerobic conditions 25 mg (23 μmol) of **1** and 47.6 mg (0.23 mmol) of **A** were dissolved in 4 mL of thf and toluene, respectively. Optionally molecular sieves were added. After exposure to an excess of dry dioxygen the reaction mixture was stirred vigorously for 6 h at r.t. The reaction was terminated by removal of all volatiles, redissolving in 30 mL of diethyl ether, and treatment of the organic phase with 20 mL of diluted HCl (4 M). Any molecular sieves employed were removed by filtering off the ether solution through a plug of Celite prior to the hydrochloric acid addition. After separating the phases the aqueous one was extracted twice with 20 mL of diethyl ether. The combined organic phases were dried with $MgSO_4$, and after filtration the solvent was removed under reduced pressure. To the resulting solid 17.9 μL (0.23 mmol) dimethylformamide were added as an internal standard, and the conversion was determined by ^{1}H NMR spectroscopy. Yields were determined from at least two replicate runs and are given with an accuracy of ±1%. Alternatively, the sodium salt of **A**, [Na(thf)O(2,4-*t*Bu)C$_6$H$_3$], **A′** (69.3 mg 0.23 mmol) was employed. Because of the mononuclear nature of the complex [(N(2,6-Me$_2$C$_6$H$_3$)C(CH$_3$))$_2$CH]Cu(MeCN) **4**, in comparison to **1** the double amount of equivalents (0.46 mmol) was used.

B: ^{1}H NMR ($CDCl_3$, 297 K): δ 1.32 (s, 18H, C(C**H**$_3$)$_3$), 1.45 (s, 18H, C(C**H**$_3$)$_3$), 7.12 (d, ^4J(H, H) = 2.5 Hz, 2H, C**H**), 7.39 (d, ^4J(H, H) = 2.5 Hz, 2H, C**H**); ^{13}C NMR ($CDCl_3$, 297 K): δ 29.6 (C(**C**H$_3$)$_3$), 31.6 (C(**C**H$_3$)$_3$), 34.4 (**C**(CH$_3$)$_3$), 35.1 (**C**(CH$_3$)$_3$), 122.4 (**C**^{Ar}), 124.7 (**C**H^{Ar}), 125.2 (**C**H^{Ar}), 136.2 (**C**^{Ar}), 142.9 (**C**^{Ar}), 149.7 (**C**^{Ar}).

Low Temperature Experiments Concerning the Reaction of 1 with O_2. *(a) UV/vis Spectroscopy.* A 1-cm-path-length quartz cuvette filled with 2 mL of a solution of **1** in thf (1 mM) was sealed with a septum and cooled to −80 °C. Dry O_2 was bubbled through it for 10 s and the spectra were recorded in an interval of 2 s. Spectroscopic changes (after 10, 30, 50, 110, 210, 610 s) are summarized in Figure 4. Either addition of 0.1 mL of a 400 mM solution of PPh_3 in thf or annealing of the sample caused decrease of the new band.

The same procedure was applied when 0.1 mL of a 2-(*tert*-butylsulfonyl)iodosylbenzene solution in CH_2Cl_2 (20 mM) or 1.8 mg of Me_3NO in 0.2 mL of thf were added instead of O_2 at −70 °C.

ε of the Cu−O−Cu intermediate was determined assuming a complete conversion of **1**; dilution effects upon substrate addition were considered.

(b) Spectrophotometric O_2 Titrations. A 1-cm-path-length quartz cuvette filled with 2 mL of a solution of **1** in thf (1 mM) was sealed with a septum and cooled to −80 °C. In one experiment, spectra were taken for more than 30 min, monitoring the absorbance at 640 and 1080 nm, to ensure that no oxygen from air diffused into the sample over a longer period of time.

Addition of 0.5 equiv of O_2 or 1 equiv of O_2 was performed by injecting a O_2-saturated thf solution (10 mM), prepared by bubbling O_2 through argon-saturated thf in a Schlenk tube for 25 min at 25 °C.[15] In case of the experiment involving 1 equiv of O_2, 200 μL of the O_2-saturated thf solution were injected into the cuvette, whereas 0.5 equiv of O_2 were added by injecting 100 μL of the O_2-saturated thf solution followed by 100 μL of an argon-saturated thf solution to keep the level of dilution constant.

The reaction was followed by monitoring the absorption band at 640 nm until no further increase was observed, which took not longer than 15 min.

The investigation of the oxygen atom-uptake from sPhIO was carried out as described above: addition of the first equiv of sPhIO was followed by injection of an excess of O_2 or a second equiv of sPhIO after equilibration with stirring.

(c) Raman Spectroscopy. A screw-cap NMR tube equipped with septum was charged with 0.5 mL of a solution of **1** in thf (46 mM or 9 mM) and cooled to −80 °C. Dry $^{16}O_2$ and $^{18}O_2$, respectively, were bubbled through the solutions for 10 s prior to the spectroscopic measurements, carried out at −80 °C.

(d) PPh_3 Oxidation. Under strictly anaerobic conditions 20 mg of (18.5 μmol) **1** were dissolved in 8 mL of thf, cooled to −80 °C and exposed to an excess of dry dioxygen under vigorous stirring. After 20 min dioxygen was removed by several vacuum/argon cycles, and a solution of 48.4 mg of (0.185 mmol) PPh_3 in 1 mL of thf was added. The reaction mixture was stirred for further 45 min at −80 °C and subsequently annealed to room temperature (r.t.). Removal of all volatiles led to a brown solid, to which 14.3 mg of (36.9 μmol) [nBu$_4$N]PF_6 were added as an internal standard, and the conversion was determined by ^{31}P NMR spectroscopy. A control experiment in the absence of **1** did not lead to phosphane oxidation.

