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Catalytic aziridinations with copper(II) salen complexes†

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Three copper(II) complexes coordinated with salen ligands are synthesized, characterized, and examined for catalytic nitrene transfer reactions with a set of olefins. All three copper(II) complexes exhibit catalytic reactivity for the aziridination of styrene with PhI=NTs. Complex **3** is the most efficient catalyst for activated olefins (up to 94% yield). This complex is additionally characterized by X-ray crystallography, showing a highly distorted octahedral ligand surrounding the Cu atom having included in its coordination sphere an acetate ligand.

Introduction

Salen ligands have been attached to a broad variety of transition metals and the resulting compounds have been successfully applied for a plethora of catalytic reactions.[1–10] Salen–copper complexes were introduced to aziridination reactions by Jacobsen *et al.* after the successful application of salen ligands in manganese-catalyzed epoxidations[3,11] (for a general equation of an aziridination reaction see eqn 1). Due to their highly regio- and stereoselective ring-opening reactions, aziridines are valuable as building blocks for the synthesis of a wide range of nitrogen-containing compounds.[12] Therefore, a general methodology for one-step formation of aziridines would be of high interest. In 1991 the copper catalyzed aziridination of olefins using (*N*-(*p*-toluenesulfonyl)imino)phenyliodane (PhI=NTs) as nitrene source had been reported. Efficient systems usually contained 5–10 mol% of a soluble copper salt such as copper triflate or copper perchlorate and a polar aprotic solvent such as acetonitrile.[13–14] Solvents with a higher polarity led to both increased reaction rates and enhanced efficiencies. In the meantime even very simple catalyst systems, containing solvent ligated Cu(I) cations and not coordinating counter ions, such as $[Cu(NCCH_3)_4][B(C_6F_5)_4]$ catalyzing the olefin aziridination quite efficiently have been described.[15] In contrast to the case of copper-catalyzed cyclopropanations where Cu(II) compounds are less successful, a variety of copper(II) salts are suitable as catalysts or catalyst precursors.[16] The successful application of metal(II) salen complexes, among them square planar Cu(II) salen complexes,[17] has for example been demonstrated for the asymmetric synthesis of α-methyl α-amino acids.[18a]

Results and discussion

Synthesis and characterization of compounds 1–3

Compounds **1–3** (see chart 1) were synthesized by the reaction of H_2L (L = salen) and $Cu(OAc)_2 \cdot H_2O$ in ethanol. Dependent on the work up procedure (see experimental part) square planar structures (**1**, **2**)[17] or a highly distorted octahedral product compound (**3**) are formed. Compounds **1** and **2** display no prominent IR signal in the region around 3400 cm^{-1} whereas compound **3** shows a quite prominent vibration at 3423 cm^{-1}, indicating a phenolic O–H vibration. Additionally, compound **3** shows strong signals at 1480 and 1452 cm^{-1}, due to the coordination of a bidentate acetyl ligand. These latter two signals are conspicuously absent in the case of the compounds **1** and **2**. The mass spectrum (MS) does not show the molecular peak in the case of compound **3**, but only the mass corresponding to the molecule after the loss of its OAc ligand. A further peak is due to the additional loss of a $C_6H_4(CH_3)OH$ fragment of the ligand L. Most of the other peaks are due to ligand fragmentation. The fragmentation of compounds **1** and **2** is similar, showing mainly ligand fragmentation and, of course, give no indication for the presence or removal of an acetate molecule.

