Efficient Aziridination of Olefins Catalyzed by a Unique Disilver(I) Compound

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Silver(I) and silver(II) complexes are frequently used as stoichiometeric oxidants for oxidation of various organic and inorganic substrates. However, these metal ions are not often used as real catalysts in oxidation or group transfer reactions that do not involve radical chemistry. Despite the fact that the silver particle is an efficient catalyst for olefin epoxidations in industry,[1,2] efficient epoxidation or aziridination reaction of unsaturated hydrocarbons mediated by silver ions in solution has yet to be realized. The nonradical oxidation reactions catalyzed by silver ions are limited, although a carbene insertion chemistry was reported recently.[3] Identifying new reactivity associated with silver ions may lead to practical synthetic processes and better understanding of silver chemistry.

We describe here an efficient olefin aziridination reaction catalyzed by a novel disilver(I) compound. Aziridines are synthetic intermediates that can be converted into important nitrogen-containing functional groups.[4] Although several efficient syntheses of aziridines from olefins have been reported,[5−14] none of these is mediated by silver ions. During our investigation of silver chemistry, we discovered that efficient aziridination of olefins could be catalyzed by mixing 1 equiv of a tridentate 4,4′,4″-tri-*tert*-butyl-2,2′:6′,2″-terpyridine (tBu_3tpy) with 1 equiv of silver(I) salt and a nitrenoid source PhI=NTs in acetonitrile at ambient temperature (Figure 1). No reaction occurred in the absence of the silver(I) salt. The reaction did not seem to be affected by the counteranions because the use of $AgNO_3$, AgOTf, $AgClO_4$, and $AgBF_4$ salts all gave the same result. Surprisingly, clean production of aziridine was only observed when tBu_3tpy was used as the ligand to silver-(I). With pyridine or 4-*tert*-butyl-pyridine as the ligand, only a trace amount of aziridine product was observed. An increasing amount of aziridine (35−50%, GC yield) could be prepared with bipyridine, 4,4′-di-*tert*-butyl-bipyridine, or 2,2′:6′,2″-terpyridine (tpy) as the ligand, but these catalytic reactions were accompanied by a variety of byproducts. When *t*Bu-bis(oxazoline) or Ph-bis(oxazoline)-pyridine was used as the ligand, no product was observed under the same reaction conditions.

To address the requirement of the tridentate ligand tBu_3tpy, we structurally characterized the catalyst or catalyst precursor from the reaction medium. Equal molar amounts of $AgNO_3$ and tBu_3tpy were mixed in acetonitrile and left to stand at room temperature for 3 days. Pale yellow single crystals were obtained from the solution. The structure was solved and revealed a dinuclear silver-(I) compound $[Ag_2(tBu_3tpy)_2(NO_3)](NO_3)$ **1** (Figure 2). The disilver-(I) center is stabilized by two tBu_3tpy ligands with Ag(1) bound to four nitrogen atoms and Ag(2) bound to two nitrogen atoms from the ligands. Both silver ions are five-coordinate if the silver−silver interaction is counted. Each ligand bridges two silver(I) ions. The Ag(1)−Ag(2) distance is 2.842(2) Å, which may indicate a fairly strong silver(I)−(I)silver interaction.[15] The space-filling model (Figure 2) shows that the two terminal positions of **1** are accessible, with one terminal side occupied by a weakly bound nitrate anion.
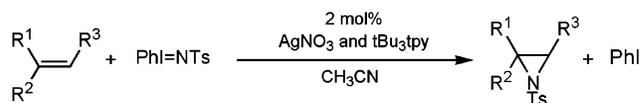
Figure 1. Silver-catalyzed olefin aziridination.
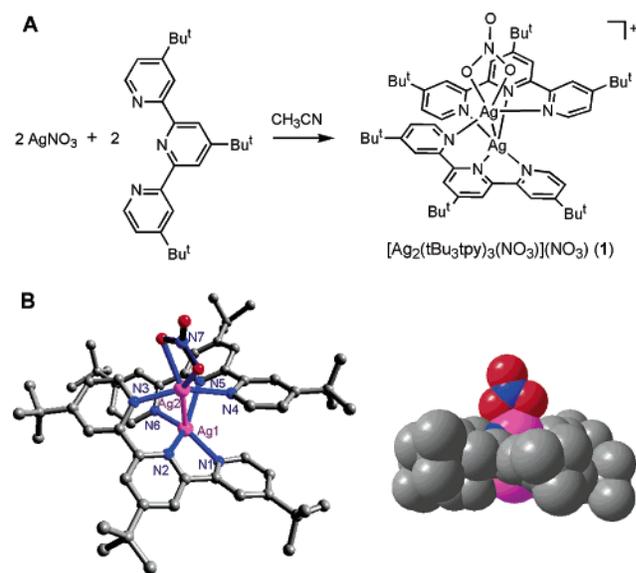
Figure 2. (A) Formation of compound $[Ag_2(tBu_3tpy)_2(NO_3)](NO_3)$ **1**. (B) The molecular structure and space-filling model of **1**.