Crystal Structure Determinations. Crystals of **1** × 4(CH_3CN) and **3** suitable for single crystal analysis were obtained from a 5:1 mixture of acetonitrile and benzene. Crystals of **2** × 6(C_7H_8) were obtained by storing a concentrated solution in toluene at 4 °C. Data collections were performed at 100 K on a Stoe IPDS 2T diffractometer using Mo-K_α radiation (λ = 0.71073 Å); radiation source was a sealed tube generator with graphite monochromator. Numerical absorption correction was applied for **1** and multiscan (PLATON[16]) absorption correction for **2**

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Table 1. Crystal Data and Experimental Parameters for the Crystal Structure Analyses of 1, 2, and 3

	1 × 4(CH_3CN)	2 × 6(C_7H_8)	3
formula	$C_{73}H_{86}Cu_2N_{10}O$	$C_{139}H_{146}Cu_2N_4OP_2$	$C_{67}H_{86}N_4Cu_2OP_2$
weight, g mol^{-1}	1246.60	2077.62	1152.42
crystal system	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2/c$	$P2_1/c$
a, Å	16.0571(8)	16.8182(9)	13.6624(4)
b, Å	16.0722(9)	15.6847(9)	28.0073(9)
c, Å	16.1381(9)	27.1407(9)	17.2399(5)
α, deg	98.674(4)	90	90
β, deg	105.632(4)	127.083(2)	107.578(2)
γ, deg	119.080(4)	90	90
V, $Å^3$	3302.9(3)	5711.5(5)	6288.8(3)
Z	2	2	4
density, g cm^{-3}	1.253	1.208	1.217
$\mu(Mo_{K\alpha})$, mm^{-1}	0.695	0.455	0.771
$F(000)$	1320	2208	2448
GoF	0.992	1.018	1.070
$R_{ind}[I > 2\sigma(I)]$	R1 = 0.0752	R1 = 0.0362	R1 = 0.0833
	wR2 = 0.1596	wR2 = 0.0907	wR2 = 0.1868
R_{ind} (all data)	R1 = 0.1369	R1 = 0.0428	R1 = 0.1082
	wR2 = 0.1829	wR2 = 0.0937	wR2 = 0.2001
$\Delta\rho_{min}/\Delta\rho_{max}$, e $Å^{-3}$	−1.11/1.36	−0.62/0.63	−1.26/1.23

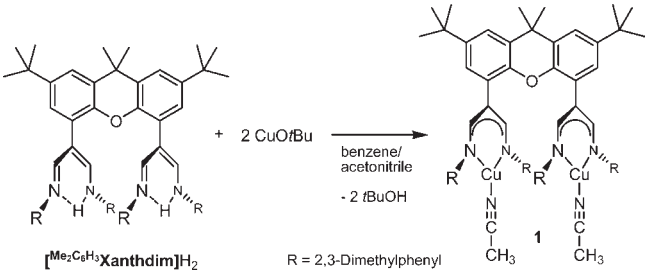
and **3**. The structures (Table 1) were solved by direct methods (SHELXS-97)[17a] and refined by full matrix least-squares procedures based on F^2 with all measured reflections (SHELXL-97).[17b] All non-hydrogen atoms were refined anisotropically. H atoms were introduced in their idealized positions and refined as riding.

RESULTS AND DISCUSSION

Complex Synthesis. First experiments on the system $[^{Me_2C_6H_3}\mathbf{Xanthdim}]^{2-}/Cu^{I}$ confirmed the suspicions with respect to disproportionation. While mononuclear diketiminato-Cu^{I} complexes were successfully synthesized in the past[18] by reactions of the corresponding lithium diketiminates with $[Cu(NCCH_3)_4]SO_3CF_3$, all attempts to react $[^{Me_2C_6H_3}\mathbf{Xanthdim}]Li_2$ with $[Cu(NCCH_3)_4]SO_3CF_3$ led to immediate disproportionation. Lee et al. successfully prepared a Cu^{I} complex of a macrocyclic ligand containing two diketiminato units[4d] in the absence of strongly coordinating solvents like acetonitrile by reacting the protonated form of the ligand in toluene with copper(I)-*tert*-butoxide. Isolation was possibly aided by the insolubility of the product. However, applying the same procedure to $[^{Me_2C_6H_3}\mathbf{Xanthdim}]H_2$ again only led to disproportionation, even when thf was chosen as the solvent to provide a stronger potential coligand for the stabilization of complexed Cu^{I} centers (toluene molecules served as coligands in the system of Lee). A successful synthesis was finally achieved by addition of acetonitrile.

Treatment of $[^{Me_2C_6H_3}\mathbf{Xanthdim}]H_2$ with 2 equiv of copper(I)-*tert*-butoxide in a mixture of benzene and acetonitrile (2:1) at r.t. immediately led to a clear yellow solution, and subsequent addition of excessive acetonitrile led to the precipitation of the product $[^{Me_2C_6H_3}\mathbf{Xanthdim}](Cu(NCCH_3))_2$, **1** (Scheme 1). **1** could be isolated in 70% yield after work up, and it is readily soluble in benzene, toluene, and thf. As expected, the complex is very sensitive to O_2, both in the solid state and in solution, and it

Scheme 1



was characterized by IR spectroscopy, elemental analysis, and NMR spectroscopy.