X-Ray structure of compound 3

The coordination of a bidentate acetate ligand to the Cu(II) atom, leaving one of the phenolic –OH groups with its proton, as already evident by the IR spectrum (see above) is confirmed by the X-ray structure of compound **3** (see Fig. 1 and Table 1). Only one of the two phenolic alcohol groups is deprotonated forming a covalent Cu–O bond. The other OH-group is acting as an electon donor to the Cu atom (donor–acceptor interaction). The acetate ligand, on the other hand, is bidentate, forcing the tetradentate salen ligand out of the equatorial plane and causing a quite distorted structure of the molecule. The

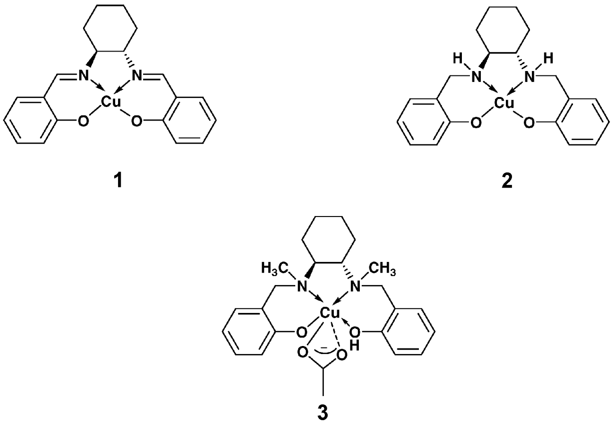

Chart 1

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† Electronic supplementary information (ESI) available: best fit of molecule 3A and inverted molecule 3B in the solid state. See DOI: 10.1039/b509568a

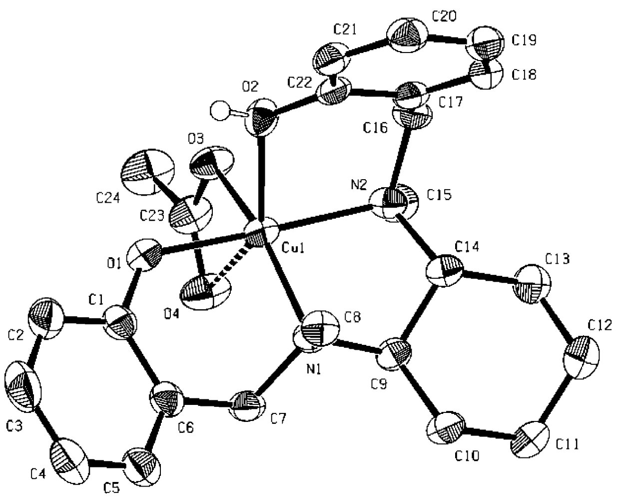
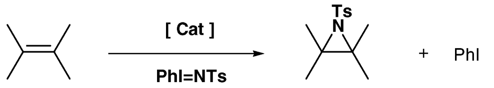


Fig. 1 ORTEP style plot[28] of compound **3A** in the solid state. Thermal ellipsoids are drawn at a 50% probability level.

different binding modes of the two phenolic oxygen atoms are evidenced by the different O–Cu bond distances (1.961(2) Å *vs* 2.320(2) Å and 1.937(2) Å *vs* 2.292(2) Å, resp., in the two crystallographic independent molecules **A** and **B**). The two oxygen atoms of the acetate ligand display two rather different O–Cu bond distances (1.960(2) Å and 1.962(2) Å *vs* 2.714(3) Å and 2.740(2) Å). In contrast to the Cu–O bond distances, the Cu–N bond distances are similar, indicating a comparable binding mode, in this case a N–Cu donor interaction, showing a bond distance of *ca.* 2.00–2.01 Å in all cases. Cu(II)–O single bonds are in the range of *ca.* 1.8–2.0 Å , Cu(II)–N donor interactions are in the range of 2.0 Å.[17–19]

Catalytic aziridination reactions

The aziridination of olefins has been often considered to be similar to cyclopropanation and epoxidation reaction, in the sense that a nitrene group is transferred to the olefin, generating the three membered ring. Complexes **1–3** were investigated as catalysts for olefin aziridination reactions (see eqn 1).



