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Silver(II) and Silver(III) Intermediates in Alkene Aziridination with a Dinuclear Silver(I) Nitrene Transfer Catalyst

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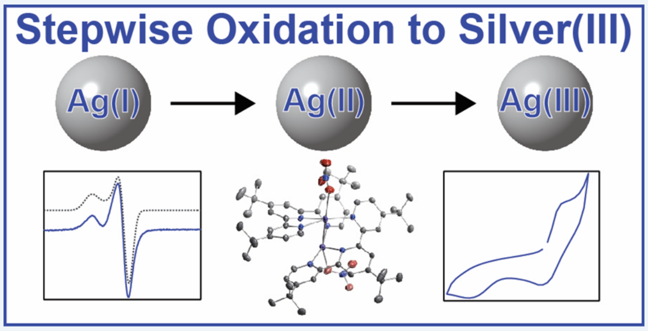
ABSTRACT: In recent years, synthetically useful homogeneous catalysis has been developed with silver, including nitrene transfer reactions for carbon−nitrogen bond formation. However, the mechanisms of silver-catalyzed redox reactions are generally still poorly understood, including a near-total lack of data on oxidized intermediates. Here, we present a detailed experimental study on the oxidation of a dinuclear silver(I) nitrene transfer catalyst with commonly used hypervalent iodine oxidants ($PhINSO_2Ar$), including structurally characterized examples of silver(II) oxidation products obtained under catalytically relevant conditions. Furthermore, the silver(I) catalyst is shown to undergo stepwise oxidation to silver(II) and silver(III) intermediates; the generation of silver(III) intermediates has not previously been demonstrated in nitrene transfer catalysis. In contrast to prior mechanistic hypotheses, our data indicates that nitrene transfer occurs from silver(III) in this reaction system.

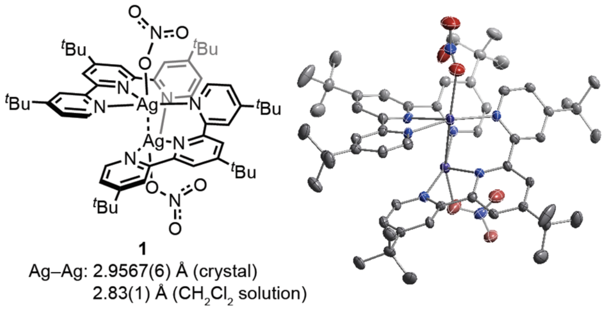


KEYWORDS: *silver, nitrene transfer, aziridination, mechanism, homogeneous catalysis*

INTRODUCTION

Although silver is a second-row transition metal, it often seems to be treated as an “honorary” first-row metal, because of its relatively low cost and its propensity for single-electron redox chemistry. Homogeneous redox catalysis with well-defined silver complexes is under-developed, compared to other late transition metals, even among the coinage metals.[1] Scattered reports over the past two decades have suggested that redox cooperation in dinuclear silver complexes may facilitate catalysis,[2,3] but there has been no experimental data on oxidation products derived from such catalysts. The challenge of understanding the oxidation chemistry of well-defined silver complexes is derived in part from the flexible coordination chemistry of d^{10} silver(I), which often leads to fluxional behavior and ambiguous relationships between solution- and solid-state structures.[4,5] Here, we present the first experimental study that characterizes oxidation products obtained from a dinuclear silver(I) nitrene transfer catalyst (**1**; see Figure 1). Through a combination of structural characterization and in situ spectroscopic analysis, we show that catalyst **1** reacts sequentially with 2 equiv of oxidant to form both silver(II) and silver(III) products. Reactivity studies indicate that nitrene transfer to an alkene substrate occurs from silver(III), which is a hypothesis that is rarely invoked in the field of redox catalysis with silver.

Beginning in 2003, work from the He group demonstrated silver-catalyzed nitrene transfer for aziridination and C−H amination.[2,6] Isolation and crystallographic analysis of two different ligated silver catalysts revealed dinuclear complexes with Ag−Ag interactions, and one of the He group’s dinuclear catalysts was subsequently used by Bolm for imination of sulfoxides and sulfides.[7] Recent work from the Pérez and Schomaker groups has greatly expanded the scope and utility



1

Ag–Ag: 2.9567(6) Å (crystal)
2.83(1) Å (CH_2Cl_2 solution)

Figure 1. Structure of dinuclear silver(I) nitrene transfer catalyst **1**, based on a combination of solid-state crystallographic and solution-phase EXAFS analysis; X-ray structure is plotted with 50% probability ellipsoids (H atoms omitted for clarity).

