Dalton Transactions

PAPER

View Article Online
View Journal | View Issue

Cite this: *Dalton Trans.*, 2014, **43**, 13578

2-Quinoxalinol diamine Cu(II) complex: facilitating catalytic oxidation through dual mechanisms†

Yuancheng Li, TaeBum Lee, Kushan Weerasiri, Tanyu Wang, Emily E. Buss, Michael L. McKee and Anne E. V. Gorden*

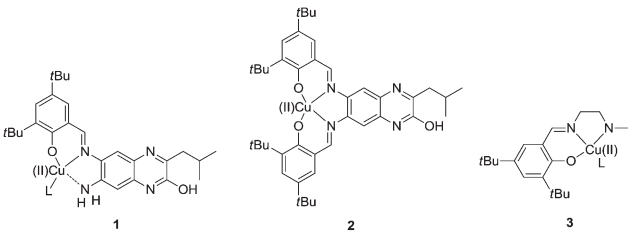
Received 5th June 2014,
Accepted 27th July 2014

DOI: 10.1039/c4dt01562b

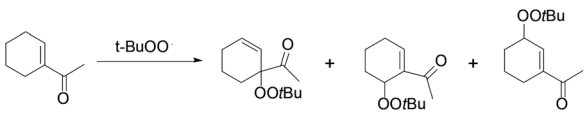
www.rsc.org/dalton

The Cu(II) complex **1**, Cu(II)-6-*N*-3,5-di-*tert*-butylsalicylidene-6,7-quinoxalinol-diamine, has been developed to address problems with current methods of catalytic oxidation using *tert*-butyl hydroperoxide (TBHP). Complex **1** demonstrated an increased capability to utilize TBHP while limiting interference from free radical reactions and was demonstrated to be highly effective in the oxidations of a variety of olefins.

Introduction



Direct transformation of an allylic CH_2 group to a carbonyl is of great importance given the versatility of the resultant α,β-unsaturated enones or 1,4-enediones as synthetic starting materials or drug precursors.[1,2] Although oxidations using organic catalysts have been reported,[3] to perform these oxidations efficiently, most often the oxidant *tert*-butyl hydroperoxide (TBHP) has been used in combination with a metal catalyst.[4] Limitations remain, including harsh reaction conditions, difficult purification procedures, toxic wastes, low functional group tolerance, and high costs. A key drawback of utilizing TBHP is the poor regioselectivity of the *tert*-butyl peroxy radical (*t*-BuOO$^{\bullet}$) that can be produced during the course of the oxidation (eqn (1)).[4–6] Here, we report a new 6-*N*-3,5-di-*tert*-butylsalicylidene-6,7-quinoxalinol-diamine Cu(II) complex catalyst **1** that can be used with TBHP in a method that diminishes the potential for free radicals in allylic oxidation.



Experimental

Materials and methods

All reagents were obtained commercially without further purification. Yields reported are for isolated mass yields after chromatography. The leucine methyl ester hydrochloride, 1,5-di-fluoro-2,4-di-nitrobenzene (DFDNB), ammonium formate, 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde, ammonium hydroxide (5.0 N), palladium on carbon (wet, 5%), *tert*-butyl hydroperoxide (TBHP, 5.0–6.0 M solution in decane) were purchased from Aldrich. The $^{18}O_2$ was purchased from Icon in a 100 mL break-seal (gas at atmospheric pressure, 98 atom %). The ^{1}H NMR and ^{13}C NMR spectra were recorded on 250 or 400 MHz instruments as solutions in $CDCl_3$ as indicated; chemical shifts (δ) are reported in ppm relative to Me_4Si. Reaction progress was monitored by thin-layer chromatography (TLC) using 0.25 mm silica gel precoated plates; spots were detected with UV light and revealed with I_2. Chromatographic purifications were performed using Fisher (60 Å, 70–230 mesh) silica gel. HRMS data were collected with electron spray ionization. All UV-Vis data was collected using a Cary 50 UV-Vis spectrophotometer with a xenon lamp with an equipment range from 200 to 1000 nm. Atomic absorption spectroscope (Varian AA240), its software (AA240FS) and hollow cathode lamp (HLC; Ni 232.0 nm, optimum working range: 0.1–20 mg L^{-1}; Mn 279.5 nm, optimum working range: 0.02–5 mg L^{-1}; Cu 324.8 nm, optimum working range: 0.03–10 mg L^{-1}) are from Varian Inc.