(1)

As nitrene source *p*-(toluensulfonyl)imino-phenyliodinate has been applied in this work as an alternative to an azide. The catalytic studies involved 2 mol% catalyst loading with regard to PhI═NTs and a styrene: PhI═NTs molar ratio of 5 : 1 at room temperature. Complex **3** proves to be the most efficient catalyst, leading to the highest product yields, while complexes **1** and **2** are found to be somewhat less reactive and the conversion of styrene to the aziridine in moderate to good yields requires more time than with catalyst **3**. This behavior is, at first glance, somewhat surprising, since compound **3** is sterically more hindered around the Cu(II) center as are the square planar compounds **1** and **2**. However, due to the different binding modes of the salen ligand, which is coordinated less symmetrically to the metal and due to the ability of the acetate to act both as a monodentate and a bidentate ligand, as indicated already by the two significantly different Cu–O bond lengths (see above), the overall situation around the Cu(II) atom seems to promote its catalytic activity. The catalytic results are displayed in Table 2.

We have also explored the conversion of simple mono and di-substituted olefins including some with electron-withdrawing groups attached to the C═C bond, using complex **3**. The olefin aziridination reactions were carried out at room temperature using 2.0 ml acetonitrile and 2 mol % of compound **3**. Styrene, α-methylstyrene, *trans*-β-methylstyrene, and *cis*-cyclooctene were found to be quite reactive under the reaction conditions applied and could be converted to the corresponding aziridines in good to excellent yields (75–94%). Even 1,2-dihydronaphthalene, in several cases described as a very slowly reacting substrate giving low yields even after prolonged reaction times,[3] could be easily converted to the corresponding aziridine in very good yields (84% after one hour reaction time, see Table 2, entry 6). The results obtained with styrene derivatives are superior to reported literature values obtained with polypyrazolylborate copper(I) complexes and hexaacetonitrile copper (II) cations, associated with non-coordinating anions.[20] The yields obtained for cyclooctene are in the same order of magnitude as the reported values, while the results for 1,2-dihydronaphthalene are considerably better. Only 1-octene could not be transformed to the corresponding aziridine in a satisfying yield. After 20 h of reaction time the yield is still low (22%, see Table 2).

Experimental

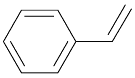
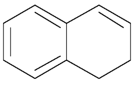
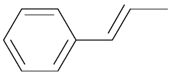
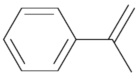
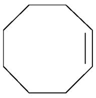
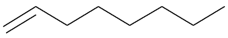
General remarks

^{1}H- and ^{13}C-NMR spectra were recorded with a 400 MHz Bruker Avance DPX-400 spectrometer. IR spectra were recorded on a Perkin-Elmer 1650 spectrometer (KBr). Elemental analyses were performed in the Mikroanalytische Labor of the Technische Universität München (M. Barth). Catalytic runs were monitored by GC-MS methods on a Hewlett-Packard instrument HP 6890/5973 GC-MS by S. Mühl.

Table 1 Selected bond distances and bond angles for compound **3** in molecule **A**. The values for molecule **B** are given in italics. The transcription for equivalent atoms of **A** to **B** is Cu(n + 1), O(n + 4), and N(n + 2)

	Bond distance (Å)		Bond angle (°)
Cu(1)–N(1)	2.016(3) *2.029(2)*	O(1)–Cu(1)–(O)2	86.36(9) *85.52(10)*
Cu(1)–N(2)	2.088(3) *2.060(3)*	O(1)–Cu(1)–O(3)	88.28(10) *87.27(10)*
Cu(1)–O(1)	1.961(2) *1.937(2)*	O(1)–Cu(1)–O(4)	85.44(9) *82.62(9)*
Cu(1)–O(2)	2.320(2) *2.292(2)*	O(1)–Cu(1)–N(1)	93.56(10) *94.52(10)*
Cu(1)–O(3)	1.960(2) *1.962(2)*	O(1)–Cu(1)–N(2)	174.97(10) *175.39(10)*
Cu(1)–O(4)	2.714(3) *2.740(2)*	O(2)–Cu(1)–O(3)	93.32(9) *97.78(9)*
		O(2)–Cu(1)–O(4)	146.26(9) *149.05(8)*
		O(2)–Cu(1)–N(1)	109.46(10) *103.16(10)*
		O(2)–Cu(1)–N(2)	89.25(9) *89.89(10)*
		O(3)–Cu(1)–O(4)	53.78(9) *53.29(8)*
		O(3)–Cu(1)–N(1)	157.21(10) *159.06(10)*
		O(3)–Cu(1)–N(2)	94.42(11) *93.76(10)*
		O(4)–Cu(1)–N(1)	103.68(9) *106.19(8)*
		O(4)–Cu(1)–N(2)	99.58(9) *101.60(9)*
		N(1)–Cu(1)–N(2)	85.60(11) *86.13(11)*