After dissolution of the ligand precursor, the protons bound inside the asymmetric diimine units rapidly flip from one N atom to the other; hence, the protons belonging to the aldimine backbone are equivalent and split to a doublet by coupling with the N−H proton in the ^1H NMR spectrum. Consequently, the observation of a singlet signal for the diiminato unit is a first indication of a successful deprotonation, and a second one is the absence of a triplet originating from the N−H unit at around 12 ppm. The ^1H NMR spectrum of **1** in CD_2Cl_2 matched these criteria and thus revealed the quantitative replacement of the N−H protons by copper ions. At the same time it pointed to a highly symmetric structure. Two singlets are observed for all methyl groups bonded in 2- and 3-positions of the aryl rings, shifted to lower field in comparison to the corresponding signals in $[^{Me_2C_6H_3}\mathbf{Xanthdim}]H_2$. The acetonitrile ligands at the copper centers also show only one singlet. Addition of a large excess of degassed water to such an NMR sample (CD_2Cl_2 as the solvent) revealed also water-sensitivity of **1**, albeit not to an extent that could have been expected in view of the rather basic character of

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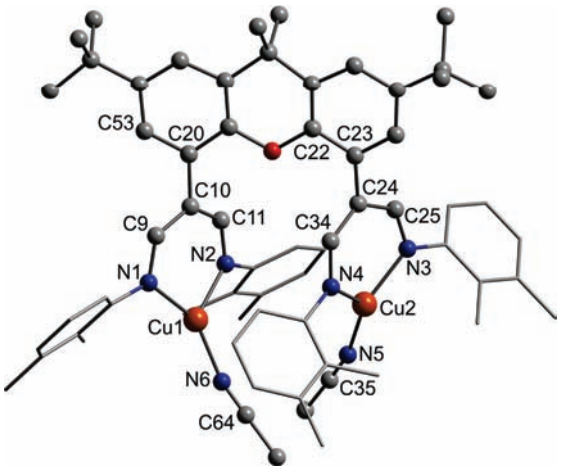
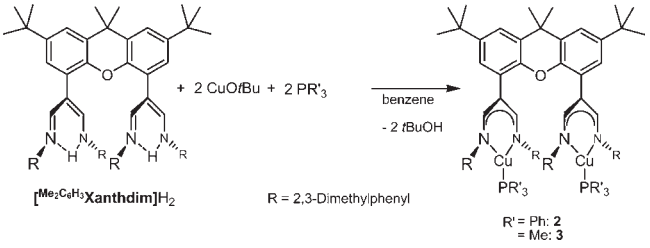


Figure 1. Molecular structure of **1** co-crystallized with four molecules of acetonitrile. All hydrogen atoms and solvent molecules have been omitted for clarity. Selected bond lengths [Å] and angles [deg]: Cu1−Cu2 4.7739(10), Cu1−N1 1.952(4), Cu1−N2 1.990(4), Cu2−N3 1.953(4), Cu2−N4 1.979(4), Cu1−N6 1.882(5), N6−C64 1.141(7), Cu2−N5 1.867(2), N5−C35 1.159(8), N1−C9 1.338(6), N2−C11 1.315(6), C9−C10 1.393(7), C10−C11 1.423(7), N3−C25 1.333(6), N4−C34 1.328(6), C25−C24 1.399(7), C24−C34 1.402(8), N1−Cu1−N2 96.87(17), N1−Cu1−N6 142.6(2), Cu1−N6−C64 164.6(5), N3−Cu2−N4 97.30(18), N3−Cu2−N5 136.7(2), Cu2−N5−C35 165.5(5), N1−C9−C10 127.5(4), C9−C10−C11 125.3(4), N2−C11−C10 126.2(5), N3−C25−C24 128.4(5), C25−C24−C34 124.7(5), N4−C34−C24 126.7(5), C9−C10−C20-C53 −44.8(7), C34−C24−C23-C22 62.8(8), C10−C9−N1−Cu1 11.1(8), C24−C25−N3−Cu2 9.7(8), C9−N1−Cu1−N6 150.5(5), C34−N4−Cu2−N5 −149.6(4), N1−Cu1−N2−C11 21.4(5), N3−Cu2−N4−C34 22.8(5).

the β-diiminato ligands: After 30 min the ^{1}H NMR spectrum shows signals for three different species: **1**, the mononuclear complex [^{Me_2C_6H_3}**Xanthdim**]H(Cu(NCCH$_3$)), and [^{Me_2C_6H_3}**Xanthdim**]H$_2$ in an approximate ratio of 1:2:3. Complete hydrolysis of **1** occurs within 48 h, and it is accompanied by the formation of an orange colored precipitate. Single crystals of **1** could be grown by storing a solution of **1** in a 5:1 mixture of acetonitrile and benzene at r.t., and the result of the X-ray diffraction analysis is shown in Figure 1. The two copper ions show a distorted trigonal planar coordination geometry with chelating binding angles of 96.87(17)° (N1−Cu1−N2) and 97.30(18)° (N3−Cu2−N4). The Cu−Cu separation of 4.7739(10) Å is comparable to the one observed in an analogous (three-coordinated) zinc complex [^{Me_2C_6H_3}**Xanthdim**](ZnEt)$_2$ (4.8654(7) Å).[6] Furthermore, it can be seen that the binding pockets are indeed oriented parallel to each other without any distortion because of the quite low steric demand of the coordinating acetonitrile ligands.

As for a large number of the diketiminato-copper chemistry reported so far, mononuclear Cu^I-acetonitrile complexes were employed (since the acetonitrile ligand is readily replaced),[3,18] **1** can be envisaged as a valuable precursor for novel multicopper chemistry and O_2 activation studies (also compare below). In this context it seemed worthwhile to examine the influence of the coligands L in [^{Me_2C_6H_3}**Xanthdim**](CuL)$_2$ on the stability and O_2-reactivity. Phosphane ligands have been shown to replace acetonitrile ligands at diketiminato-Cu^I units leading to complexes with retarded reactivity, which, however, were often