Department of Chemistry and Biochemistry, Auburn University, Auburn, AL 36849-5319, USA. E-mail: anne.gorden@auburn.edu

†Electronic supplementary information (ESI) available: Experimental details, cyclic voltammetry, GC-MS spectra, and calculation details. See DOI: 10.1039/c4dt01562b

All products have been previously described, and ^{1}H, ^{13}C NMR, and IR data are in accordance with literature data.

Synthetic procedures

Synthesis of 6-*N*-3,5-di-*tert*-butylsalicylidene-6,7-quinoxalinol-diamine Cu(II) complex 1. The ligand was synthesized in accordance with a previously published procedure.[1] In a 100 mL round-bottomed flask charged with a stirring bar, 0.20 mmol of ligand (89.6 mg) and 0.24 mmol of $Cu(OAc)_2{\cdot}H_2O$ were dissolved with 20 mL of dichloromethane and 20 mL of methanol. After 1.2 mmol of triethylamine was added, the reaction was stirred for 2 h at reflux temperature. After solvent was removed, the resulting dark red solid was washed with water and cold ether 3 times each. A product of 93.2 mg of solid was obtained (82%). HRMS was obtained from high yields of these microcrystalline samples inappropriate for characterization by X-ray diffraction.

6-*N*-3,5-Di-*tert*-butylsalicylidene-6,7-quinoxalinol-diamine Cu(II) complex 1. UV-Vis ($CHCl_3$): 334 nm (ε = 9000 M^{-1} cm^{-1}). Formula (M + H): $C_{29}H_{39}N_4O_4Cu$. HRMS: found 571.2351 (M + H), calcd 571.2346 (M + H).

Representative procedure for allylic oxidation of olefins using complex 1. To a 50 mL round-bottomed flask charged with a stirring bar, were sequentially added complex **1** (2.5 μmol), CH_3CN (10 mL), 1-acetyl-1-cyclohexene (0.5 mmol), and *t*-BuOOH (1.5 mmol). After the reaction was stirred at 70 °C for 1 h, solvent was removed under reduced pressure. The residue was purified by flash column chromatography with hexane–ethyl acetate as eluent to yield product as yellowish oil.

3-Acetyl-2-cyclohexenone (entry 1, Table 1). ^{1}H NMR: δ 6.58 (bs, 1 H), 2.50 (m, 2 H), 2.48 (m, 2 H), 2.41 (s, 3 H), 2.00 (m, 2 H). ^{13}C NMR: δ 201.5, 200.1, 154.6, 132.5, 37.9, 26.2, 23.4, 21.9. Formula: $C_8H_{10}O_2$. HRMS: found 138.0687, calcd 138.0681.

3-Phenyl-2-cyclohexenone (entry 2, Table 1). ^{1}H NMR: δ 7.55–7.53 (m, 2 H), 7.42–7.41 (m, 3H), 6.43 (t, J = 1.2 Hz, 1 H), 2.78 (m, 2 H), 2.49 (t, J = 6.0 Hz, 2 H), 2.18–2.13 (m, 2 H). ^{13}C NMR: δ 200.0, 159.9, 139.0, 130.0, 128.8, 126.1, 125.5, 37.3, 28.1, 22.8. Formula: $C_{12}H_{12}O$. HRMS: found 172.0881, calcd 172.0888.

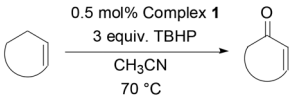
3-Acetoxy-2-cyclohexenone (entry 3, Table 1). ^{1}H NMR: δ 5.92 (s, 1 H), 2.54 (t, J = 6.8 Hz, 2 H), 2.42 (t, J = 6.4 Hz, 2 H), 2.23 (s, 3 H), 2.09 (m, 2 H). ^{13}C NMR: δ 200.0, 170.0, 167.4, 117.5, 36.6, 28.3, 21.2, 21.2. Formula: $C_8H_{10}O_3$. HRMS: found 154.0626, calcd 154.0630.