Table 2 Catalytic results obtained with compounds **1–3** in aziridination reactions[a]

Entry	Substrate	Catalyst	Time (h)	Yield(%)[b]
1		**1**	5	75
2		**2**	6	74
3		**3**	3.5	94
4		**1**	10	54
5		**2**	10	47
6		**3**	1	84
7		**3**	6.5	82
8		**3**	3	76
9		**3**	24	88
10		**3**	20	22

[a] Olefin (2.5 mmol), (188.0 mg, 0.5 mmol) PhI=NTs and (0.01 mmol) catalyst (**1–3**) were stirred in 2.0 ml acetonitrile at the room temperature. [b] Isolated yield.

All organic and inorganic starting materials were purchased from Aldrich or Acros and used without further purification. The salen ligand for compound **3** was prepared as described in the literature.[21–23]

X-ray crystallography

Crystal data: $C_{49}H_{68}Cl_2Cu_2N_4O_9$, $M_r = 1055.07$, monoclinic, $a = 21.3987(1)$, $b = 11.1987(1)$, $c = 21.5985(2)$ Å, $\beta = 106.0160(3)^\circ$, $U = 4974.91(7)$ Å^3, $T = 173$ K, space group $P2_1/c$ (no. 14), Z = 4, $D_c = 1.409$ g cm^{-3}, μ(Mo–K$_\alpha$) = 1.021 mm^{-1}. *Data collection:* Suitable single crystals for the X-ray diffraction study were grown by standard techniques from a saturated mixture of hexane–dichloromethane at room temperature. A clear dark green fragment was stored under perfluorinated ether, transferred in a Lindemann capillary, fixed, and sealed. Preliminary examination and data collection were carried out on a KappaCCD device (NONIUS MACH3) with an Oxford Cryosystems cooling device at the window of a rotating anode (NONIUS FR591) with graphite monochromated Mo–K$_\alpha$ radiation ($\lambda = 0.710\ 73$ Å). Data collection[24] was performed at 173 K (OXFORD CRYOSYSTEMS) within a θ-range of $1.94^\circ < \theta < 25.36^\circ$. The detector to crystal distance was set to 40 mm. Nine data sets in rotation scan modus with $\Delta\varphi/\Delta\omega = 1.0^\circ$ were measured and a total number of 112470 intensities were integrated. Raw data were corrected for Lorentz, polarization, and, arising from the scaling procedure,[25] for latent decay and absorption effects. After merging ($R_{int} = 0.076$) a sum of 9110 (all data) and 7377 [$I > 2\sigma(I)$], respectively, remained and all data were used. *Solution:* The structure was solved by a combination of direct methods[26] and difference-Fourier syntheses.[27] All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms bound to oxygen atoms were found and were allowed to refine freely with individual isotropic displacement parameters. All other hydrogen atoms were calculated in ideal positions (riding model). *Refinement:* Full-matrix least-squares refinements with 617 parameters were carried out by minimizing $\Sigma w(F_o^2 - F_c^2)^2$ with the SHELXL-97 weighting scheme and converged with $R1 = 0.0498$ ($I_o > 2\sigma(I_o)$), w$R2 = 0.1115$ (all data), GOF = 1.046, and a shift/error of <0.001. The final difference Fourier map shows no striking features ($\Delta e_{min/max} = +0.56/-0.92$ e Å^{-3}). Besides two crystallographic independent molecules **A** and **B** of **3** we found in the solid state additionally one molecule of solvent CH_2Cl_2 and one molecule of water. The overall geometry of the two molecules **A** and **B** is identical within the esd's (see supporting material†). CCDC reference number 277167. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b509568a