Scheme 2



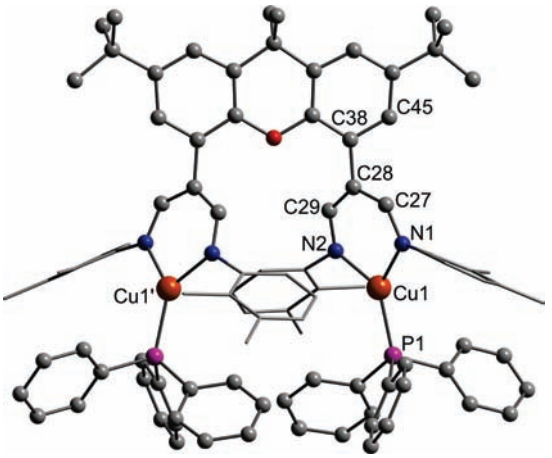


Figure 2. Molecular structure of **2** co-crystallized with six molecules of toluene. All hydrogen atoms and solvent molecules have been omitted for clarity. Selected bond lengths [Å] and angles [deg]: Cu1−Cu1′ 6.6303(4), Cu1−N1 1.9633(12), Cu1−N2 1.9699(12), Cu1−P1 2.1748(4), N1−C27 1.3251(19), N2−C29 1.3227(19), C27−C28 1.407(2), C28−C29 1.402(2), N1−Cu1−N2 96.65(5), N1−Cu1−P1 131.05(4), N1−C27−C28 128.17(13), C27−C28−C29 124.89(13), N2−C29−C28 126.15(13), C45−C38−C28-C29 127.2(2), C28−C27−N1−Cu1 −4.6(3), C27−N1−Cu1−P1 −173.26(12), N1−Cu1−N2−C29 2.33(16).

employed as precursors for oxidation chemistry, too. Hence, our investigations were extended to PPh_3 and PMe_3 ligands.

When the reaction shown in Scheme 1 was performed in the absence of acetonitrile but in the presence of 2 equiv of triphenylphosphane, again a yellow solution was formed, from which yellow [^{Me_2C_6H_3}**Xanthdim**](Cu(PPh$_3$))$_2$, **2**, could be precipitated (Scheme 2) via addition of acetonitrile (75% yield after workup).

Compound **2** shows similar solubilities as **1** but it is significantly more stable against air: a solution changes color from yellow to brown only after several minutes, and the solid is stable in air for hours. **2** has been characterized by NMR spectroscopy, IR spectroscopy and elemental analysis. Naturally, the ^{1}H NMR spectrum obtained for **2** only shows slight differences in comparison to the one recorded for **1**. The phosphane ligands give rise to a singlet resonance at 3.52 ppm in the ^{31}P NMR spectrum, which thus compares well to the signals found for other diketiminato-Cu-phosphane complexes.[19] Single crystals suitable for X-ray diffraction could be grown by storing a concentrated solution of **2** in toluene at 4 °C, and Figure 2 shows the molecular structure.

Complex **2** crystallizes as a toluene solvate in the centrosymmetric space group $P2/c$ with the complex molecule lying on a

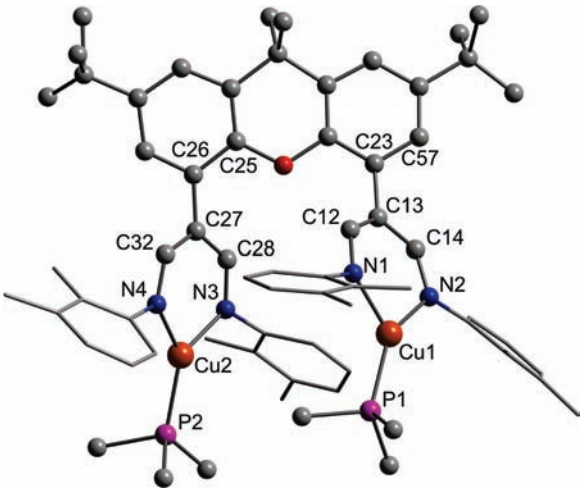


Figure 3. Molecular structure of **3**. All hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [deg]: Cu1−Cu2 5.6670(11) Cu1−N1 1.967(4), Cu1−N2 1.959(4), Cu2−N3 1.967(5), Cu2−N4 1.934(5), Cu1−P1 2.1499(17), Cu2−P2 2.1437(19), N1−C12 1.314(6), N2−C14 1.330(7), C12−C13 1.418(7), C13−C14 1.398(7), N3−C28 1.313(7), N4−C32 1.331(7), C27−C28 1.410(7), C27−C32 1.405(8), N1−Cu1−N2 95.96(17), N1−Cu1−P1 122.61(13), N3−Cu2−N4 96.96(18), N3−Cu2−P2 126.45(15), N1−C12−C13 125.9(5), C12−C13−C14 124.2(4), N2−C14−C13 128.3(5), N3−C28−C27 126.0(5), C32−C27−C28 123.9(5), N4−C32−C27 128.4(5), C57−C23−C13−C14 −36.7(7), C25−C26−C27−C28 −50.7(8), C13−C12−N1−Cu1 −10.5(8), C27−C28−N3−Cu2 3.5(8), C12−N1−Cu1−P1 −154.2(4) C32−N4−Cu2−P2 −165.0(4), N1−Cu1−N2−C14 −17.0(4), N3−Cu2−N4−C32 11.7(5).

2-fold axis. Both copper ions display a trigonal planar coordination sphere, which is distorted because of the acute angle N1−Cu1−N2 of 96.65(5)°. The Cu−Cu distance amounts to 6.6303(4) Å, which is considerably longer than the distance observed for **1** × 4(CH_3CN) (4.7739(10) Å). This is due to the steric bulk of the triphenylphosphane ligands that obviously push the Cu centers (including the corresponding binding pockets) apart. For the same reason, the Cu ions are positioned somewhat outside the planes defined by the diiminato binding pockets ((C28−C27−N1−Cu1) = −4.6(3)°. As already derived from the NMR data, these diiminato units are quite symmetric showing equally long C−C and C−N bonds, respectively. The Cu−N and Cu−P bond distances are comparable to those observed in diketiminato-Cu-phosphane complexes.[19]

Phosphane ligands are stronger σ-donors and also better π-acceptors than acetonitrile, and this might account for the increased stability of **2** against air. In fact, phosphane ligands have been shown to replace O_2 coordinated to a mononuclear diketiminato-copper complex, while O_2 replaces acetonitrile.[12] On the other hand, the Cu centers are well protected within **2**, and this might contribute, too.

