

Supporting Material.

Mechanistic Studies of Copper-Catalyzed Alkene Aziridination

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The oxidation state of copper and the PES of the dicationic system 4a.

Results.

Table S1. Potential energy surface of the dicationic system 4a (kcal/mol).^a

Species	BSI	BSII	BSIII
5	-42.0	— ^b	— ^b
6	0.0	0.0	0.0
8	-70.7	-54.5	-55.0
10	-168.4 ^c	— ^b	— ^b
11	-153.8	-145.0	-143.4
6	-56.2	-58.9	-58.1

^aAll species in the doublet state.

^bNot determined.

^cOptimized to a ring-closed structure possessing the five-membered S^I-O-C-C-N=S^I unit.

Discussion.

Calculations using dicationic **4** as the model system is strongly influenced by electrostatic effects as expected and therefore, the energies shown in Table S1 should be treated with some caution. However, some interesting conclusions can be drawn from the energies. First of all, the naked Cu(II) complex **6** indeed reacts with PhINTs. However, as indicated by the spin densities of the doublet state of the complex shown in Figure S1, PhINTs is not capable of fully oxidizing Cu(II) to Cu(IV), instead, this complex could be viewed as a Cu(II) complex of a triplet nitrene. The vertical excitation energy to the quartet state is only 16 kcal/mol at BSI, but optimization of this quartet results in extrusion of a nitrogen atom and lowering of the energy by 20 kcal/mol indicating that a dicationic copper-nitrene species would, if ever formed, be very labile indeed. Optimizing the intermediate carbon centered radical **10**, which could serve as a route to isomerized aziridines, resulted in ring-closure to the corresponding five-membered $S^1-O-C-C-N=S^1$ structure, which in fact is the most stable species on the entire dicationic PES.

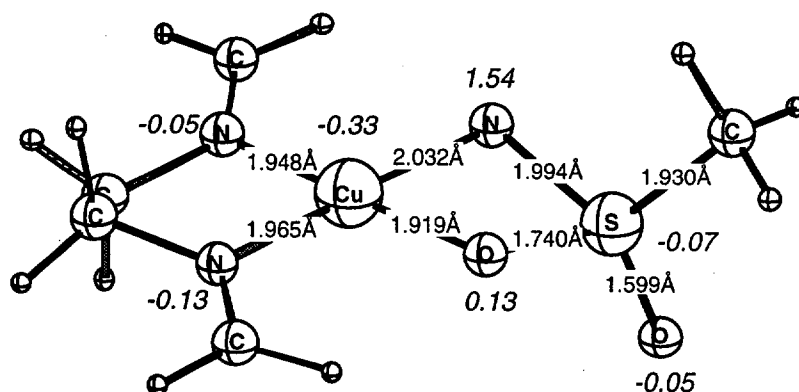


Figure S1. Doublet nitrene intermediate **8** formed in the reaction between the Cu(II)-diimine complex **6** and PhINSO₂Me (Mulliken spin densities from B3LYP/BSIII in italics).

The formation of aziridine from the copper-nitrene complex is very exothermic as expected from the pronounced radical character of the nitrene and the long Cu-N bond in **8**. For a catalytic cycle to continue, the next step is to replace the product with a new nitrene. This step could be expected to be reasonably well described by gas phase calculations, as there is no change in the number of atoms bound to copper, and was calculated to be endothermic by 30 kcal/mol. The great endothermicity of this step may be attributed to the comparatively weak Cu-nitrene bond, and prompted us to conclude the catalytic cycle does not involve dicationic species.

Conclusions

Calculations on a dicationic Cu(II)-diimine system strongly suggest that the Cu(II)-diimine does not take part in the reaction mechanism of the Cu-catalyzed aziridination of olefins. The catalytic cycle is blocked by a very strong product binding that makes the regeneration of the active Cu-nitrene highly endothermic (30 kcal/mol). Solvent effects should be of minor importance for this step, since the number of atoms bound to copper remains unchanged.