Procedure for the synthesis of the complexes 1, 2

A solution of H_2L (1 mmol) and $Cu(OAc)_2 \cdot H_2O$ (1 mmol) in 20 ml of ethanol was heated to reflux for 3 h. The precipitated solids were isolated by vacuum filtration and rinsed with ethanol several times. The solid was collected and dried in vacuum to get the complexes **1** and **2**. The spectroscopic data of compound **1** of this work are identical to those described in the literature [18] for the compound named **1e** in the latter paper.

Complex **1**, Anal. Calc. for $C_{20}H_{20}CuN_2O_2$: C, 62.57; H, 5.25; N, 7.30. Found: C, 62.25; H, 4.84; N, 7.26%. IR (KBr, cm^{-1}): 2929 (w), 1631 (s), 1604 (m), 1541 (m).

Complex **2**, Anal. Calc. for $C_{20}H_{24}CuN_2O_2$ C, 61.92; H, 6.24; N, 7.22. Found: C, 61.69; H, 6.19; N, 7.15%. IR (KBr, cm^{-1}): 3206 (s), 1589 (s), 1477 (s).

General procedure for the synthesis of the complex 3

A solution of H_2L (1 mmol) and $Cu(OAc)_2 \cdot H_2O$ (1 mmol) in 20 ml of ethanol was heated to reflux for 3 h. The resulting dark green solution was subsequently evaporated under oil pump vacuum. The remaining residue was extracted with CH_2Cl_2, filtered *via* cannula, and the resulting liquid was brought to dryness under oil pump vacuum to get a dark green solid. Single crystals suitable for X-ray analysis were obtained by recrystallization from a CH_2Cl_2–hexane mixture. Anal. Calc. for $C_{24}H_{32}CuN_2O_4 \cdot H_2O$: C, 58.34; H, 6.94; N, 5.67. Found: C, 58.07; H, 6.78; N, 5.74%. IR (KBr, cm^{-1}): 3423 (s), 2936 (s), 1594 (s), 1480 (*vs*), 1452 (*vs*), 1293 (s), 864 (s); CI-MS (70 eV): m/z (%): 414 (8) $[M - O_2CCH_3]^+$; 354 (2) $[LH]^+$; 309 (4) $[M - O_2CCH_3 - C_6H_4(CH_3)OH]^+$; 248 (41) $[LH_2 - C_6H_4(CH_2)O]^+$; 107 (100) $[C_6H_4(CH_2)OH]^+$.

General procedure for the olefin aziridination reaction

Olefin (2.5 mmol; *e.g.* 260.0 mg styrene), (188.0 mg, 0.5 mmol) PhI=NTs and (0.01 mmol) catalyst (**1–3**, resp.,) were stirred at room temperature in 2.0 ml acetonitrile for the time spans given in Table 1. Then the product was purified by silica gel column chromatography (hexane : ethyl acetate = 5 : 1) and yields were determined by weighting the isolated product. The structure of pure product was determined by ^{1}H-NMR and GC-MS.

Conclusions

Dependent on the product workup, copper(II) salen compounds can be isolated with or without an additional acetate ligand. All examined complexes are applicable as catalysts in the aziridination of styrene, where the acetate ligated complex **3** is found to display the highest product yield. Complex **3** is also an active catalyst for the aziridination of several activated olefins.

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