To clarify the effect of the steric bulk, trimethylphosphane was also tested as a coligand, as it is far less sterically demanding and at the same time a better σ-donor than triphenylphosphane. To synthesize a corresponding PMe_3 complex, benzene was added to copper(I)-*tert*-butoxide and [^{Me_2C_6H_3}**Xanthdim**]H_2, and the resulting solution, which lacks of proper σ-donor molecules, was quickly frozen to avoid disproportionation of the unstable dinuclear complex initially formed. Excessive trimethylphosphane was condensed on top of the frozen mixture, and the reaction vessel was allowed to anneal. This resulted in a bright orange colored solution, from which all volatiles were removed subsequently. Redissolution in benzene and treatment with excessive acetonitrile then gave a yellow precipitate [^{Me_2C_6H_3}**Xanthdim**](Cu(PMe_3))$_2$, **3**, that could be isolated in 67% yield (Scheme 2). Compound **3** was characterized by means of NMR and IR spectroscopy as well as by elemental analysis. The ^{1}H NMR spectrum of **3** is differing from the one observed for **2** principally only in two aspects: instead of the resonances belonging to the triphenylphosphane ligands a doublet is observed at 0.81 ppm for the trimethylphosphane ligand, and the protons belonging to the aldimine units cause a doublet signal (because of the long-range coupling with the P atoms, that does not occur in case of **2**).

Storing a solution of **3** in a 5:1 mixture of acetonitrile and benzene at r.t. led to the formation of single crystals, which were examined by X-ray diffraction, and the result of the corresponding structure analysis is shown in Figure 3.

As expected the Cu−Cu distance is significantly shorter (5.6670(11) Å) than the one in **2** as the trimethylphosphane ligands are less bulky and thus allow a closer approach of the two Cu centers. Accordingly, also the Cu−P distances are somewhat shorter for **3** (2.1499(17) and 2.1437(19) Å) than for **2** × 6(C_7H_8) (2.1748(4) Å), as there are less steric clashes within the binding pocket. Otherwise the structural data of the diiminato-Cu moieties correspond well to those observed for **2** × 6(C_7H_8). As in that case, the Cu atoms are not located within the plane defined by the diiminato framework ((C13−C12−N1−Cu1) = −10.5(8)° and (C27−C28−N3−Cu2) = 3.5(8)°). However, while the Cu atoms turn away from each other in **2** they are oriented in the same direction within **3**.

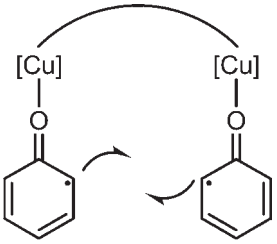
Like **2**, complex **3** is only slightly sensitive to air. Thus, the stability of **2** and **3** may mainly originate from electronic rather than steric effects.

Activity of 1 As a Catalyst for the Oxidative Coupling of Phenols. The coupling of arenes is of great importance for general organic synthesis, and the copper-catalyzed phenol coupling to arrive at chiral biphenol derivatives is used extensively as a test reaction for the catalytic activity of new copper complexes.[20] These reactions usually start from Cu^I compounds and are assumed to involve an initial O_2 activation to yield Cu^{II} centers, which oxidize either free phenols via a proton-coupled (outer-sphere) electron-transfer[21] or by formation of a dinuclear Cu^{II} phenoxo complex.[22] For the subsequent coupling both a free radical type reaction and an alternative pathway including the decomposition of binuclear Cu^{II} phenoxo species are discussed (Chart 3).[21,22] Assuming that indeed the decisive coupling step requires the contact of two such units, it is also reasonable to assume that dinuclear catalysts may have advantages in this context, and in fact dicopper(I) complexes, specifically synthesized by employing dinucleating ligands, were shown to couple 2,4-di-*tert*-butylphenol, **A**, to the corresponding bisphenol derivative **B** (Scheme 3) in most of the cases reported so far.[23]

It was thus of particular interest to test the potential of **1** with respect to this kind of reactivity. Since the reaction shown in Scheme 3 could be expected to produce also water (if not H_2O_2 is formed[22]), and **1** is not stable against water over longer periods of time, we have initially used the sodium salt of **A**, sodium 2,4-di-*tert*-butylphenolate **A′**.

Accordingly, a solution of **1** and 10 equiv of sodium 2,4-di-*tert*-butylphenolate in 4 mL of thf was stirred for 6 h at r.t. under an

Chart 3



Scheme 3

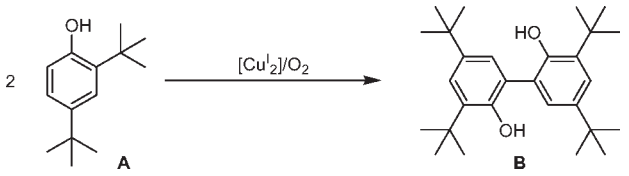


Table 2. Oxidative Coupling of 2,4-Di-*tert*-butylphenol, A, Catalyzed by 1 (10 mol %)[c]

line	solvent	molecular sieves	yield [%]	turnover number
1[a]	thf	no	39	3.9
2	thf	no	27	2.7
3	thf	yes	31	3.1
4	toluene	no	53	5.3
5	toluene	yes	74	7.4
6[b]	toluene	yes	62	6.2

[a] Sodium 2,4-di-*tert*-butylphenolate, **A′**, was used instead of 2,4-di-*tert*-butylphenol, **A**, as a substrate. [b] The mononuclear catalyst **4** was employed instead of **1** with a doubled concentration. [c] The data refer to a reaction time of 6 h at r.t.

atmosphere of dioxygen. After workup, **B** was identified as the reaction product by means of ^{1}H and ^{13}C NMR spectroscopy with a yield of 39% (based on **A′**, Table 2, line 1).

