# Copper−Nitrenoid Formation and Transfer in Catalytic Olefin Aziridination Utilizing Chelating 2-Pyridylsulfonyl Moieties

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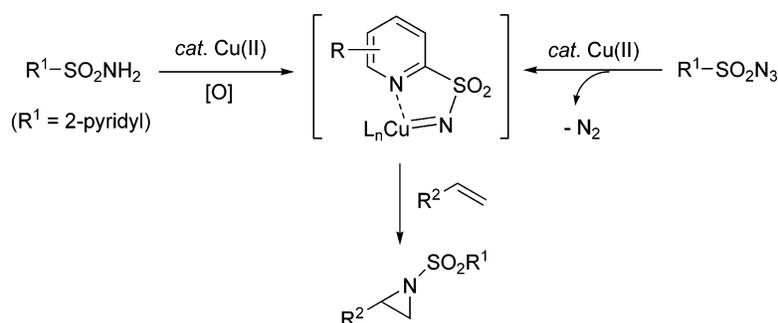
We have developed an efficient protocol for copper-catalyzed olefin aziridination using 5-methyl-2-pyridinesulfonamide or 2-pyridinesulfonyl azide as the nitrenoid source. The presence of a 2-pyridyl group significantly facilitates aziridination, suggesting that the reaction is driven by the favorable formation of a pyridyl-coordinated nitrenoid intermediate. Using this chelation-assisted strategy, synthetically acceptable yields of aziridines could be obtained with a range of aryl olefins even in the absence of external ligands. Importantly, a large excess of olefin is not required. X-ray crystallography, ESI-MS, Hammett plot analysis, kinetic studies, and computational undertakings strongly support that the observed aziridination is driven by internal coordination.

I. Introduction

The aziridine group is found in a number of important naturally occurring molecules, such as ficellomycin,[1a] porfiromycin,[1b] mitomycin,[1c] miraziridine,[1d] azinomycine,[1e] FR-66979,[1f] FR-900482,[1g] and maduropeptin.[1h] In addition to being synthetic endpoints, aziridines are also highly important building blocks in organic synthesis.[2] This utility has stimulated the development of a wide range of preparative procedures of aziridines via either traditional syntheses[3] or catalytic routes.[4]

A range of catalytic aziridination reactions of olefins have been developed using transition metal species including Cu,[5] Ag,[6] Au,[7] Ru,[8] Rh,[9] Mn,[10] Fe,[11] Co,[12] Pd,[13] Ni,[14] Re,[15] or In[16] in combination with suitable oxidants and coordinating ligands.

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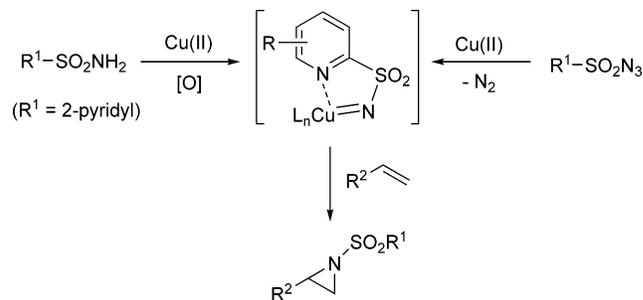
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Catalyst options have been expanded in recent years, but known nitrenoid sources remain limited. Thanks to the pioneering work of Mansuy,[17] *N*-(*p*-toluenesulfonyl)imino phenyliodinane (PhI = NTs) has been most widely employed as an efficient nitrenoid precursor in the olefin aziridination procedures.[18] Although there are several advantages of using PhI = NTs, some drawbacks limit its practical utility, for example, sensitivity to moisture or air, generation of side products such as oxygenated molecules, or difficulty in scaling up.[19] As a result, for reasons of convenience, practicality, and environmental concerns, N-halogenated sulfonamide salts such as chloramine-T and bromamine-T have emerged as alternative nitrogen sources in some N-transfer reactions.[20] However, these pathways are frequently low yielding due to the competition between hydrogen abstraction and insertion reactions.

To overcome these drawbacks, various more convenient nitrenoid sources have been investigated including sulfonamides,[21] carbamates,[22] and sulfamate derivatives[23] in combination with iodonium salts[24] and/or suitable additives.[25] However, reactions are sought that use more user-friendly oxidants,

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equivalent olefin amounts, and no external ligands.[26] In addition, the mechanism of aziridination has not been studied as much as that for epoxidation[27] or cyclopropanation.[28]

There are mounting examples showing that the presence of directing groups adjacent to reacting sites has significant influence on the reaction outcomes, thus leading to a dramatic change in efficiency and/or selectivity.[29] Nitrogen-containing organic functional groups readily coordinate to numerous transition metal species,[30] so that they are widely utilized as effective chelating units.[31] Among these, 2-pyridyl groups have attracted much attention as an effective chelating group.[32] We also have successfully utilized 2-pyridyl moieties in the Ru-catalyzed hydroesterification and hydroamidation of olefins and alkynes.[33] We previously reported initial results of chelation-assisted Cu-catalyzed aziridination using 2-pyridinesulfonamides as a nitrenoid source.[34] Described herein are our detailed studies on the aziridination using 2-pyridinesulfonyl azides and 2-pyridinesulfonamides (Scheme 1), focusing on reaction scope and mechanism.