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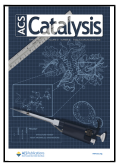

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of silver-catalyzed nitrene transfer.[8,9] In particular, work from the Schomaker group has shown how the dynamic behavior of silver(I) complexes in solution can affect selectivity in catalysis, influenced by factors such as ligand choice and metal:ligand ratio.[4,9a] However, despite these advances, there remains a fundamental lack of mechanistic understanding, particularly with regard to identification of high-valent silver complexes that are relevant to catalysis. This report focuses on studying the oxidation of dinuclear silver(I) complex **1** with hypervalent iodine nitrene transfer reagents ($PhINSO_2Ar$), which is a catalyst system that has been used for alkene aziridination.[2a] Prior mechanistic investigations of nitrene transfer reactions catalyzed by **1** have addressed possible high-valent intermediates through computational studies only.[9c]

■ RESULTS AND DISCUSSION

Isolation of Silver(II) Oxidation Products. Our investigations began with efforts to isolate and structurally characterize oxidation products obtained from **1** and $PhINSO_2Ar$, using solvents that have been reported for nitrene transfer reactions with this catalyst (CH_2Cl_2 and MeCN). Combining **1** and PhINTs in CH_2Cl_2 produces a color change from pale yellow to dark brown, and the dark color persists for several days if the mixture is held at low temperature under inert atmosphere. Slow diffusion of hexanes into the reaction mixture at −35 °C produced dark brown needle-shaped crystals in 39% isolated yield after 1 week. The resulting crystals are thermally and atmospherically sensitive, and were also found to decompose during X-ray data collection using an in-house diffractometer; a complete dataset was obtained by collecting rapid frames using a synchrotron source. Single-crystal X-ray analysis revealed the structure to be a silver(II)•PhINTs adduct (**2**), featuring an unprecedented Ag(II)−N−I(III) core (see Figure 2). The Ag center in **2** adopts a square-planar geometry, as expected for d^9 silver(II),[10] with a nitrate ion weakly coordinated to one of the apical sites. A second nitrate anion coordinates to the iodine center, which has a typical T-shaped geometry.[11] Consistent with the square planar silver(II) structure, X-band EPR of a polycrystalline sample at 77 K shows a broad axial spectrum for **2**, with $g_\perp$ = 2.038 and $g_\parallel$ = 2.186.[12,13]