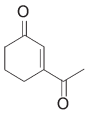
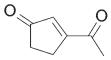
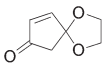
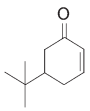
3-Acetyl-2-cyclopentenone (entry 4, Table 1). ^{1}H NMR: δ 6.67 (t, J = 2.0 Hz, 1 H), 2.83–2.80 (m, 2 H), 2.56–2.51 (m, 2 H), 2.50 (s, 3 H). ^{13}C NMR: δ 210.6, 197.3, 169.3, 137.0, 35.4, 27.8, 26.3. Formula: $C_7H_8O_2$. HRMS: found 124.0520, calcd 124.0524.

4-Cyclopentene-1,3-dione monoethylene ketal (entry 5, Table 1). ^{1}H NMR: δ 7.20 (d, J = 6.0 Hz, 1 H), 6.19 (d, J = 6.0 Hz, 1 H), 4.03 (m, 4 H), 2.60 (s, 2 H). ^{13}C NMR: δ 204.0, 156.3, 135.4, 111.6, 65.2, 45.2. Formula: $C_7H_8O_3$. HRMS: found 140.0465, calcd 140.0473.

3-Cyano-2-cyclohexenone (entry 6, Table 1). ^{1}H NMR: δ 6.52 (s, 1 H), 2.57 (dt, J = 6.0 Hz, 2.0 Hz, 2 H), 2.54 (t, J = 6.2 Hz, 2 H). 2.13 (m, 2 H). ^{13}C NMR: δ 196.6, 138.6, 131.1, 117.0, 37.2, 27.6, 22.0. Formula: C_7H_7NO. HRMS: found 121.0525, calcd 121.0528.

Table 1 Complex **1** catalyzed allylic oxidation of olefins



Entry	Substrate	Product	Time (h)	Isolated yield (%)
1			1	96
2			1	85
3			2	72
4			3	96
5			1	91
6			3	89
7			1	75
8			2	54[a]
				10[a]
9			2	60

[a] Yield as found by gas chromatography (GC).

3-Methyl-2-cyclohexenone (entry 7, Table 1). ^{1}H NMR: δ 5.87 (d, J = 1.6 Hz, 1 H), 2.33 (t, J = 6.4 Hz, 1 H), 2.31–2.28 (m, 2 H), 2.02–1.98 (m, 2 H), 1.96 (s, 3 H). ^{13}C NMR: δ 199.6, 162.8, 126.5, 36.8, 30.8, 24.4, 22.5. Formula: $C_7H_{10}O$. HRMS: found 110.0725, calcd 110.0732.

5-Methyl-2-cyclohexenone (entry 8, Table 1). ^{1}H NMR: δ 6.98–6.94 (m, 1 H), 6.03–6.00 (m, 1 H), 2.51–2.39 (m, 2 H), 2.27–2.17 (m, 1 H), 2.15–1.99 (m, 2 H), 1.07 (d, J = 6.4 Hz, 3 H). ^{13}C NMR: δ 200.1, 149.3, 129.6, 46.2, 34.0, 30.3, 21.2. Formula: $C_7H_{10}O$. HRMS: found 110.0722, calcd 110.0732.

5-*tert*-Butyl-2-cyclohexenone (entry 9, Table 1). ^{1}H NMR: δ 7.05–7.00 (m, 1 H), 6.04–6.01 (m, 1 H), 2.56–2.38 (m, 2 H), 2.17–2.08 (m, 2 H), 1.89–1.82 (m, 1 H), 0.92 (s, 9 H). ^{13}C NMR: δ 201.1, 150.8, 129.2, 45.2, 40.0, 32.3, 27.5, 26.9. Formula: $C_{10}H_{16}O$. HRMS: found 152.1192, calcd 152.1201.

Cyclic voltammetry

Electrochemical measurements were carried out at room temperature using a three electrode set-up in a home built glass cell (20 mL total volume). The supporting electrolyte was 0.1 M tetrabutyl ammonium tetrafluoroborate in 5 mL CH_2Cl_2 with 1 mM ferrocene as internal standard, the reference electrode was home made Ag/AgCl wire, and the counter electrode was Pt gauze (A = 0.77 cm^2). The working electrode was a glassy carbon disk (d = 0.3 cm, A = 0.071 cm^2). Before electrochemical measurements, the solution was purged with N_2 for 15 min. Cyclic voltammogram of 1 mM Cu(II) salqu was recorded in 5 mL CH_2Cl_2 described above between 0.0 V and 1.7 V using a scan rate of 100 mV s^{-1}.