Encouraged by these results we have also used the phenol **A** itself for comparison. Under the same conditions as described above, **B** was formed in 27% yield (line 2). Hence, the conversion decreases somewhat because of the deleterious effect of the water produced concomitantly, albeit not to an extent that could have been envisaged. This finding can be explained assuming that the Cu^{II} intermediates formed during catalysis are somewhat more resistive toward hydrolysis than **1**. To test whether hydrolysis can be avoided completely, in the next step the catalytic oxidations were performed in the presence of molecular sieves, which were supposed to remove the water formed during the reaction. The coupling of **A** proceeded slightly more effectively then with a 31% yield of **B** (line 3) which, however, is still less than that achieved with **A′** (vide supra).

Variation of the solvent showed that performance of the coupling in a less strongly coordinating solvent allows for considerably higher conversions: in toluene 53% **B** (line 4) is obtained and the coupling activity of **1** can be further increased by addition of molecular sieves leading to a maximum value of 74% yield (line 5). The resulting turnover number (TON) of

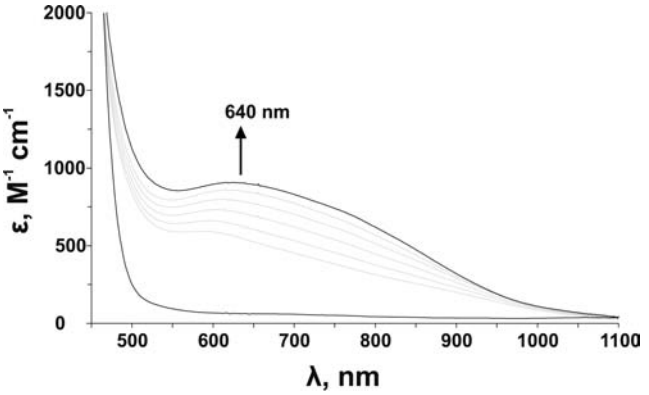


Figure 4. UV/vis spectra monitoring the reaction of **1** in thf (1 mM) with excessive O_2 at −80 °C. The various traces in the direction of the arrow represent the spectra recorded before O_2 addition and 10, 30, 50, 110, 210, and 610 s subsequent to O_2 addition.

7.4 is somewhat higher than those reached by other dinuclear Cu^{I} systems.[23] Comparison with the coupling yields/efficiencies of more simple copper based systems employed in organic synthesis is difficult because of the quite different reaction conditions.[24] However, it becomes obvious that their TOFs are lower while their robustness is higher, so that higher maximum TONs can be reached. For further comparison we also carried out this reaction with the known β-diketiminato-Cu^{I} complex, $[(N(2,6\text{-}Me_2C_6H_3)C(CH_3))_2CH]Cu(MeCN)$ **4**, as a catalyst.[18] To keep the quantity of copper equivalents constant, the molar percentage was doubled (with respect to the one employed for **1**). Toluene was chosen as the solvent, and molecular sieves were added such that the yield of 62% (line 6) has to be compared with line 5. The comparison shows that the prearranged dinuclear species brings out only a small advantage.

Identification of the Primary Product in Contact with O_2. In principle, the system **1**/**A**/O_2 also could have led to ortho-hydroxylations, which, however, were not observed. Such tyrosinase activity requires the formation of a CuO_2Cu intermediate and an accessible coordination site for phenolate binding.[21,25] To investigate whether the reaction of **1** with O_2 leads to a CuO_2Cu core, **1** was dissolved in thf and treated with O_2 at −80 °C. Notably, the formation of a green solution was observed, which changed color to brown upon annealing to r.t. Low-temperature UV/vis measurements (Figure 4) showed that during the reaction of **1** with O_2 at −80 °C a new band at about 640 nm (ε = 1000 M^{-1} cm^{-1}) evolves.

A band at this wavelength cannot arise from a Cu(μ-O)$_2$Cu entity, as corresponding complexes usually absorb around 420 nm. The extinction coefficient points either to a Cu^{II} d-d transition of a Cu(μ-O)Cu species or to a ligand-to-metal charge transfer (LMCT) band that should be expected for Cu^{II} peroxo units.[3b,18,26,27] Copper peroxide complexes should be characterized by further bands (e.g., at ca. 350 nm for Cu(μ-η^2:η^2-O_2)Cu units or at ca. 520 nm for Cu(μ-η^1:η^1-O_2)Cu moieties),[27,28] but the corresponding regions of the spectrum of **1** are masked by ligand absorptions, so that this did not aid the assignments. Spectrophotometric O_2 titration experiments indicate that complete conversion of **1** to the intermediate requires 0.5−1 equiv of O_2 per dicopper unit (after addition of 1 equiv excessive O_2 does not lead to a further increase of the 640 nm band, see Supporting Information, Figures S1−S3). Hence, this finding does not hint unequivocally into one or the other direction; it might be due to

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partial decay of initial O_2 adducts like those depicted in Scheme 4 or to equilibria, for instance, between $\mathbf{1}/O_2$ and the Cu(μ-O)Cu species. However, treatment of **1** at −70 °C with 1 equiv of a soluble derivative of iodosobenzene, 2-(*tert*-butylsulfonyl)iodosylbenzene (sPhIO),[29] caused the development of the same UV/vis band at 640 nm as observed after O_2 addition, which argues in favor of a Cu(μ-O)Cu species (Scheme 4). This reaction proceeds very slowly, though, so that it could not be brought to completion within 6 h as indicated by the sudden increase of the characteristic absorption band when O_2 was added after that time. Almost quantitative conversion was possible when an excess of sPhIO (10 equiv) was employed, and the final spectrum showed no additional features as compared to the one recorded on treatment with 1 equiv, which yet again supports the formation of a Cu(μ-O)Cu complex. The same observations were made employing Me_3NO as the OAT reagent.