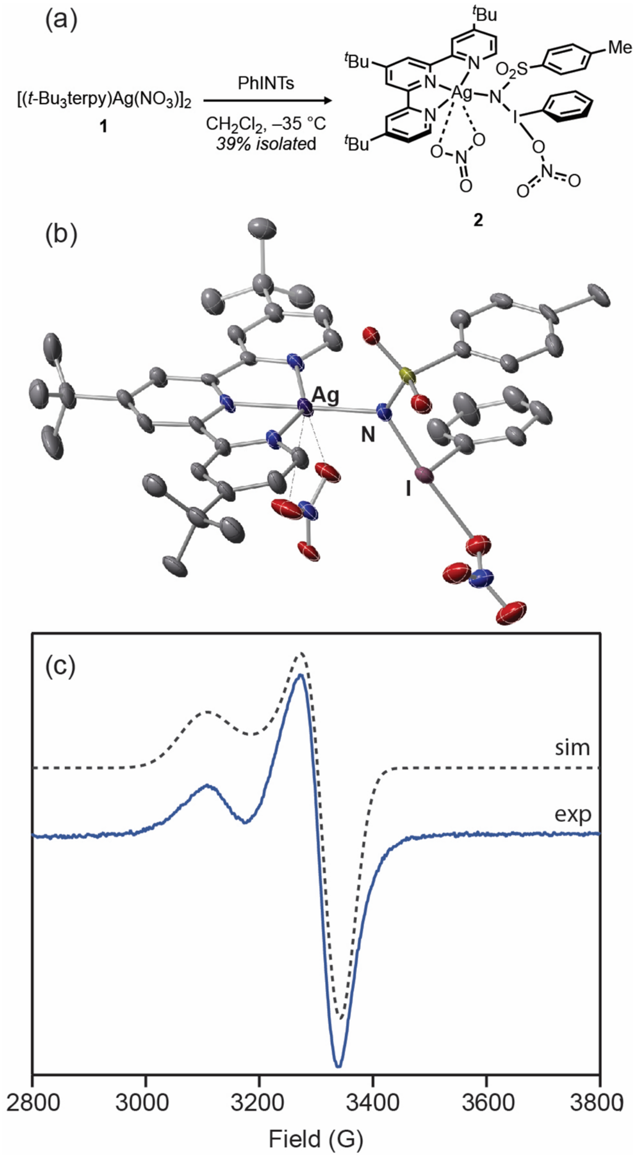

Figure 2. (a) Synthesis, (b) crystal structure, and (c) X-band EPR spectrum of silver(II)•PhINTs adduct **2** (50% probability ellipsoids; H atoms and solvent molecules omitted for clarity).

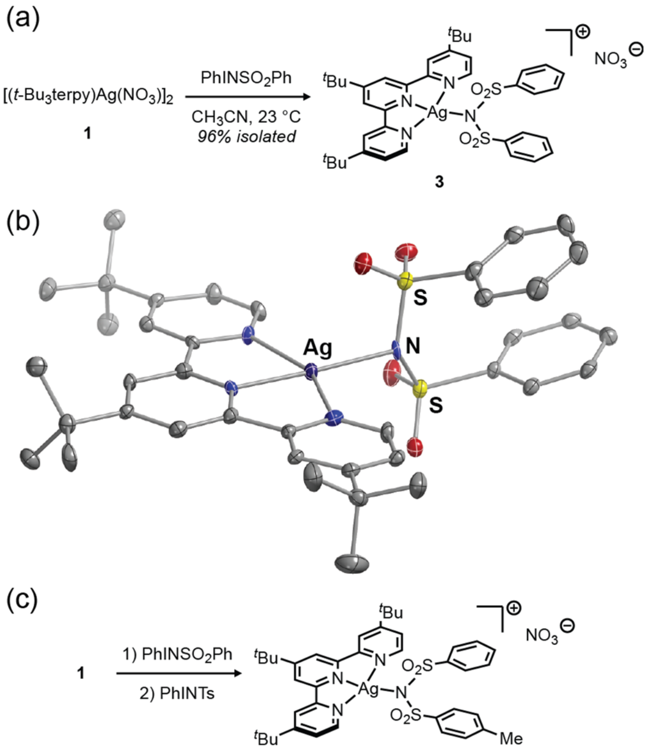

Figure 3. (a) Synthesis and (b) crystal structure of silver(II) complex **3** (50% probability ellipsoids; H atoms, solvent, disorder, and noncoordinated nitrate anion omitted for clarity); (c) sequential addition of two different $PhINSO_2Ar$ derivatives leads to the formation of a mixed sulfonimide ligand.

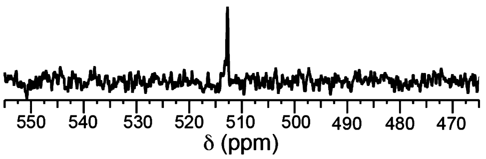

Figure 4. ^{109}Ag NMR spectrum of **1** in CD_3CN (23 °C, 18.6 MHz).