Results and discussion

Previously, we have developed a ligand that incorporates a 2-quinoxalinol backbone into a salen framework with a typical O–N–N–O coordination salen core, abbreviated "salqu" (*e.g.*, **2**), for use as catalyst in allylic oxidations with TBHP as terminal oxidant.[7,8] Complex **1** was designed to have a more flexible backbone to better accommodate the reduction of the square planer Cu(II) to tetrahedral Cu(I) over the course of the reaction.[7] On further characterization, complex **2** was found to exhibit two quasi-reversible peaks that can be ascribed to the sequential one-electron oxidations of the two phenolic moieties of the complex. Since complex **2** possessed the same cyclic voltammogram as the simple Cu(II) salen complex,[7,9] and the half unit salen-type Cu(II) complex **3** exhibited one pair of quasi-reversible peaks (see Fig. 1 above), one CV redox peak was expected for the new complex **1** for its phenolic moiety. Interestingly, a pair of very small redox peaks was observed for complex **1** (see Fig. 2 above).

These electrochemical results are in agreement with the spectroscopic results. In the UV-Vis spectra in $CHCl_3$, the salqu ligand (free base of **2**) had an absorption band at 371 nm (ε = 24 100 M^{-1} cm^{-1}), while its Cu(II) complex (**2**) had two UV-Vis absorptions at 327 nm (ε = 20 000 M^{-1} cm^{-1}) and 450 nm (ε = 13 000 M^{-1} cm^{-1}) (Fig. 3). The ligand absorption can be ascribed to the electron excitation from the HOMO to the LUMO, and upon binding of Cu(II), the salqu complex **2** exhibited two absorptions. The one at 450 nm can be ascribed to the electron excitation from the HOMO of complex to the LUMO, while the other at 327 nm is typical of a ligand-to-metal charge transfer (LMCT) transition.[10] The absorptions at 371 nm for the salqu ligand and at 450 nm for salqu Cu(II) complex **2** correspond to the CV peaks for the salqu ligand and complex **2**, respectively. As seen in the CV experiment, the salqu ligand exhibited one redox pair within the scan window, and its Cu(II) complex **2** exhibited two quasi-reversible peaks. For complex **1**, only one UV-Vis absorption was observed at

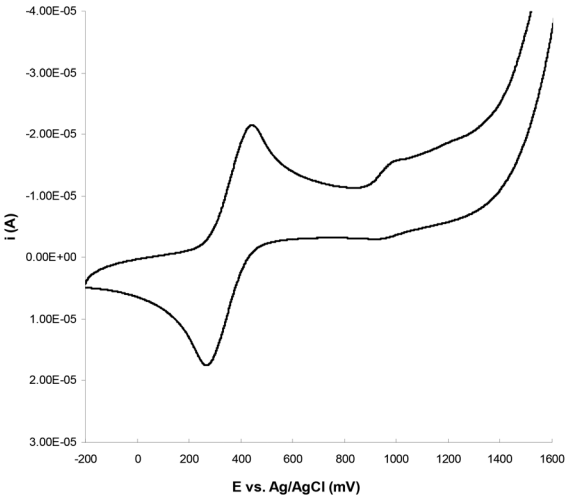


Fig. 2 Cyclic voltammogram of Cu(II) complex **1** with supporting electrolyte 0.1 M tetrabutyl ammonium tetrafluoroborate in 5 mL CH_2Cl_2 and 1 mM ferrocene internal standard, reference Ag/AgCl, counter electrode Pt gauze (A = 0.77 cm^2), and the working electrode was a glassy carbon disk (d = 0.3 cm, A = 0.071 cm^2).

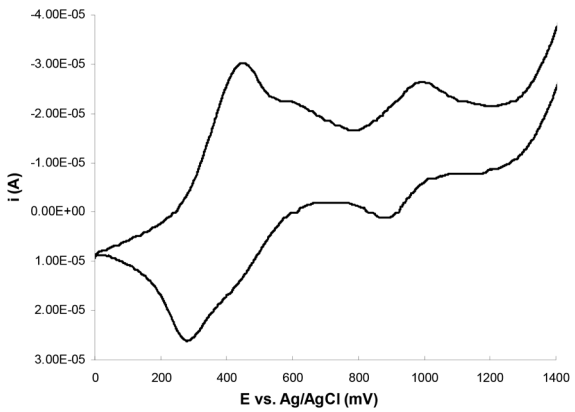


Fig. 1 Cyclic voltammogram of Cu(II) complex **3** with supporting electrolyte 0.1 M tetrabutyl ammonium tetrafluoroborate in 5 mL CH_2Cl_2 and 1 mM ferrocene internal standard, reference Ag/AgCl, counter electrode Pt gauze (A = 0.77 cm^2), and the working electrode was a glassy carbon disk (d = 0.3 cm, A = 0.071 cm^2).