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SCHEME 2.   Aziridination of Styrene with Various Nitrenoid Sources
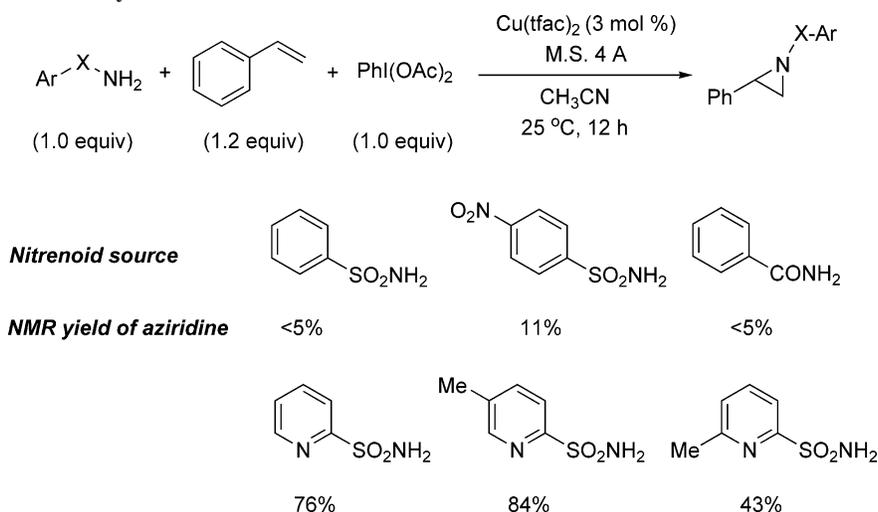
II. Results and Discussion

II.A. Aziridination with 2-Pyridinesulfonamides. At the outset of our studies, it was envisioned that the introduction of a 2-pyridyl unit into nitrenoid precursors such as arenesulfonamides and aromatic amides could significantly influence the course of metal-mediated aziridination through pyridyl-*N* metal chelation (eq 1). It was anticipated that both nitrenoid generation and subsequent alkene aziridination would be favorably driven by coordination effects, resulting in efficient catalysis even in the absence of added ligands.
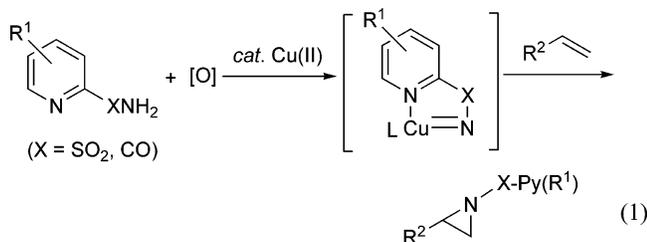

We first investigated the chelation effects of a range of nitrenoid sources in combination with mild oxidants such as PhI(OAc)$_2$ in the copper-catalyzed aziridination reactions (Scheme 2). To examine the feasibility of such chelation, only 1.2 equiv of styrene was employed. Aziridination was sluggish when benzenesulfonamide and its *p*-nitro derivatives were employed in the absence of external ligands. This low reactivity was not improved by increasing the amount of olefin employed (up to 10 equiv). Reaction with benzamide did not afford the desired aziridine under the same conditions.

In sharp contrast, efficiency of the transformation is significantly enhanced when 2-pyridinesulfonamide and its derivatives are employed. For example, the use of 2-pyridinesulfonamide resulted in high yield of the corresponding aziridine (76% yield) using 3 mol % of Cu(tfac)$_2$ catalyst. Among a variety of transition metal species previously known to catalyze aziridination, it was found that Cu(tfac)$_2$ exhibited the highest catalytic activity in acetonitrile in the presence of molecular sieves.[35] Introduction of a methyl group at C-5 of the 2-pyridyl moiety slightly improved the yield to 84%, as monitored by NMR spectroscopy. However, the use of 6-methyl-2-pyridinesulfona-

(35) See the Supporting Information for details.

mide gave a lower product yield (43%), implying that steric bulkiness near the coordination site of the 2-pyridyl group has a detrimental influence on the reaction efficiency. It should be noted that copper(I) species could also carry out the reaction, albeit with slightly lower activities compared to that of Cu(II) catalysts. In fact, the product yield was 66% with Cu(OTf)•PhH and 58% with [Cu(CH$_3$CN)$_4$][PF$_6$] in the reaction of styrene with 5-methyl-2-pyridinesulfonamide under otherwise the same conditions.

A similar propensity was also observed in the Cu-catalyzed aziridination with 1-naphthalene- and 8-quinolinesulfonamide (eq 2). A significantly improved product yield was observed when 8-quinolinesulfonamide was employed, whereas only negligible aziridine was obtained using 1-naphthalenesulfonamide, clearly indicating the crucial effect of chelation.
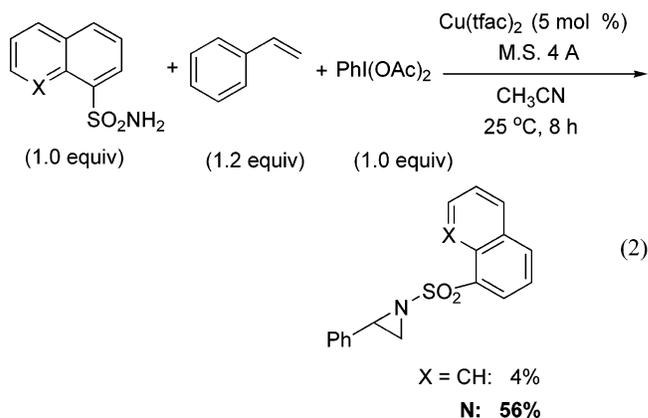
The olefin aziridination procedure optimized above using 5-methyl-2-pyridinesulfonamide (**1**) was successfully applied to a range of aromatic terminal olefins, resulting in moderate to high product yields. However, internal olefins reacted less efficiently compared to monosubstituted alkenes, and relatively large excesses of olefin substrates were required to obtain satisfactory yields. Whereas aziridination of *trans-β*-methyl styrene gave only *trans*-aziridine product, that of *cis*-olefin took place non-stereoselectively to provide a mixture of *cis/trans* isomeric products, suggesting that the nitrene transfer process in our system proceeds via a stepwise radical pathway.[36] In contrast to aryl olefins, the aziridination of aliphatic olefins was