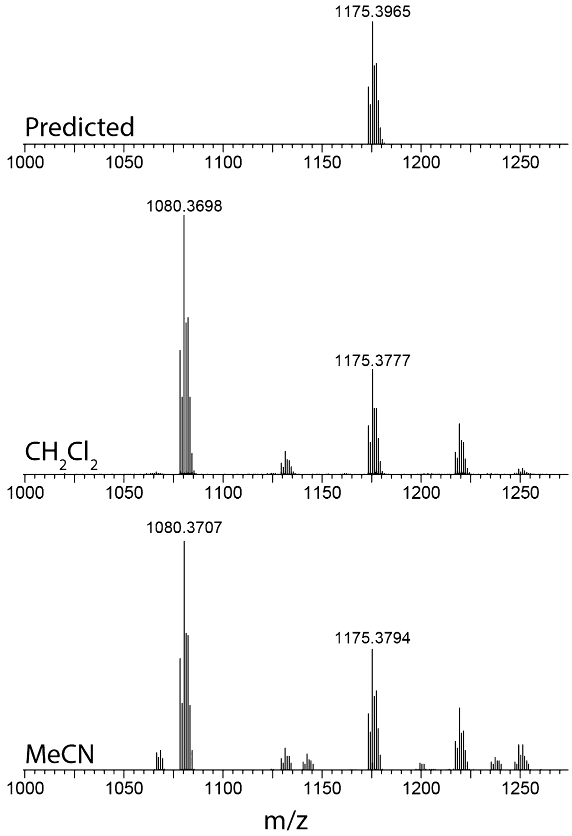

Figure 5. In situ mass spectrometry analysis (ESI+) of the initially formed reaction mixture between **1** and $PhINSO_2Ph$: (top) predicted spectrum for the dinuclear nitrenoid product $[(t\text{-}Bu_3terpy)_2Ag_2(NSO_2Ph)]^+$; (middle) experimental spectrum in CH_2Cl_2; (bottom) experimental spectrum in MeCN. The peak at m/z = 1080 corresponds to the molecular ion of **1**.

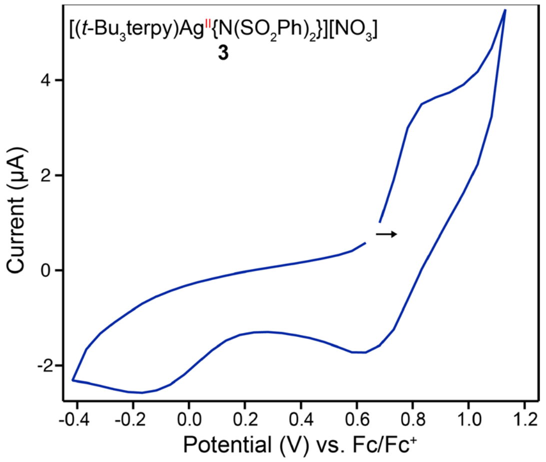

Figure 6. Cyclic voltammogram (0.1 M $TBAPF_6$/MeCN) of silver(II) complex **3**: the reversible redox couple at 0.73 V is assigned to silver(II)/silver(III), and irreversible reduction to silver(I) is observed at −0.12 V. The starting point and direction of the scan are indicated by an arrow.

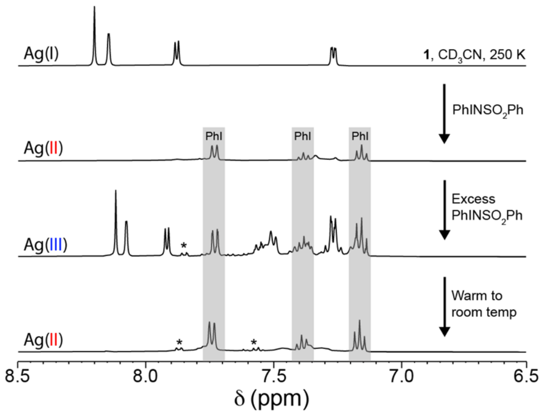

Figure 7. ^1H NMR spectra (400 MHz) showing stepwise formation of paramagnetic silver(II), followed by diamagnetic silver(III) products, when **1** is subjected to reaction with multiple equivalents of $PhINSO_2Ph$. The in-situ-generated silver(III) product persists briefly at low temperature, but decomposes rapidly to silver(II) upon warming. The peaks indicated by an asterisk (*) correspond to trace amounts of $PhSO_2NH_2$.

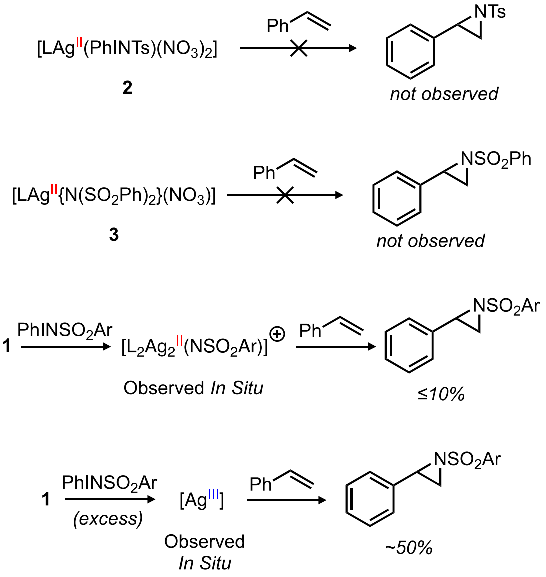

Figure 8. Chemical competency for styrene aziridination of isolated and in-situ-generated silver products derived from **1** and $PhINSO_2Ar$ (yields determined by ^1H NMR, and reported with respect to the silver starting material; L = t-Bu_3terpy).

