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Copper-catalyzed aziridination with redox-active ligands: molecular spin catalysis

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Abstract: Small-molecule catalysts as mimics of biological systems illustrate the chemists' attempts at emulating the tantalizing abilities displayed by Nature's metalloenzymes. Among these innate behaviours, spin multistate reactivity is used by biological systems as it offers thermodynamic leverage towards challenging chemical reactivity but this concept is difficult to translate into the realm of synthetic organometallic catalysis. Here we report a rare example of molecular spin catalysis involving multistate reactivity in a small-molecule biomimetic copper catalyst applied to aziridination. This behaviour is supported by spin state flexibility enabled by the redoxactive ligand.

Of all the tricks up Nature's sleeve, multistate reactivity^[1] as a means to control reactivity within enzymatic active sites is perhaps among the most astute and difficult behaviour to emulate. Metalloenzyme-promoted mitigation of reactivity with stability is handled through the occurrence of spin-flip events, mostly metal-based, for example from a singlet to a triplet state. A classic example of such reactivity is found in epoxidation of double bonds performed by cytochrome P450.[1a,2] Metalcatalysed aziridination -which, unlike epoxidation, does not have a biological counterpart- relies on the use of noble metals such as Rh and Ru or cheaper first-row transition metals as Fe, Co, Ni, Cu and Mn.^[3] Recent work from the Arnold group on aziridination performed by an engineered bacterial cP450 obtained through in vitro evolution casts a light on the productive merger of bioinspired systems and bona fide synthetic applications.^[4] Because aziridination is electronically closely related to epoxidation, for which metal-oxo complexes of first row transition metals have proved highly efficient, chemists have developed synthetic approaches relying on metals in conjunction with nitrene precursors. While the mechanism remains a subject of debate, a consensus revolves around the implication of metalnitrene species, whose electronic structure can be described as either metal nitride M=N or metal-nitrene radical M-N^{•,[5]} The former is usually associated with a concerted mechanism while

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the latter favors a stepwise mechanism through radical intermediates. Copper nitrene species are elusive^[6] and the need to isolate metal-nitrene adducts introduces a disconnect between off-site spectroscopic interrogation of their electronic structure and their actual involvement in the catalytic cycle.

Redox-active ligands have received sustained attention due to their ability to perform biologically inspired transformations implying ligand-based electronic participation akin to that encountered in metalloenzymatic redox co-factors. This research area stems from an early interest in bioinspired catalytic systems and has morphed into broader synthetic pursuits.^[7] The use of cobalt (II)–porphyrin complexes for nitrene transfer has been reported by Zhang and de Bruin and mechanistic studies have provided information on key porphyrin-Co(III)-nitrene intermediates involved in which the porphyrin ligand acts as a redox-active ligand in a bis-nitrene species.^[8] A well-established family of redox-active ligands are aminophenols^[9] which can shuttle between three distinct redox states: amidophenolate (AP), iminosemiquinone (SQ), and iminobenzoquinone (BQ).^[10] Complex **1** Cu(L_{SO})₂ is a stable three-spins system with a Cu^{II} centre and two biradical SQ species^[11] which has been shown to promote ligand-based redox events.^[12] Here, we report on the ability of this three-spins system to carry out aziridination through molecular spin catalysis,^[13] wherein the redox-active ligands mediate electronic transfer from the nitrene source to the metal complex.

Our initial studies began with the observation that complex 1 can perform aziridination of 4-chlorostyrene. The influence of the nitrene source was first investigated (Table 1). In the presence of 5 mol% of complex 1, an excess of 4-chlorostyrene (4 equiv.) in dichloromethane at room temperature, tosyliminoiodinane (entry 3) gives access to aziridine 2 in 65 % yield, whereas chloramine-T (entry 1) and sulfonyle azide (entry 2) are not converted. An increase in substrate concentration, from 1 M to 5 M, enabled to obtain 78 % of aziridine 2 (entry 4). Similar yields were also obtained when diminishing the catalytic load to 2 mol% (entry 5). Then, we turned our attention to the reaction time: after 2 hours, iminoiodinane was totally converted and aziridine 2 was obtained in 89 % yield with 1 mol% of catalyst (entry 6), and in 90 % yield with 0.5 mol% of catalyst (entry 7), thus demonstrating the rapid evolution of the reaction. The reaction is not air-sensitive (entry 8). Switching dichloromethane for acetonitrile afforded reduced reaction times as the reaction was complete in 20 min with a quantitative yield of aziridination substrate (entry 9). This could be due to degradation or side reactivities of the aziridination product under prolonged reaction conditions, although no other product was detected.