much more sluggish, giving only moderate to low yields of the corresponding products.[37] The aziridination also was shown to be possible on larger scale. For instance, reaction of styrene (12 mmol) with 5-methyl-2-pyridine sulfonamide (**1**, 10 mmol) afforded the corresponding aziridine (2.2 g, 81%) under the optimized conditions.

II.B. Aziridination with 2-Pyridinesulfonyl Azides. Organic azides have been extensively utilized in various synthetic areas such as peptide synthesis, combinatorial chemistry, and cycloaddition reactions.[38,39] Despite their high utility in synthetic chemistry, transition-metal-mediated aziridination reactions using sulfonyl azides have been far less studied,[40] mainly due to the lack of suitable protocols for the controlled thermal[41] or photolytic[42] generation of reactive nitrenoids. Since molecular nitrogen is released as a byproduct from aziridination reactions using sulfonyl azides, this approach is very attractive from an environmental perspective. In 1967, Khan and Kwart reported that tosyl azide was decomposed upon the addition of Cu catalysts in cyclohexene to afford aziridine and allylic insertion species, strongly implying the intermediacy of a copper−nitrenoid species.[43] In 1995, Jacobsen and co-workers revealed that chiral copper catalysts bearing bidentate ligands induce asymmetric aziridination of olefins when sulfonyl azides are used,[36b] again clearly implying the presence of a copper−nitrenoid. More recently, Katsuki and co-workers utilized various azides for the development of efficient nitrogen transfer reactions such as aziridination, sulfimidation, and intramolecular C−H amination reactions under mild conditions without photolysis.[44] In particular, they developed an elegant protocol of Ru-catalyzed asymmetric aziridination using sulfonyl azides.

We were intrigued by the possibility of developing a facile aziridination procedure using chelating 2-pyridyl-containing sulfonyl azides. Whereas the reaction of styrene with benzenesulfonyl azide using Cu(acac)$_2$ (10 mol %) resulted in only a negligible yield of aziridine (Table 1, entry 1), the use of 2-pyridinesulfonyl azide (**2**) enabled the formation of the corresponding aziridine in a synthetically acceptable yield, even

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TABLE 1. Aziridination of Styrene with Various Sulfonyl Azides

entry	X	Y	R	yield (%)[a]
1	CH	SO$_2$	H	<5
2	N	SO$_2$	H	69
3[b]	N	SO$_2$	H	43
4	CH	SO$_2$	4-NO$_2$	7
5	N	SO$_2$	4-Me	70
6	N	SO$_2$	5-Me	72
7	N	SO$_2$	6-Me	9
8	N	SO$_2$	5-CF$_3$	29
9	CH	CO	H	<5
10	N	CO	H	<5

[a] ^{1}H NMR yield using an internal standard (anisole). [b] In the presence of 1,10-phenanthroline (0.4 equiv).

in the absence of external ligands (entry 2). Copper species exhibited the most satisfactory activities among a wide range of transition metal catalysts examined.[35] In particular, Cu(acac)$_2$ in acetonitrile at 50 °C gave the best results. It was interesting to note that the addition of an external coordinating ligand slightly decreased product yield (entry 3), suggesting competitive copper coordination between the added external ligand and the 2-pyridyl moiety of the nitrenoid precursor. Binding of the external ligand would interfere with nitrenoid precursor chelation. When an electron-deficient benzenesulfonyl azide was employed under the same conditions, small amounts of aziridine formed (entry 4).

The presence of a 4- or 5-methyl substituent on the 2-pyridinesulfonyl group resulted in a slight increase of product yields (entries 5−6). However, 6-methyl substitution afforded the aziridine in poor yield (entry 7). In addition, when 5-trifluoromethyl-2-pyridinesulfonyl azide was employed, a significant decrease in product yield was observed (entry 8). Efficiency of aziridination became poor when acyl azides were employed (entries 9 and 10).

Aziridination of styrene with 8-quinolinesulfonyl azide smoothly gave the desired aziridine in reasonable yield, whereas it was very sluggish with 1-naphthalenesulfonyl azide under otherwise identical conditions, again underscoring the role of nitrogen atom chelation (eq 3).

$$(3)$$

X = N: 69%

CH: <1%

The scope of chelation-assisted olefin aziridination using 2-pyridinesulfonyl azide (**2**) was subsequently investigated using more optimized conditions (Table 2). Reaction of aromatic terminal olefins (3 equiv to azide **2**) took place smoothly with

TABLE 2. Aziridination of Olefins with 2-Pyridinesulfonyl Azide

| entry	olefin	product	yield(%)[a]
1			61
2			56
3			52
4			69
5			68
6			59
7			43
8			49
9[b]			58
10[b]			41[c]
11[b]			10

[a] Isolated yields. [b] Ten equivalents of olefin was used. [c] A mixture of *trans/cis* isomer (2:1).