Oxidation of **1** in MeCN produced a similar color change from pale yellow to dark brown, followed by further development of a deep brick-red color. The red color persists for at least several days at room temperature, even after exposure to ambient atmosphere. EPR analysis of the red product showed a broad axial spectrum similar to **2**, indicative of silver(II) (see Figure S4 in the Supporting Information). Crystallization of the product obtained using $PhINSO_2Ph$ afforded dark red needles in 96% isolated yield, and single-crystal X-ray diffraction (SCXRD) analysis revealed mononuclear silver(II) complex **3**, featuring a newly formed dibenzenesulfonimide ligand (Figure 3).

A noteworthy feature of oxidation products **2** and **3** is that they both must be formed via reaction of **1** with 2 equiv of $PhINSO_2Ar$. First, while the Ag center in **2** is in the 2+ oxidation state, the PhINTs fragment is ligated to silver but not reduced. Oxidation of silver must occur in a separate step from PhINTs coordination. This conclusion is also supported by the generation of PhI in the reaction mixture, prior to isolation of **2** (see Figure S8 in the Supporting Information). Second, formation of the dibenzenesulfonimide ligand observed in **3**

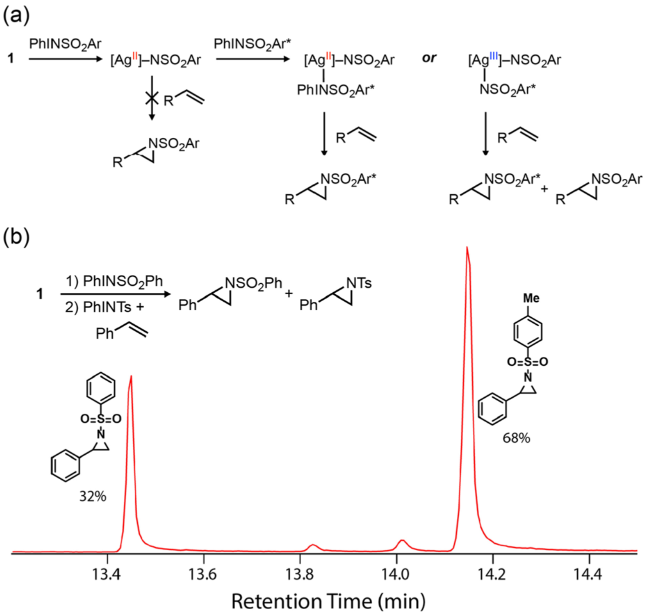

Figure 9. (a) Conceptual scheme for double labeling experiment, and (b) representative GC trace demonstrating significant incorporation of nitrene groups from both PhINSO$_2$Ar derivatives.

can only proceed via coupling of NSO$_2$Ar fragments from 2 equiv of oxidant, and our data suggests that formation of the $[N(SO_2Ar)_2]^-$ anion occurs from a high-valent silver intermediate. When **1** was treated with 1 equiv of PhINSO$_2$Ph, a dark brown color developed; further treatment with 1 equiv PhINTs led to the characteristic brick red color. Mass spectrometry analysis of the reaction mixture revealed formation of the mixed-sulfonimide ligand $[(Ts)N(SO_2Ph)]^-$ (see Figure 3c, as well as Figure S7 in the Supporting Information). While both **2** and **3** are off-cycle products that do not directly participate in aziridination catalysis, their formation indicates the reactivity of **1** with multiple equivalents of oxidant, a finding that is indeed relevant to our mechanistic studies (vide infra).