| Table ' | Optimization | conditions | for | the | aziridination | of | 4-chlorostyrene |
|----------|----------------------------------|---------------------------------------|-----|-----|---------------|----|-----------------|
| catalyze | ed by complex 1 | I Cu(L _{SQ}) ₂ . | | | | | |

| entry ^[a] | [Styrene] | Nitrene source | Catalyst (x mol%) | time | Yield (%) ^[b] |
|----------------------|-----------|------------------------------------|----------------------|--------|-----------------------------|
| 1 | 1 M | AcN-SO ₂ N ₃ | 5 | 18h | - |
| 2 | 1 M | Chloramine-T | 5 | 18h | - |
| 3 | 1 M | PhINTs | 5 | 18h | 65 |
| 4 | 5 M | PhINTs | 5 | 18h | 78 |
| 5 | 5 M | PhINTs | 2 | 18h | 80 |
| 6 | 5 M | PhINTs | 1 | 2h | 89 |
| 7 | 5 M | PhINTs | 0.5 | 2h | 90 |
| 8 ^[c] | 5 M | PhINTs | 1 | 2h | 87 |
| 9 ^[d] | 5 M | PhINTs | 1 | 20 min | 99 |

^[a] 4 equiv. styrene, ^[b] NMR yields, calculated considering nitrene source as limiting reactant, ^[c] Reaction performed under air, ^[d] Acetonitrile as solvent.

The scope of the reaction was assessed on a variety of substrates and found to be quite large. Mono-substituted aziridines were obtained in excellent to moderate yields depending on the Csp2 or Csp3 hybridization of the substituting group (substrates **2**, **3**, **10**). Di-substituted aziridines could be isolated with yields up to 86% (**4**, **5**, **6**, **7**, **8**, **11**, **13**, **14**) and several motifs can be accommodated (aldehyde, ester, ketone). Also, the methodology could be extended to more challenging gem-disubstituted (**12**) and tri-substituted (**9**, **15**, **16**) scaffolds. Running the reaction on geranyl acetate, which possesses two triply-substituted double bonds afforded an overall aziridination yield of 67% divided between products **15** (15%) and **16** (52%), the latter is preferentially formed presumably for steric reasons.



Scheme 1. Scope of the aziridination performed under optimized conditions.

In UV-Vis-NIR, complex 1 [Cu(L_{SQ})₂] displays a characteristic intervalence charge transfer (IVCT) band at 795 nm (Fig. 1). Upon addition of 4-chlorostyrene, no evolution is detected. Addition of increasing amounts of PhINTs (1, 2, 3 and 10 equiv.) induces the disappearance of the IVCT band, which reaches its minimum value upon addition of 2 equiv., followed by the growth of a new broad band shifted to 720 nm. These results suggest the consecutive formation of two distinct complexes, presumably corresponding to mono- and bis-nitrene species,^[8] upon addition of increasing amounts of PhINTs. From TDDFT calculations, the low-energy transition in the bis-nitrene spectrum can be assigned to a interligand charge transfer rather than a IVCT between the two nitrene as the donor state involves predominantly the copper center and the nitrene ligands while the acceptor state is distributed over the benzoquinone moieties (see SI). Reaction between PhINTs and complex 1 [Cu(L_{SQ}]₂] is very slow to reach its equilibrium. Spectra recorded for 0.5 and 1 equiv. mixtures show that these two species coexist under substoichiometric conditions (See SI for detailed studies and DFT).



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Figure 1. UV-Vis-NIR spectra of complex 1 and upon addition of increasing amounts of PhINTs in DCM under argon atmosphere ([1]= 0.075 mM).

The X-band spectrum of complex 1 in solution at 293 K displays a main feature around g=2, which corresponds to an apparent S=1/2 ligand centered radical (fig S13). Evolution of this EPR spectrum upon reaction with PhINTs was monitored for three distinct substoichiometric nitrene to copper ratios (0.25:1, 0.5:1 and 0.75:1) (Fig. 2A). RT spectrum for the lowest concentration displays a five lines pattern centered at g=2.0042, indicating a species (presumably mono-nitrene 17) with two quasi equivalent nitrogens coupled to an organic radical. Under stoichiometric conditions (Fig. 2B), a drastic change in the EPR spectrum occurs, indicating the formation of a new species, presumably bis-nitrene 18. At the 1:1 ratio, the RT spectrum is typical for a Cu(II) species. Increasing PhINTs (2 to 5 equiv.) results in an increase of this signal. Under catalytic conditions (Fig. 2C), a copper pattern with $A_{iso Cu}$ = 70 Gauss and a g factor of 2.13 remain throughout the reaction, thus indicating no change in the environment of the copper complex. After 20 hours, the copper (II) signal disappears and the five lines pattern is observed,

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consistent with regeneration of mono-nitrene **17**, which seems to be the resting state of the catalysis.

Figure 2. X-band EPR studies of A) formation of the mono-nitrene species 17 under substoichiometric conditions, B) formation of bis-nitrene species 18, C) aziridination reaction under operando conditions, D) 2D HYSCORE spectra recorded at 5K. Conditions: 5 mM [Cu] in CH₂Cl₂.