10 mol % of Cu(acac)$_2$ catalyst at 50 °C, providing the corresponding monosubstituted aziridines in moderate to good yield (entries 1−5). The plausible chelation effect was not significantly altered by the electronic and/or steric environment of the olefins. The reaction conditions demonstrated tolerance of some functional groups such as halides or acetate. 2-Vinyl-naphthalene was also a viable substrate, albeit with a moderate efficiency (entry 8). The reaction of *trans-β*-methylstyrene (10 equiv) afforded the corresponding *trans*-aziridine in an acceptable yield (entry 9). When *cis-β*-methylstyrene was subjected to the reaction conditions, a mixture of two stereoisomeric aziridne products was obtained with 2:1 ratio (*trans/cis*, entry 10). The reactivity of aliphatic olefins was low even when the olefin was used in large excess (entry 11). Although no direct comparison of reaction efficiency between two nitrenoid sources

of 2-pyridinesulfonamide and 2-pyridinesulfonyl azide can be made, the reaction with azides affords slightly lower aziridine yields in general.

II.C. Mechanistic Studies of Chelation-Assisted Aziridination. The intrigue of transition-metal-mediated aziridination of olefins lies in determining validity of the postulated metal−nitrenoid intermediates, elucidating the oxidation state of the metal centers, and understanding the comprehensive reaction course of nitrene transfer. Even though involvement of the metallonitrene intermediate is now well accepted, there is a paucity of concrete experimental evidence, compared to that for epoxidation and cyclopropanation reactions. Recently, Prortasiewicz and co-workers reported a mechanistic detail of aziridination by isolating an iodinane species in the copper-catalyzed routes.[45] Scott and co-workers have investigated the oxidation state of active copper catalytic species in the aziridination via Hammett plot analysis, UV spectroscopy, and theoretical calculations.[46] More recently, Che and co-workers utilized a Ru−porphyrin system to elucidate mechanistic pathways in the olefin aziridination by utilizing various spectroscopic tools such as NMR, ESI-MS, UV, X-ray crystallography, and cyclic voltammetry (CV).[8] Warren and co-workers also tried to verify the presence of transient Cu−nitrene intermediates from discrete dicopper nitrenes.[47] Despite these significant contributions, more tangible evidence for the existence of the presumed metal−nitrenoid is highly desirable for better understanding of the catalytic processes.

We envisaged that our present chelation-assisted system would be suitable for the mechanistic studies of aziridination since the copper−nitrenoid species was postulated to be stabilized by the intramolecular coordination of the metal center to the pyridyl nitrogen atom of 2-pyridylsulfonamide or its azide analogue. At the outset of our studies using **1**, we tried to capture intermediate metal−nitrenoids by allowing **1** to react with a stoichiometric oxidant PhI(OAc)$_2$ in the presence of 0.5 equiv of copper complex Cu(tfac)$_2$ (eq 4).

(4)
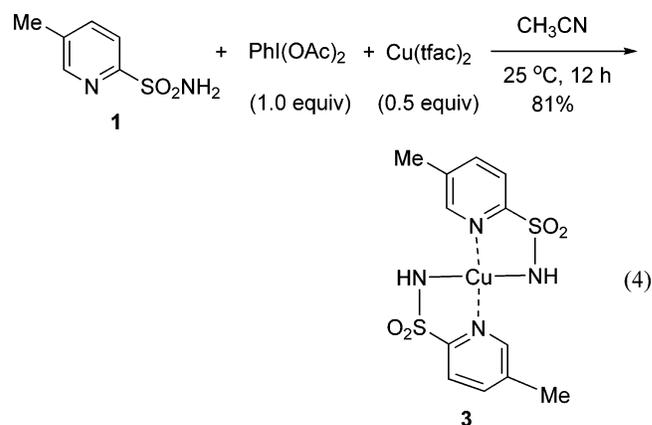
A green solid (**3**) was isolated from the reaction mixture in 81% yield, and its structure was determined by the X-ray crystallographic analysis (Figure 1). It reveals that the copper-(II) complex **3** forms a pseudo-square-planar geometry with two 2-pyridinesulfonamido groups positioned *trans* to each other.

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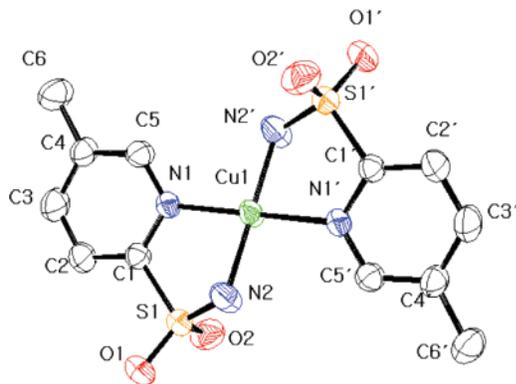(47) Badiei, Y. M.; Krishnaswamy, A.; Melzer, M. M.; Warren, T. H. *J. Am. Chem. Soc.* **2006**, *128*, 15056−15057.

FIGURE 1. Structural diagram of compound **3**.