In Situ Spectroscopic Characterization. In addition to the isolation and characterization of oxidation products obtained from **1** and PhINSO$_2$Ar, we have used in situ characterization methods to interrogate high-valent silver intermediates that may be relevant to catalysis. We have previously reported a solution-phase EXAFS study of silver(I) nitrene transfer catalysts, which indicates that **1** maintains a dimeric structure with a close silver−silver interaction in CH$_2$Cl$_2$ solutions (as depicted in Figure 1).[5] In contrast, however, **1** displays a predominantly monomeric form in MeCN solutions: X-ray absorption spectroscopy data shows the complete lack of a silver−silver contact in this solvent (Figures S13 and S14 in the Supporting Information). Furthermore, the ^{109}Ag spectrum of **1** in CD$_3$CN displays a single resonance at 513 ppm, with no $J(^{109}\text{Ag}-^{107}\text{Ag})$ coupling that is characteristic of dimers with silver−silver interactions (see Figure 4).[14] No ^{109}Ag NMR signal is observed for **1** in CD$_2$Cl$_2$, which we attribute to exchange broadening, likely due to rapid dimer/monomer equilibrium. EXAFS and DOSY-NMR studies clearly establish that the dimer form is favored in this solvent (see refs 5 and 9a). Taken together, these data indicate a dimer/monomer equilibrium for **1**, which favors the dimeric form in CH$_2$Cl$_2$ but the monomeric form in MeCN.

Mass spectrometry analysis of the dark reaction mixture initially obtained from **1** and PhINSO$_2$Ph in both CH$_2$Cl$_2$ and MeCN shows a peak consistent with the formation of a dinuclear silver(II)-nitrenoid product with the formula $[(t\text{-Bu}_3\text{terpy})_2\text{Ag}_2(\text{NSO}_2\text{Ph})]^+$ (see Figure 5). These mass spectrometry findings are consistent with data from the He group in their initial reports of catalyst **1**.[2b] EPR analysis of the same reaction mixtures also shows a signal consistent with silver(II), overall indicating a net two-electron oxidation of **1** (see Figures S5 and S6 in the Supporting Information). Crystallization from these reaction mixtures ultimately affords silver(II) complexes **2** or **3**, as described above.

Because the structures of isolated oxidation products **2** and **3** indicate the reactivity of **1** with multiple equivalents of PhINSO$_2$Ar, we sought to determine if the initially formed silver(II) products can undergo further oxidation. While silver(III) is rarely discussed in the homogeneous catalysis literature,[15] presumably due to the assumption that the required oxidation potentials are prohibitively high, our data suggests that silver(III) is quite accessible with the ligand set used in this system. For example, cyclic voltammetry studies of isolated silver(II) complex **3** show that reversible oxidation to silver(III) occurs at a fairly mild potential of 0.73 V (vs Fc/Fc$^+$; see Figure 6).

^{1}H NMR analysis further indicates that the initially formed silver(II) products obtained from **1** and PhINSO$_2$Ar can undergo reaction with additional oxidant. Sequential addition of 2 equiv of PhINSO$_2$Ph to **1** at room temperature was conducted. As previously observed, addition of the first equivalent of oxidant produced silver(II) products and 1 equiv of PhI. After addition of the second equivalent, NMR-silent silver(II) products were still present (formation of complex **3** occurs under these conditions, vide supra). However, generation of a second equivalent of PhI was

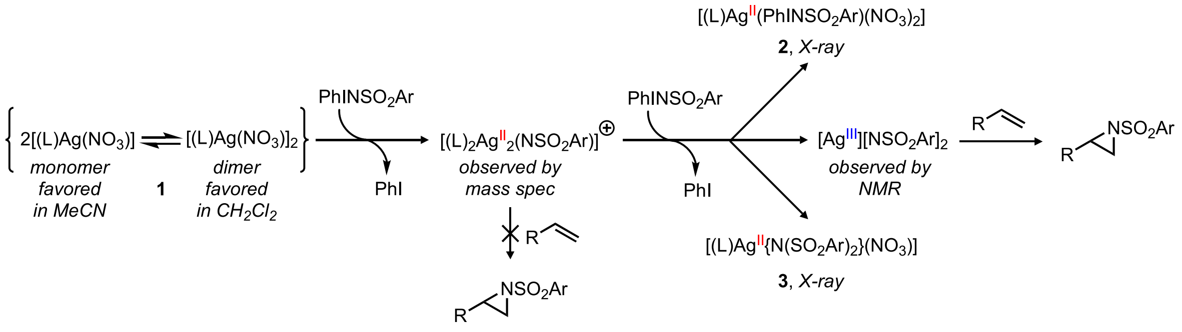

Figure 10. Summary of the reactivity pathways observed between silver(I) catalyst **1** and PhINSO$_2$Ar (L = t-Bu$_3$terpy).

observed by integration relative to an internal standard, indicating the formation of an unstable oxidized species that is not detected at room temperature (see Figure S8 in the Supporting Information).