To probe the solution structure of **1**, we recorded the ^{1}H NMR of **1** in CD_3CN and compared it to the spectrum of a mixture of equal molar amounts of $AgNO_3$ and tBu_3tpy in the same solvent (Figure S1). The two spectra were identical if the solution generated in situ was allowed to stand for 5 min. If the spectrum was taken immediately after mixing the ligand and silver salt, broader peaks were observed, which may indicate that the system was still equilibrating (Figure S1). Crystals of compound **1** were dissolved in acetonitrile and exhibited the same activity in catalyzing the olefin aziridination reaction as the mixed compound. The disilver compound could also be isolated by flash chromatography after completion of the catalytic reaction. Single-crystal X-ray structural analysis of the isolated complex revealed a similar disilver(I) core structure (Figure S4; OTf was used as the anion in this case). All these results suggest that the disilver(I) compound is the precatalyst present in the reaction solution and the structure is retained after the reaction.

We also found that the same disilver(I) compound can epoxidize olefins and oxidatively activate inert C−H bonds.[16] Silver compounds with other ligands either showed no activity or gave a mixture of oxidized products.

Although the geometry of the disilver(I) compound could be a factor in mediating the reactivity of the silver ions, we suspect that the electronic communication between two silver ions may play an important role in controlling the reactivity of compound **1**. We

Table 1. Disilver(I)-Catalyzed Aziridination of Olefins

Entry	Substrate	Product	Yield[a]
1			66
2			71
3			81
4			88
5			91(89)[b]
6			74
7			80
8			90
9			86
10			88
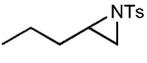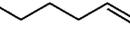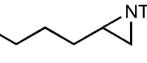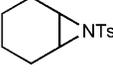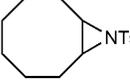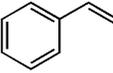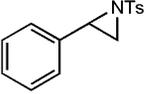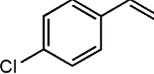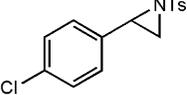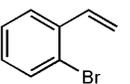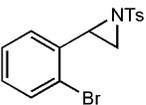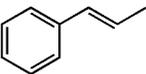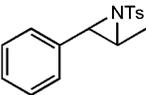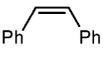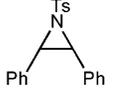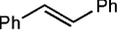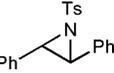
[a] All reactions were conducted at 0 °C to r.t. in CH_3CN with 2 mol % of $AgNO_3$ and tBu$_3$tpy. The isolated yields are reported here (%). [b] The yield in the parentheses was obtained by using 2 mol % compound **1** crystal as the catalyst.

envision that a transient Ag=NTs group may form on the open coordination sites of the disilver(I) core upon reacting with PhI=NTs. The electronic interaction between the two silver ions may help generate this species and tune its reactivity. It is well-known that pyridine-based ligands can stabilize high-valent silver species.[17] High-valent silver intermediates could be involved in this reaction. No product was observed if 1 equiv of zinc(II) was mixed with 1 equiv of tBu$_3$tpy and used as the catalyst in the aziridination reaction. Therefore, the metal does not serve as a simple Lewis acid catalyst. A color change from pale yellow to brown was observed upon mixing compound **1** with PhI=NTs in acetonitrile (Figure S2), which may indicate the involvement of a high-valent silver species. Further mechanistic investigations are required to reveal the nature of the intermediate.

This silver-catalyzed aziridination reaction proceeds in good to excellent isolated yields with a range of olefin substrates (Table 1). Terminal alkene substrates can be converted into aziridines in good yields.