Whereas the Cu−N$_{pyridyl}$ bond distance was determined to be 2.034 Å, the Cu−N$_{sulfonamido}$ length of 1.928 Å is slightly shorter.[48] Infrared spectroscopy of **3** showed that the vibrational peaks for SO$_2$ of 2-pyridinesulfonyl group are shifted from 1329 and 1170 cm^{-1} to 1303 and 1142 cm^{-1}, respectively, indicating the existence of the copper−amido bond.[49]

A series of experiments were subsequently carried out, using the isolated copper complex **3** as a mechanistic probe. When a stoichiometric amount of **3** was allowed to react with excess styrene in the presence of PhI(OAc)$_2$, the aziridine was obtained in 56% (eq 5), implying that **3** is readily transformed into the active nitrenoid species under the reaction conditions.
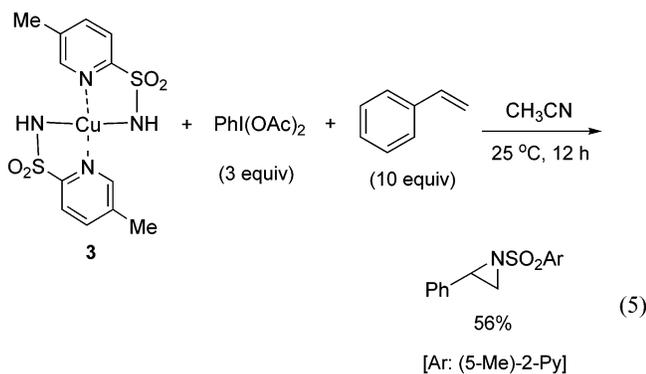
In addition, when a catalytic amount of **3** was employed under the aziridination conditions, aziridine product could be obtained in 86% yield (eq 6).
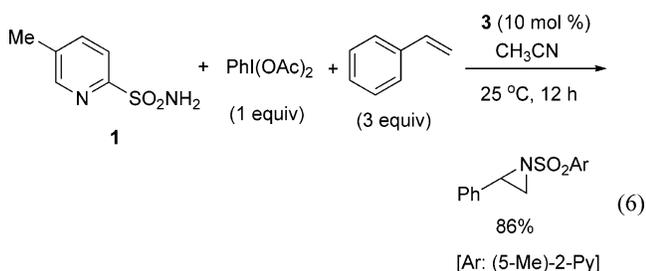
In order to further prove the putative chelation between the copper and nitrogen atom of the 2-pyridyl moiety, we next utilized an ESI-MS method since this analysis has been

increasingly employed as an important tool for mechanistic studies.[50] After treating a solution of **1**, PhI(OAc)$_2$ (1.2 equiv), and styrene (1.0 equiv) in CH$_3$CN (0.01 M) with Cu(tfac)$_2$ (0.5 equiv), aliquots were taken and subjected to ESI-MS analysis. An intense ion at $m/z = 590$ was observed after 10 min, which was assigned to copper species **4**, (tfac)Cu−PhINSO$_2$(2-Py)-(5-Me). In addition, a peak at $m/z = 464$ was detected, which was assigned as a bis(sulfonamido)copper complex bearing one acetate ligand (**3** + OAc). The observed isotopic distribution of each peak is in good agreement with that of the calculated ratio.[35] After 60 min, the aziridine peak ($m/z = 275$) appeared with concomitant decrease in the intensity of the peak at $m/z = 590$ (Figure 2b).

Competition experiments with a series of *p*-substituted styrene derivatives indicate that electron-withdrawing substituents slowed the reaction with a ρ value of -0.60 (Figure 3).[35] This result suggests an asynchronous transition state model for the Cu-mediated nitrene transfer reaction in accord with the previous reports.[51]

Kinetic studies of styrene aziridination using **1** showed that the reaction is first-order in olefin and second-order in copper catalyst.[35] This rate order dependence on the olefin concentration is in good agreement with Jacobsen's results,[5e] in which it was argued that the rate-limiting step is the transfer of copper−nitrenoid to double bonds. Thus, nitrenoid transfer of copper intermediates to olefin may be also the rate-limiting process in our case.

On the basis of our experimental results above, we propose a mechanism that requires the pyridyl chelation (Scheme 3). It is envisioned that copper binds to the 2-pyridinesulfonamide group, leading to facile ligand exchange to afford a copper amido species (**A**). We postulate that conversion of **A** to an active copper−nitrenoid species (**C**) is accelerated by chelation assistance upon the release of iodobenzene and acetic acid through **B**. It should be noted that the 2-pyridyl binding in **C** is in contrast to Norrby's postulate for the reaction with benzenesulfonyl precursors, in which nitrenoid copper center binds to a sulfonyl oxygen atom (**D**).[52] It is believed that the isolated copper diamido species (**3**) can be converted into the active copper−nitrenoid intermediate (**C**) by the action of additional oxidant under the reaction conditions, supported by our observations described above.

Although it is not explicitly presented in Scheme 3, the final nitrenoid transfer to copper-coordinated olefin is assumed to take place via a stepwise sequence involving radical species, evidenced by the generation of two stereoisomeric products in the reaction of *cis-β*-methylstyrene.[34] It is assumed that, since the reaction is second-order in copper concentration, the copper−nitrenoid is transferred onto the double bond that is probably coordinated to a second copper species.

In order to rationalize the postulated chelation effects on the aziridination pathway, geometry optimization of certain putative intermediates and transition states was performed with both ab initio at the Hartree−Fock (HF) level and DFT (B3LYP) levels