While catalysis occurs at room temperature, HYSCORE experiments were performed at 5K in order to get structural insights on the various species involved. For 1 alone, a weak coupling signal with proton and carbon is observed in the quadrant (+,+) (Fig. S10). Additionally, a ¹⁴N A_{iso} = 3.2 MHz is measured in the (-,+) quadrant. At low PhINTs concentration, a 15 MHz coupling due to nitrogen is observed in both quadrants (Fig. S11). For 5 equiv., a new nitrogen correlation peak appears in the (-,+) quadrant, indicating that a second nitrene has been incorporated (Fig. S12). Additionally, a coupling with ¹H is observed with a maximum value of 11 MHz arising from the tosyl group. The spectra of Figures S11 and S12 are thus representative of mono-nitrene 17 and bis-nitrene 18, respectively. A HYSCORE spectrum recorded at 5K on frozen reaction aliquots displays a new ligand-centered S=1/2 signal and only weak ¹³C and ¹H couplings in the (+,+) quadrant. Interestingly, in the low frequency region, we can observe two peaks centered at 1.4 and 2.8 MHz respectively, arising from a coupling with the chlorine atom of 4-chlorostyrene (Fig. 2D). This spectrum is in agreement with the formation of intermediate 19, as proposed in the catalytic cycle (Fig. 3), resulting from the reaction of the nitrene radical in 17 with the alkene.

DFT calculations were undertaken to gain insight into the species observed during catalysis. The structures of the putative species were subjected to geometry optimization. Their electronic properties were investigated using Broken-Symmetry calculations to evaluate the ground spin and first excited states of each intermediate. Complex 1 displays a quasi square planar geometry (Fig. S16) and the spin density plot (Fig. S17) is compatible with a Cu(II) center bound to two redox-active iminosemiquinone (SQ) ligands. In agreement with previous $\mathsf{studies}^{[11,12b]}$ the system is characterized by a doublet $\mathsf{S=1/2}$ ground spin state due to strong antiferromagnetic coupling between the SQ moieties (Table S1). A quartet S=3/2 state is close enough in energy to be thermally accessible, as experimentally observed by SQUID technique.^[11] The theoretical structure of complex 17 is trigonal bipyramidal (Fig. S18) and its electronic structure shows a Cu(II) center interacting with an SQ moiety and a NTs radical (Fig. S19). The computed geometry for 17 does not allow for an IVCT band neither between the NTs radical and the SQ ligand nor between the SQ and BQ ligands in agreement with UV-vis data. A ferromagnetic interaction dominates in 17 resulting in a quartet S=3/2 ground spin state and the energetic separation with the first doublet S =1/2 state is consistent with its observation at RT (Table S1). Complex 18 displays an octahedral geometry (Fig. S20) and the spin density

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plot (Fig. S21) is compatible with a Cu(II) center bound to two NTs radicals. The system is characterized by a doublet S=1/2 ground spin state due to antiferromagnetic coupling between the NTs moieties (Table S1). The theoretical structure of complex **19** is also trigonal bipyramidal (Fig. S22) and its electronic structure shows a Cu(II) center interacting with an SQ moiety and a styrene-based radical (Fig. S23). An antiferromagnetic interaction dominates in **19** resulting in a doublet S=1/2 ground spin state in agreement with HYSCORE measurements (Table S1).

Together with DFT calculations, variable temperature EPR experiments (see SI) indicate that all the species (1, 17, 18, 19) involved in the reaction have a complex electronic structure due to the interaction of two ligand radicals (S=1/2) and one metal centre (S=1/2), leading to a mixture of populated spin states at room temperature. Small changes in the coordination sphere have been shown to have an impact on the spin states of related complexes.^[14] Interestingly, while starting complex **1**, bis-nitrene 18 and intermediate 19 present a doublet ground state, mononitrene 17 has a quadruplet ground state. In a classical approach, reaction between $[Cu(L_{SO})_2]$ and PhINTs to form mono-nitrene 17 should be spin forbidden, and thus extremely slow. However, due to its unique electronic structure, the excited state S=1/2 of 17 becomes accessible, as attested by the observed radical centered S=1/2 signature at RT (Fig. S14). Hence, through multistate configuration, the reaction becomes spin allowed, ensuring fast kinetics for each step. The implication of redox-active ligands in spin-forbidden processes has been discussed by de Bruin.^[15] We thus propose the following mechanism in which each intermediate has been spectroscopically identified, and the electronic structures confirmed by DFT calculations (Fig. 3). Two-state reactivity of copper-nitrenes involving two spins systems has been studied by Pérez,^[16] Norrby^[17] and Ray in aziridination,^[18] and by Ray in alkane hydroxylation.^[19] Norrby has proposed a Cu¹/Cu^{III} redox cycle in aziridination. Strikingly, in our system, a Cu^{II} oxidation prevails throughout the catalytic cycle and this metal redox homeostasis is enabled by the fact that redox variations are all ligand-based.

In conclusion, we report here a rare example of molecular spin catalysis in copper-catalyzed aziridination performed by a copper complex bearing two redox-active iminosemiquinone ligands. This unique behaviour is enabled by the spin fluxionality exhibited by the starting complex and the intermediates involved in the reaction, which is allowed by the redox-active nature of the ligands. This work showcases the ability of redox-active catalytic manifolds to perform otherwise well-known reactions through distinct and unconventional mechanisms and opens wide perspectives in redox and biomimetic catalysis.

Figure 3. Mechanistic proposal for the aziridination reaction outlining the spin configuration of the involved species with DFT inserts. SQ: iminosemiquinone, BQ: iminobenzoquinone.



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