Comparison with the spectral data reported for the few known examples of Cu(μ-O)Cu complexes, as summarized in Table 3, also confirms the assignment of the 640 nm band to a Cu(μ-O)Cu species.

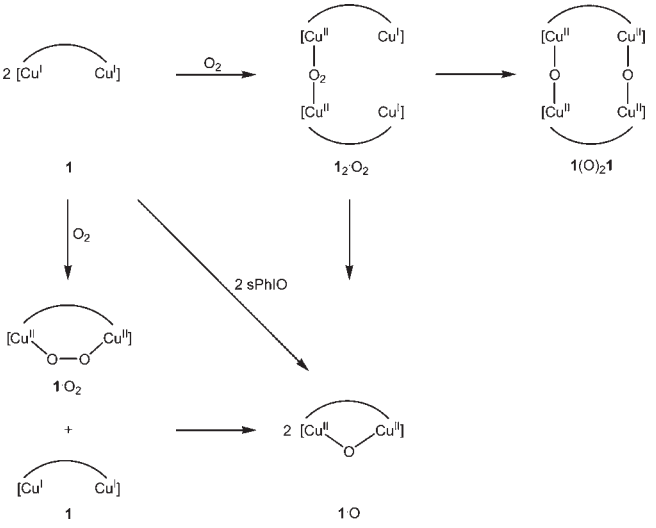
Further support is derived from low-temperature Raman and resonance Raman spectroscopy (−80 °C, thf). After reaction of **1** with $^{16}O_2$ a new band at 593 cm^{-1} was observed in the Raman spectrum (1064 nm excitation) that decays upon annealing at ambient temperature. In addition, the band shifts down to 568 cm^{-1} when the reaction is carried out with $^{18}O_2$ (Figure 5). No other isotopically sensitive signals could be detected. Raman bands at around 600 cm^{-1} were reported for Cu(μ-O)$_2$Cu compounds, but, as outlined above, these complexes do not exhibit UV−vis absorption bands between 600 and 700 nm.[18,5,27] To distinguish between Cu(μ-O)$_2$Cu and Cu(μ-O)Cu species we have performed an additional experiment with a 1:2:1 mixture of $^{18}O_2$:$^{16}O^{18}O$:$^{16}O_2$ (12.5% in argon). Because of the dilution by argon, the signal-to-noise ratio of the spectra obtained from these experiments was distinct as compared to those in Figure 5, but sufficient to identify the two bands at 568 and 593 cm^{-1}. Some additional Raman activity was noted between these bands; however, a 1:2:1 intensity distribution for a triplet with band components at 568, ~580, and 593 cm^{-1}, as expected for a Cu(μ-O)$_2$Cu moiety, could safely be ruled out.

Unfortunately, no vibrational spectra have been reported in the literature for the Cu−O−Cu compounds in Table 3 that might further back the assignment. The only literature data including vibrational frequencies refer to oxygen-activated Cu-ZSM-5 that has been shown to selectively oxidize methane to methanol. Here, a $[Cu_2O]^{2+}$ core was identified as the active site, which gives rise to an electronic transition at 441 nm, and to ^{18}O-sensitive resonance Raman bands at 456 and 870 cm^{-1}, assigned to the symmetric and asymmetric (Cu−O−Cu) stretching mode, respectively (Table 3).[9a] We like to point out that Raman spectra of oxygenation product of **1**, obtained with 1064- or 647-nm excitation, do not display ^{18}O-sensitive bands in the regions around 450 or 850 cm^{-1}.

Thus, both the vibrational spectra and the electronic spectra of Cu-ZSM-5 differ substantially from the intermediate state analyzed in this work, and evidently reflect the differences in electron density distribution and geometry of a Cu−O−Cu unit as a part of a zeolite on the one hand and within the N-donor sphere of a coordination compound on the other hand.

Further Raman experiments were carried out with 647 nm excitation, that is, in resonance with the 640 nm absorption band.

Scheme 4. Possible Routes to a Cu^{II}−O−Cu^{II} Intermediate



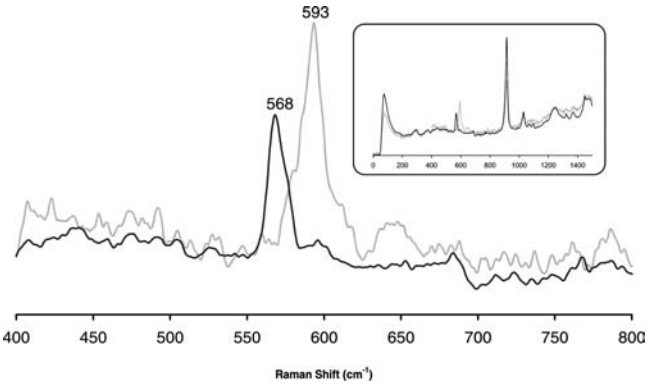


Figure 5. Raman spectra recorded after oxygenation of **1** (λ_{ex} = 1064 nm, thf, 46 mM, −80 °C) with $^{16}O_2$ (gray line) and $^{18}O_2$ (black line).

The conjugate bands at 593 (^{16}O) and 568 cm^{-1} (^{18}O) are readily detected, but there is not significant enhancement for these modes. However, 647 nm excitation allows detecting two additional bands at 612 and 640 cm^{-1} which, upon reaction with $^{18}O_2$, shift down to 598 and 622 cm^{-1}, respectively (see Supporting Information, Figure S4). The quite similar frequencies of these band pairs suggest structurally similar complexes and thus a heterogeneity of the intermediate, presumably originating from a distribution of **1**·**O** aggregates, although the involvement of Cu(μ-O)$_2$Cu moiety cannot rigorously be ruled out.