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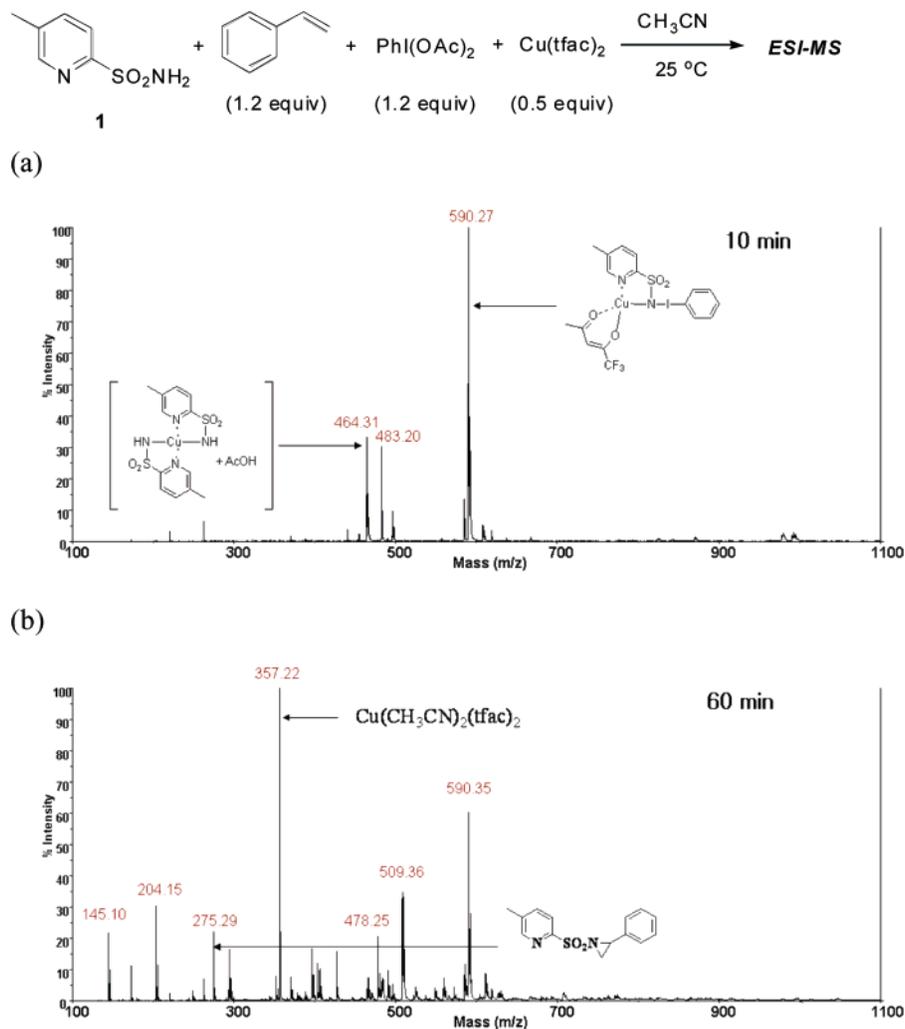
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FIGURE 2. ESI-MS analysis of the aziridination (including 0.1% acetic acid in the positive mode): (a) 10 min and (b) 60 min.
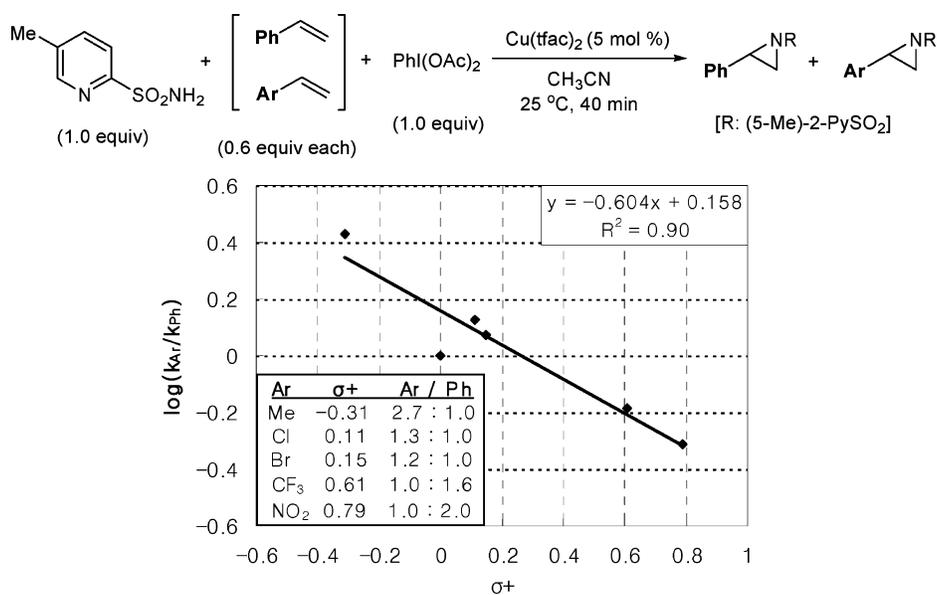

FIGURE 3. Hammett plot fit against σ^+ values.

using the 6-31G(d) basis set.[53] The calculated structure for **3** agreed well with that of its X-ray structure (Figure 1), proving that this method is suitable for the mechanistic studies in the aziridination with 2-pyridinesulfonamide as a model reagent. According to the B3LYP/6-31G(d) computation, the difference of bond dissociation energy (BDE) between an olefin-bound