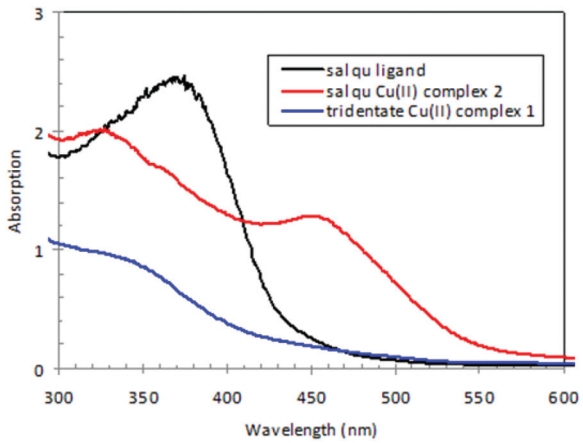
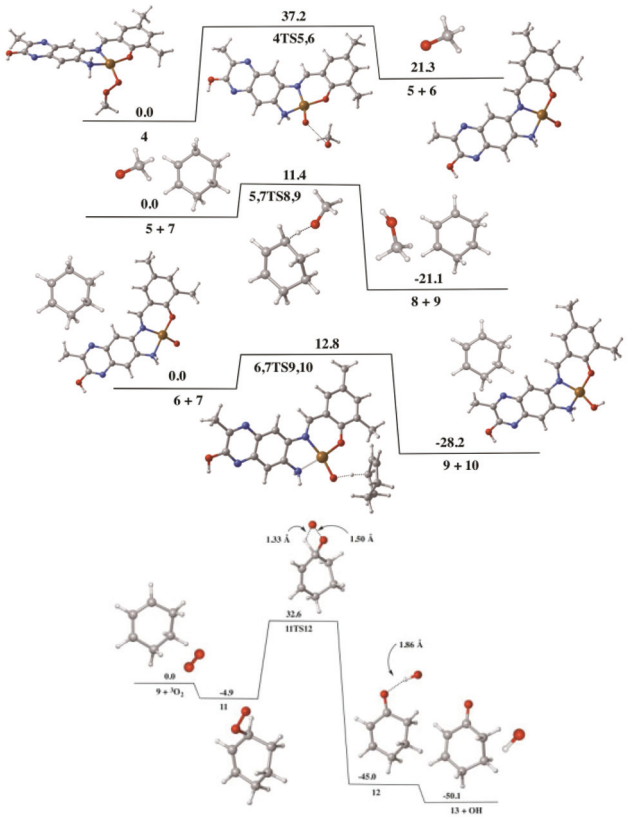


Fig. 3 UV-Vis spectra of salqu ligand, salqu Cu(II) complex **2**, and Cu(II) complex **1**. Samples were prepared as 0.1 mM solution in $CHCl_3$.