There are several options how a Cu−O−Cu complex can be formed from **1** and O_2. A transient **1**·O_2 species may be formed that transfers one O atom onto an unreacted molecule of **1**. On the other hand O_2 activation could also proceed between two different molecules of **1** to give a transient $\mathbf{1}_2$·O_2 species, whose CuO_2Cu moiety gets reduced in an intramolecular process by the two pendant Cu^I centers to finally yield in two molecules of **1**·O. Moreover we cannot rule out that the Cu−O−Cu species contains Cu centers belonging to two different molecules of **1**, in which case it would correspond to a tetranuclear **1**$(O)_2$**1** complex (Scheme 4).

In any case, according to the observations described above the Cu−O−Cu species generated from **1** is unstable and

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Table 3. Summary of UV/vis and Raman Spectral Data of Known Cu(μ-O)Cu Species

complex	solvent	λ_{max} (nm) (ε (M^{-1} cm^{-1}))	ν(Cu−^{16}O) (cm^{-1}) (ν(Cu−^{18}O) (cm^{-1}))	ref.
[((Bpy2)Cu)$_2$O]	CH_2Cl_2	660 (760)		30b
[((Bpi)Cu)$_2$O]	CH_2Cl_2	650 (180)		30c
[((TMEDA)Cu)$_2$O]	$PhNO_2$	600 (130)		30d
[((TEEDA)Cu)$_2$O]	$PhNO_2$	640 (140)		30d
[((TPEDA)Cu)$_2$O]	$PhNO_2$	625 (80)		30d
[((TMPDA)Cu)$_2$O]	$PhNO_2$	650 (240)		30d
[((HB(3,5-Me$_2$pz)$_3$)Cu)$_2$O]	CH_2Cl_2	660 (105)		30e
[((MePY2)Cu)$_2$O]	thf	680 (100)		30f
1 + O_2 at −80 °C	thf	640 (1000)	593 (568)	this work
			612 (598),[a] 640 (622)[a]	
Cu-ZSM-5 after O_2 activation		441	456 (448), 870 (830)	9a,9d

[a] Only observed with 647 nm excitation, (Bpy2) = *N*-benzyl-2-(pyridin-2-yl)-*N*-(2-(pyridin-2-yl)ethyl)ethanamine, Bpi = biphenyl-2,2′-di(carb(2-(2-pyridyl)ethylimine, TMEDA = *N*,*N*,*N*′,*N*′-tetramethylethylendiamine, TEEDA = *N*,*N*,*N*′,*N*′-tetraethylethylendiamine, TPEDA = *N*,*N*,*N*′,*N*′-tetrapropylethylendiamine, TMPDA = *N*,*N*,*N*′,*N*′-tetramethyl-1,3-propanediamine, MePY2 = *N*-methyl-*N*,*N*′-bis[2-(2-pyridyl)ethyl]amine.

decomposes at ambient conditions to give unknown products. This finding is not surprising considering that some of the few Cu−O−Cu compounds isolated so far also decompose very easily.[30a,e] The chemical behavior of this Cu−O−Cu intermediate is also in good agreement with corresponding reports in the literature since, for example, it was found to show O atom transfer reactivity: Treatment with 10 equiv of PPh_3 for 30 min at −80 °C followed by annealing to r.t. gave **2** and O=PPh_3 (33%, referenced to the amount of **1** employed) as evidenced by UV/vis and NMR spectroscopy.

Formation of a Cu−O−Cu species as the primary product instead of Cu−O−O−Cu or Cu(μ-O)$_2$Cu intermediates could also explain why no tyrosinase activity has been observed for **1**. Nevertheless, the findings reported here are still of substantial bioinorganic interest. In the context of the Cu-ZSM-5/O_2 and pMMO work described above it was suggested that "future research should focus on how the Cu^{II}−O−Cu^{II} species possibly translates to the context of protein environments; the structure will likely become a focus of a bioinorganic field invigorated by the proposal."[9b] Furthermore it was noted: "The mixed-valent oxodicopper(II/III) or simple oxodicopper(II) centers are both candidates for the enzyme active site methane oxidizer. The former has not yet been identified or isolated among the known crop of Cu_2O_2 synthetic model compounds; the latter has some precedent, but does not have a developed chemistry."[8b] The work presented here makes a contribution to the, as can be judged from these quotations, important but scarcely investigated field of Cu−O−Cu compounds.

CONCLUSIONS

A procedure has been developed that allows for the synthesis and isolation of novel, dinuclear Cu^I complexes based on the bis(diiminato) framework provided by the ligand [^{Me_2C_6H_3}**Xanthdim**]$^{2-}$. Despite the pronounced tendency of Cu^I compounds to undergo disproportionation reactions (especially in case of dinuclear cores) complexes [^{Me_2C_6H_3}**Xanthdim**](Cu(L))$_2$ (L = CH_3CN, **1**, PPh_3, **2**, PMe_3, **3**), once synthesized, proved stable against corresponding decomposition reactions. As envisaged, **1** shows a high reactivity toward dioxygen that is retarded by replacement of the acetonitrile coligands by phosphane ligands as in **2** and **3** because of electronic reasons. **1** proved an efficient catalyst for the oxidative coupling of phenols in the presence of O_2, and a closer inspection of the reactivity of **1** in contact with O_2 at low temperature showed that an unstable Cu−O−Cu complex is formed during the initial steps. Future work will now focus on the utilization of complexes like **1** as building-blocks for the modeling of multicopper enzymes.

ASSOCIATED CONTENT

Supporting Information. X-ray crystallographic data in cif format. Further details are given in Figures S1−S4. This material is available free of charge via the Internet at http://pubs.acs.org.

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DEDICATION

[†]Dedicated to Prof. Erhard Kemnitz on the occasion of his 60th birthday.

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