SCHEME 3. Proposed Pathway of the Chelation-Assisted Aziridination (L = CH₃CN or tfac)
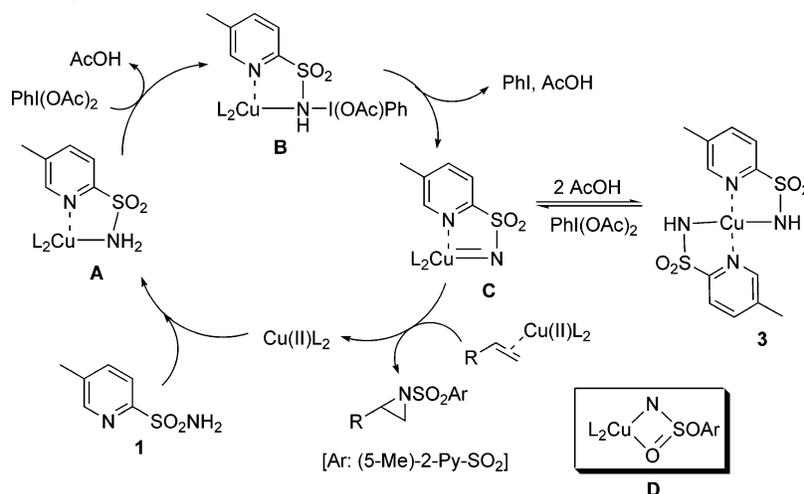
copper−nitrenoid complex derived from benzenesulfonamide (**Ph-5**) and that obtained from 2-pyridinesulfonamide (**Py-8**) was determined to be 15.5 kcal/mol, revealing the stability produced by chelation (Figure 4). In each case, styrene was employed as olefin for the computation. It should be noted that the copper center in **Ph-5** is assumed to be coordinated with the nitrenoid *N* and sulfonyl *O* based on Norrby's postulate.[52]

Optimized geometries of transition states **Ph-6** and **Py-9** for the nitrenoid transfer step resulting from olefin-bound copper−nitrenoid complexes **Ph-5** and **Py-8**, respectively, are also depicted in Figure 4. It is interesting to note that, during the transfer step, the bond length of Cu−N(nitrenoid) derived from the benzenesulfonamide precursor is significantly elongated from 1.75 Å (**Ph-5**) to 3.34 Å (**Ph-8**), whereas this difference becomes very small, changing from 1.81 Å (**Py-8**) to only 1.84 Å (**Py-9**) in case of the 2-pyridyl-bound process. The difference in

bond dissociation energy between the two transition states of **Ph-6** and **Py-9** (ΔBDE = 34.2 kcal/mol) turned out to be larger than that between the prior states (**Ph-5** and **Py-8**). Two aziridine products (**Ph-7** and **Py-10**), while being assumed to be bound to copper species, were also geometrically optimized using the computational study.

The overall energy profile along the reaction coordinates is illustrated in Figure 5, showing that there are significant chelation effects on the reaction progresses. The 2-pyridyl group-chelated nitrenoid was calculated to be greatly stabilized by the presence of the internal coordination. More importantly, the transition states are found to be also dramatically influenced by the postulated chelation effects, revealing that the 2-pyridyl-sulfonyl moiety contributes to reduce the activation energy of the aziridination reaction compared to the corresponding ben-
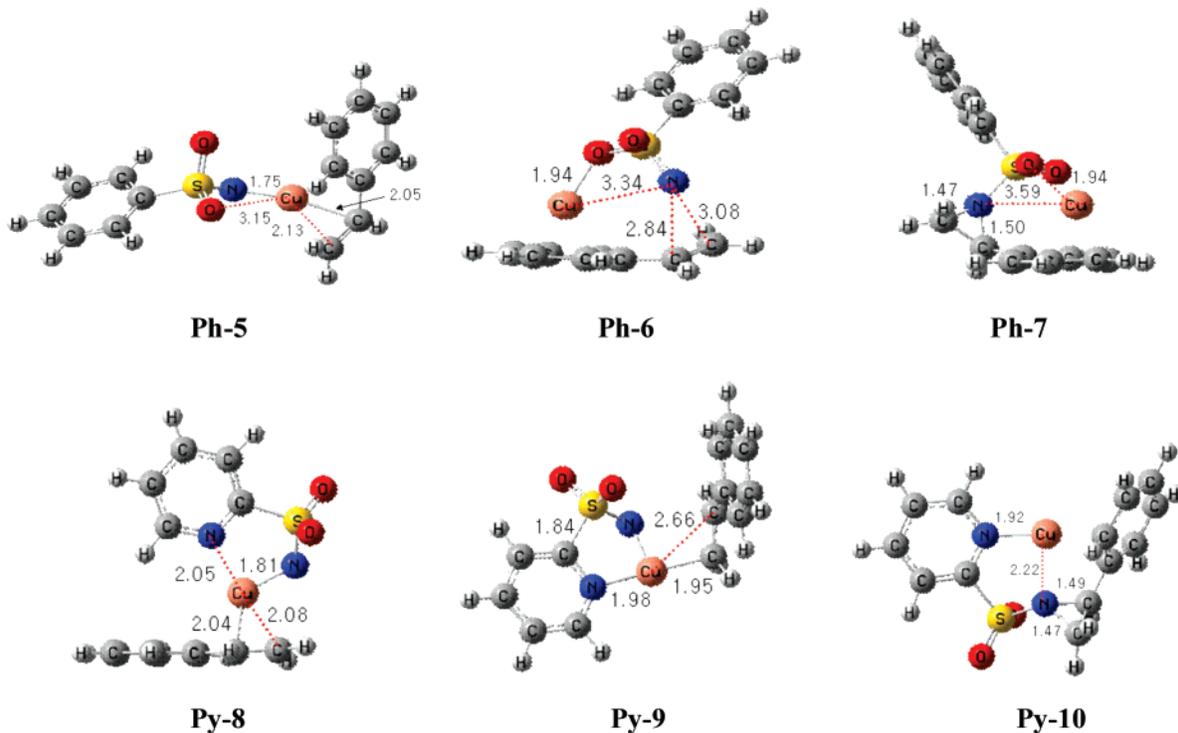
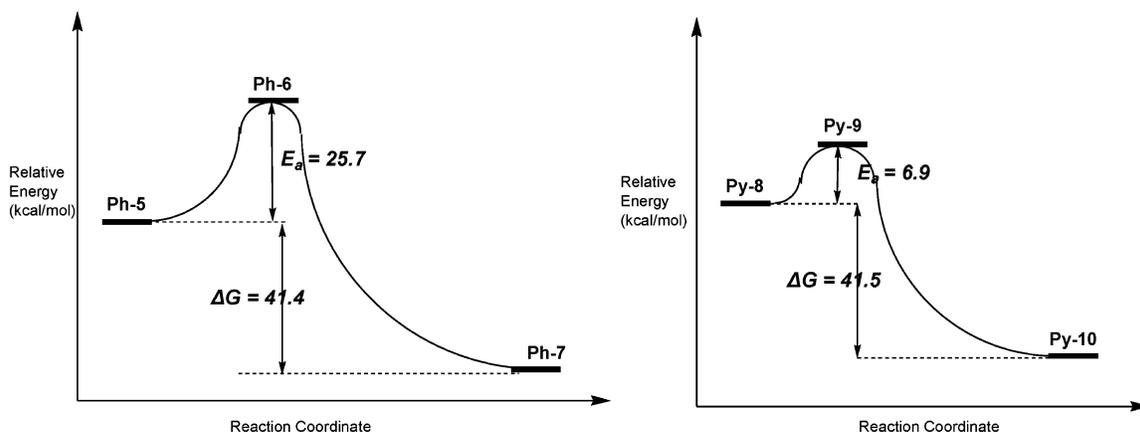**FIGURE 4.** Optimized structures of **Ph-5**−**7** and **Py-8**−**10**.