It is intriguing that the disilver(I) compound **1** exhibits the well-controlled oxidation reactivity. A diRh(II) compound, Rh$_2$(OAc)$_4$, was previously shown to catalyze similar olefin aziridination reactions.[6,14,18,19] The diRh(II) compound is used widely to catalyze other types of oxidation reactions.[6,20] The nature of the reactive intermediates in the diRh(II) system remains unclear in these reactions. It is interesting that both Rh$_2$(OAc)$_4$ and the disilver compound **1** have short metal−metal distances and accessible coordination sites at the terminal positions. The two systems may share similar mechanistic characteristics. We are in the process of exploring other catalytic reactivity and are engaged in performing mechanistic investigations of the disilver compound described here. The study may help advance oxidation catalysis in general.

Supporting Information Available: Experimental details, ORTEP diagram of [Ag$_2$(tBu$_3$tpy)$_2$(NO$_3$)](NO$_3$) **1** and [Ag$_2$(tBu$_3$tpy)$_2$(OTf)]-(OTf) **2** (PDF), and X-ray crystallographic data of **1** and **2** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) van Santen, R. A.; Kuipers, H. P. C. *Adv. Catal.* **1987**, *35*, 265−321.
(2) Stinson, S. *Chem. Eng. News* **1995**, *73*, 7.
(3) Dias, H. V. R.; Browning, R. G.; Polach, S. A.; Diyabalanage, H. V. K.; Lovely, C. J. *J. Am. Chem. Soc.* **2003**, *125*, 9270−9271.
(4) Zwanenburg, B.; ten Holte, P. In *Stereoselective Heterocyclic Synthesis III*; Metz, P., Ed.; Topics in Current Chemistry; Springer: Berlin, 2001; Vol. 216, pp 93−124.
(5) Jacobsen, E. N. In *Comprehensive Asymmetric Catalysis*; Jacobsen, E. N., Pfaltz, A., Yamamoto, H., Eds.; Springer-Verlag: Berlin, 1999; Vol. 2, pp 607−618.
(6) Müller, P.; Fruit, C. *Chem. Rev.* **2003**, *103*, 2905−2919.
(7) Evans, D. A.; Faul, M. M.; Bilodeau, M. T. *J. Am. Chem. Soc.* **1994**, *116*, 2742−2753.
(8) Jeong, J. U.; Tao, B.; Sagasser, I.; Henniges, H.; Sharpless, K. B. *J. Am. Chem. Soc.* **1998**, *120*, 6844−6845.
(9) Li, Z.; Conser, K. R.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1993**, *115*, 5326−5327.
(10) Siu, T.; Yudin, A. K. *J. Am. Chem. Soc.* **2002**, *124*, 530−531.
(11) Au, S. M.; Huang, J. S.; Yu, W. Y.; Fung, W. H.; Che, C. M. *J. Am. Chem. Soc.* **1999**, *121*, 9120−9132.
(12) Ali, S. I.; Nikalje, M. D.; Sudalai, A. *Org. Lett.* **1999**, *1*, 705−707.
(13) Antilla, J. C.; Wulff, W. D. *J. Am. Chem. Soc.* **1999**, *121*, 5099−5100.
(14) Guthikonda, K.; Du Bois, J. *J. Am. Chem. Soc.* **2002**, *124*, 13672−13673 and references therein.
(15) Zheng, S. L.; Zhang, J. P.; Wong, W. T.; Chen, X. M. *J. Am. Chem. Soc.* **2003**, *125*, 6882−6883 and references therein.
(16) Cui, Y.; He, C., 2003. The University of Chicago, IL. Unpublished results.
(17) Po, H. N. *Coord. Chem. Rev.* **1976**, *20*, 171−195.
(18) Müller, P.; Baud, C.; Jacquier, Y. *Can. J. Chem.* **1998**, *76*, 738−750.
(19) Liang, J. L.; Yuan, S. X.; Chan, P. W. H.; Che, C. M. *Org. Lett.* **2002**, *4*, 4507−4510.
(20) Doyle, M. P. In *Catalysis by Di- and Polynuclear Cluster Complexes*; Adams, R. D., Cotton, F. A., Eds.; Wiley-VCH: New York, 1998; pp 249−282.

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