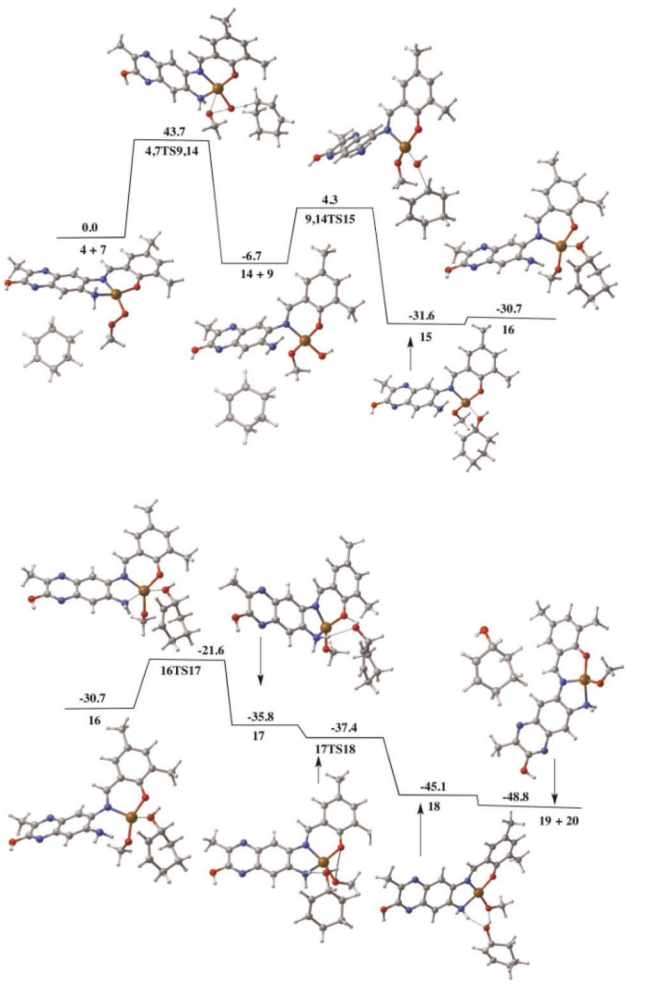
334 nm (ε = 9000 M^{-1} cm^{-1}). This band is assigned to the LMCT transition, and is close to the LMCT band of the complex **2**. Since complex **2** has two phenolic moieties contributing to the LMCT, while complex **1** has only one, the intensities are in accordance with these assignments.

Density functional theory (DFT) calculations in acetonitrile media at the B3LYP/6-311+G(2df,p)//B3LPY/6-31G(d) level were conducted to characterize the catalytic mechanism using complex **1**. For these calculations, the alkyl groups on complex **1** were replaced with methyl groups and the TBHP was replaced with methyl hydroperoxide as a means to decrease the complexity of the calculations. Two possible reaction pathways with a very small difference in free energy barrier (37.2 and 43.7 kcal mol^{-1}) were obtained. In the first possible pathway (see Scheme 1 below), the reaction is initiated by the formation of a Cu(II) peroxo complex **4** that can be obtained from the binding of peroxide to Cu(II) complex **1**. The homolytic cleavage of the O–O bond of the peroxide results in the methoxyl radical **5** and the LCu(II)–oxyl biradical **6**. The species **6** is in the triplet state after the cleavage of the O–O bond. The singlet intermediate **6** can be formed afterwards through intersystem crossing (ISC). The energy of the singlet state is 2.9 kcal mol^{-1} lower than the triplet state form. The triplet state corresponds to this LCu(II)–oxyl biradical species, while the singlet state corresponds to the LCu(III)=O species. This facile ISC is in agreement with previously reported research on the equilibrium between LCu(II)–O$^{\bullet}$ and LCu(III)=O in solution.[11] The methoxyl radical **5** can react with the substrate cyclohexene **7** abstracting the H atom at the allylic position, yielding methanol **8** and the cyclohexenyl radical **9**. This step is thermodynamically favoured, the products are 21.1 kcal mol^{-1} lower in free energy, and the energy barrier for this step (**5,7** → **5,7TS8,9** → **8,9**) is 11.4 kcal mol^{-1}. The substrate **7** can also react with LCu(II)–O$^{\bullet}$ **6** through H atom abstraction at the allylic position. Cyclohexenyl radical **9** will be obtained along with the LCu(II)–OH **10**. Such LCu(II)–OH complexes have been reported to carry out the ligand exchange with peroxides to form LCu(II)–peroxo species.[12,13] Under our reaction conditions, LCu(II)–OH **10** can be converted to LCu(II)–peroxo **4** to maintain the catalytic activity. The reaction between dioxygen and the cyclohexenyl radical **9** is spontaneous. Finally, the enone product **13** is obtained. This involvement of dioxygen is supported by observations seen in earlier work.[7]

A second potential pathway (Scheme 2) involves H atom abstraction from the allylic site by the ligating oxygen atom of



Scheme 1 DFT calculated reaction pathway **1** for allylic oxidation using complex **1** as the catalyst in acetonitrile media at the B3LYP/6-311+G-(2df,p)//B3LYP/6-31G(d) level.