FIGURE 5. The energy profiles in the aziridination with PhSO$_2$NH$_2$ (left) and 2-PySO$_2$NH$_2$ (right).

zenesulfonyl group ($\Delta E_a = 18.8$ kcal/mol). These theoretical results agree well with our experimental studies including kinetic data.

III. Conclusion

We have developed a new chelation-assisted Cu-catalyzed aziridination protocol. New precursors of nitrenoid species bearing a chelating group, such as 2-pyridinesulfonamide and 2-pyridylsulfonyl azide, are successfully utilized in combination with a mild oxidant, PhI(OAc)$_2$. A wide range of aryl terminal alkenes could be readily employed under the optimized mild conditions to provide satisfactory yields of aziridines in the absence of external ligands. X-ray crystallography, ESI-MS, competition experiments, kinetic and computational studies support that the copper-catalyzed aziridination with 2-pyridyl-sulfonamides and 2-pyridinesulfonyl azides is chelation-driven.

IV. Experimental Section

General Procedure for the Olefin Copper-Catalyzed Aziridination with 5-Methyl-2-pyridinesulfonamide. A mixture of 5-methyl-2-pyridinesulfonamide (86.1 mg, 0.5 mmol), iodobenzene

diacetate (161 mg, 0.5 mmol), copper(II) trifluoroacetylacetonate (9.2 mg, 0.025 mmol), olefin (0.6 mmol), and molecular sieves (4 Å, 500 mg) in anhydrous CH$_3$CN (1 mL) was stirred for 12 h under N$_2$. After filtration through a pad of Celite, the filtrate was concentrated in vacuo. The residue was purified by flash column chromatography (EtOAc/hexane, 1:2) to give the desired aziridine.

General Procedure for the Copper-Catalyzed Olefin Aziridination with 2-Pyridinesulfonyl Azide. A mixture of 2-pyridine-sulfonyl azide (100 mg, 0.54 mmol), Cu(acac)$_2$ (14 mg, 10 mol %), olefin (1.62 mmol, 3 equiv), and molecular sieves (4 Å, 500 mg) in anhydrous CH$_3$CN (1 mL) was stirred for 12 h at 50 °C under N$_2$. After filtration through a pad of Celite, the filtrate was concentrated in vacuo and the residue was purified by flash column chromatography (EtOAc/hexane, 1:2) to give the desired aziridine.

N-(2-Pyridinesulfonyl)(2-chlorophenyl)aziridine (Table 2, entry 2): Colorless solid; mp 64−66 °C; ^{1}H NMR (300 MHz, CDCl$_3$) δ 2.40 (1H, d, $J = 4.6$ Hz), 3.23 (1H, d, $J = 7.2$ Hz), 4.24 (1H, dd, $J = 7.2$, 4.6 Hz), 7.12−7.33 (4H, m), 7.56−7.58 (1H, m), 7.97 (1H, td, $J = 7.8$, 1.5 Hz), 8.15 (1H, d, $J = 7.8$ Hz), 8.74 (1H, d, $J = 4.1$ Hz); ^{13}C NMR (100 MHz, CDCl$_3$) δ 36.0, 39.2, 123.0, 126.9, 127.5, 127.6, 129.1, 132.8, 133.7, 138.1, 150.3, 155.6; IR (KBr pellet) 3061, 2923, 1596, 1578, 1480, 1452, 1428, 1379 cm^{-1}; *m/z* (FAB) found [M + H]$^+$ 295.0311/297.0276, C$_{13}$H$_{12}$ClN$_2$O$_2$S requires *m/z* 295.0308/297.0281.

Supporting Information Available: Detailed experimental procedures, characterization data of products, copies of ^{1}H and ^{13}C NMR spectra of the obtained aziridines, X-ray crystallographic data of complex **3**, and *XYZ* coordinates for the calculated intermediates and transition states. This material is available free of charge via the Internet at http://pubs.acs.org.

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