Scheme 2 DFT calculated reaction pathway 2 for allylic oxidation using complex **1** as the catalyst in acetonitrile media at the B3LYP/6-311+G-(2df,p)//B3LYP/6-31G(d) level.

the peroxide in complex **4**. The cyclohexenyl radical **9** is formed as in the first pathway, while a different intermediate **14** is formed. At the transition state (**4,7TS9,14**), in addition to the H atom abstraction, the O–O bond of peroxide breaks, the bond between the Cu and the remote oxygen atom is formed, and the NH_2 group from the ligand is dissociated. The cyclohexenyl radical **9** can further react with the hydroxide of the intermediate **14**, leading to complex **15** with the Cu ion bound to an allylic alcohol. After the dissociated NH_2 group is bound to the Cu center again (16TS17), allylic alcohol **19** was released, and complex **20** was obtained with a methoxide group attached. In a fashion much the same as the LCu(II)–OH species, LCu(II)–OMe can also be converted to LCu(II)–peroxo complex with the presence of TBHP.[12,14] The catalytic activity of the Cu complex is therefore maintained. The allylic alcohol **19** can be further oxidized to the enone product **13**, however, this is outside of the scope of this research.

One distinct factor differentiating the two pathways is how the peroxide is utilized. In the first, peroxide is used to coordinate with the Cu center to produce the LCu(II)–O$^{\bullet}$/LCu(III)=O and a methoxyl radical. Both the Cu–oxygen species and the methoxyl radical are responsible for the H atom abstraction; however, it is the oxygen molecule that oxidizes the substrate to yield the final enone product. Hence, the oxygen of the enone product is from oxygen molecule. In the second pathway, although the allylic H atom of the substrate is still abstracted by LCu(II)–peroxo complex **4**, the resulting allylic radical species is oxidized by the hydroxide bound to the Cu center, leading to the allylic alcohol compound. The oxygen atom of the enone product is from the peroxide.

Since the two pathways lead to the same product but with the oxygen atoms having different sources, the oxidation of 1-phenyl-1-cyclohexene in acetonitrile degassed with argon under $^{18}O_2$ atmosphere was performed to elucidate the oxygen source of the product. Natural TBHP was used as the oxidant. If the oxygen incorporated into the product is from the TBHP, only the ^{16}O product would be obtained; otherwise, ^{18}O containing enone will be the product. After 1 hour of reaction time, the reaction solution was analyzed by GC-MS (ESI†). Both ^{16}O and ^{18}O containing products were observed. The ratio of ^{16}O to ^{18}O products is 3 : 1, indicating that both pathways are possible during the course of the oxidation reaction. The ratio of ^{16}O product to ^{18}O product indicates that the second pathway is more favoured.

Oxidations of different olefin substrates were tested to prove the efficacy of complex **1** as catalyst. The reactions were performed on a millimole scale for the ease of comparison with previous results. When 0.5 mol% of complex **1** was used as the catalyst and 3 equiv. of TBHP was used as the oxidant, all of the substrates were effectively converted to corresponding enone products in excellent yields within a short reaction time (Table 1). Olefins with a variety of functional groups have been successfully oxidized to the corresponding enone products in a very short time (1 to 3 hours) with excellent yields (up to 96%). In the oxidation of 3-methylcyclohexene (entry 7), the most thermodynamically stable product 3-methyl-2-cyclohexenone is produced. The influence of the steric effect of substrates was also examined in comparing 4-methylcyclohexene and 4-*tert*-butylcyclohexene (entries 8 and 9). For 4-*tert*-butylcyclohexene, given the strong steric hindrance of the *tert*-butyl group, 5-*tert*-butyl-2-cyclohexenone was obtained as the only oxidation product. When the *tert*-butyl group was replaced by a methyl group (entry 8), the steric hindrance was greatly decreased; however, the oxidation of 4-methylcyclohexene still took place at the less hindered site, yielding the 5-methyl-2-cyclohexenone as the major product (54%) and the 6-methyl-2-cyclohexenone as the minor product (10%). Since the methyl group provides less steric bulk, the great difference in reactivities at different sites for 4-methylcyclohexene has been ascribed to the structure of the complex **1**. The bulkiness of the ligand around the Cu makes complex **1** very sensitive to the steric condition of the substrate. As we observed in the case of 4-methylcyclohexene, this catalytic system showed significant selectivity for the major product (5.4 : 1) even with the small steric effect of the methyl group.

Conclusions

The Cu(II) complex **1** has exhibited unique properties in cyclic voltammetric experiments and UV-Vis spectroscopy, indicating the electronic effect introduced by the 2-quinoxalinol backbone to the Cu(II) complex that has not been reported previously. This catalytic system demonstrated its sensitivity to the bulkiness of the substrate at different sites and is a potentially attractive synthetic alternative with high yields, short reaction times, when regioselective oxidations and mild conditions are required.

Acknowledgements

We thank Professor Christian Goldsmith for his assistance and use of gas chromatography and Professor Curtis Shannon for helpful discussions about electrochemistry. Financial support from Auburn University is also gratefully acknowledged.

Notes and references

1 (*a*) Y. B. Liu, X. H. Liu, M. Wang, P. He, L. L. Lin and X. M. Feng, *J. Org. Chem.*, 2012, **77**, 4136; (*b*) J. Lv, H. Wu and Y. M. Wang, *Eur. J. Org. Chem.*, 2010, 2073; (*c*) M. Nakada and A. Nakamura, *Synthesis*, 2013, 1421; (*d*) V. Weidmann and W. Maison, *Synthesis*, 2013, 2201.

2 (*a*) J. Salva and D. J. Faulkner, *J. Org. Chem.*, 1990, **55**, 1941; (*b*) R. Ballini and G. Bosica, *Tetrahedron Lett.*, 1996, **37**, 8027.

3 (*a*) T. Dohi, N. Takenaga, A. Goto, H. Fujioka and Y. Kita, *J. Org. Chem.*, 2008, **73**, 7365; (*b*) T. Zhao, P. Zhao and M. P. Doyle, *J. Food Prot.*, 2010, **73**, 2010.

4 (*a*) J. A. R. Salvador and J. H. Clark, *Chem. Commun.*, 2001, **33–34**, 33; (*b*) T. K. M. Shing, Y.-Y. Yeung and P. L. Su, *Org. Lett.*, 2006, **8**, 3149; (*c*) J. Q. Yu, H. C. Wu and E. J. Corey, *Org. Lett.*, 2005, **7**, 1415; (*d*) E. C. McLaughlin and M. P. Doyle, *J. Org. Chem.*, 2008, **73**, 4317; (*e*) A. J. Catino, R. E. Forslund and M. P. Doyle, *J. Am. Chem. Soc.*, 2004, **126**, 13622; (*f*) X. Han, Z. Zhou, C. Wan, Y. Xiao and Z. Qin, *Synthesis*, 2013, 615; (*g*) J. A. S. Coelho, A. F. Trindade, R. Wanke, B. G. M. Rocha, L. F. Veiros, P. M. P. Gois, A. J. L. Pombeiro and C. A. M. Afonso, *Eur. J. Org. Chem.*, 2013, 1471.

5 M. Harre, R. Haufe, K. Nickisch, P. Weinig and H. Weinmann, *Org. Process Res. Dev.*, 1998, **2**, 100.

6 E. C. McLaughlin, H. Choi, K. Wang, G. Chiou and M. P. Doyle, *J. Org. Chem.*, 2009, **74**, 730.

7 Y. C. Li, T. B. Lee, T. Y. Wang, A. V. Gamble and A. E. V. Gorden, *J. Org. Chem.*, 2012, **77**, 4628.

8 Y. C. Li, X. H. Wu, T. B. Lee, E. K. Isbell, E. J. Parish and A. E. V. Gorden, *J. Org. Chem.*, 2010, **75**, 1807.

9 R. C. Pratt and T. D. P. Stack, *J. Am. Chem. Soc.*, 2003, **125**, 8716.

10 R. C. Pratt and T. D. P. Stack, *Inorg. Chem.*, 2005, **44**, 2367.

11 T. Storr, P. Verma, R. C. Pratt, E. C. Wasinger, Y. Shimazaki and T. D. P. Stack, *J. Am. Chem. Soc.*, 2008, **130**, 15448.

12 L. E. Cheruzel, M. R. Cecil, S. E. Edison, M. S. Mashuta, M. J. Baldwin and R. M. Buchanan, *Inorg. Chem.*, 2006, **45**, 3191.

13 J. E. Pate, R. W. Cruse, K. D. Karlin and E. I. Solomon, *J. Am. Chem. Soc.*, 1987, **109**, 2624.

14 T. Fujii, A. Naito, S. Yamaguchi, A. Wada, Y. Funahashi, K. Jitsukawa, S. Nagatomo, T. Kitagawa and H. Masuda, *Chem. Commun.*, 2003, 2700.