With low-temperature handling and a larger excess of oxidant, sequential formation of silver(II) followed by silver(III) products could be observed (Figure 7). The initial paramagnetic silver(II) products formed between **1** and $PhINSO_2Ph$ display no resonances for the aromatic protons of the *t*-Bu_3terpy ligands, and only PhI is observed in the ^1H NMR spectrum. The addition of excess $PhINSO_2Ph$ to this dark brown reaction mixture produces an immediate color change to pale yellow. EPR analysis of the reaction mixture shows no signal, suggesting further oxidation to a d^8 silver(III) complex. After filtration to remove unreacted $PhINSO_2Ph$, the yellow solution persists sufficiently long for ^1H NMR analysis if held at low temperature, revealing the formation of a diamagnetic silver(III) product. In addition to clearly identifiable resonances for the *t*-Bu_3terpy ligand, new aromatic signals are observed that we tentatively assign to a silver-bound $[PhSO_2N]$ nitrenoid group. Upon warming to room temperature, the mixture rapidly darkens and converts back to silver(II), with only PhI and trace $PhSO_2NH_2$ observable in the ^1H NMR spectrum. The primary decomposition pathway appears to be generation of complex **3**, which is also consistent with the data discussed above; however, the observation of some $PhSO_2NH_2$ in the NMR spectrum also suggests that H atom abstraction from solvent may be another possible pathway. Isolation and crystallographic characterization of the silver(III) product has been unsuccessful because of a lack of long-term stability, even at low temperatures.

Reactivity and Chemical Competency Studies. In order to determine the relevance to catalysis of the various oxidation products derived from **1**, we have studied their chemical competency for nitrene transfer to an alkene substrate such as styrene. A summary of results in shown in Figure 8. Isolated silver(II) product **2** is the first structurally characterized example of a metal−iminoiodane complex for any metal, and such complexes have been proposed as relevant intermediates in nitrene transfer reactions catalyzed by other metals such as manganese, iron, and cobalt.[16] However, we find that **2** displays no reactivity toward styrene. As expected from the EPR data and basic molecular orbital considerations for a square planar complex,[13,17] a spin density plot derived from DFT calculations supports that the unpaired electron of **2** resides in an orbital of $d_{x^2-y^2}$ parentage, with respect to silver, with spin density also observed on each of the four donor N atoms of the ligands (see Figure S3 in the Supporting Information). An intermediate that is active for nitrene transfer would be expected to have more significant spin density localized on the N atom of the NTs fragment.[9c] Unsurprisingly, the highly stable silver(II) complex **3**, which lacks a reactive nitrene fragment, also shows no reaction with styrene.

As described above, treatment of **1** with $PhINSO_2Ar$ at room temperature results in the formation of silver(II) products, which mass spectrometry analysis indicates to include the dinuclear nitrenoid product $[(t\text{-}Bu_3terpy)_2Ag_2(NSO_2Ar)]^+$. When **1** was stirred with 1 equiv of $PhINSO_2Ar$ until **1** was consumed and PhI was generated (∼5 min, as determined by ^1H NMR), followed by addition of styrene, the color of the reaction mixture gradually lightened over the course of 10 min. ^1H NMR analysis of the mixture showed ≤10% production of aziridine, relative to **1** (Figure S9 in the Supporting Information).

Accurately evaluating the reactivity of the silver(III) product observed from further oxidation with $PhINSO_2Ar$ is challenging, because of the fact that this product quickly begins to decompose back to silver(II) in the absence of excess $PhINSO_2Ar$. To test for nitrene transfer reactivity, the silver(III)-containing reaction mixture was prepared at −50 °C, filtered cold to remove excess $PhINSO_2Ar$, quickly added to a chilled vial containing styrene, and then allowed to warm to room temperature. ^1H NMR analysis showed aziridine production in ∼50% yield relative to **1** (Figure S10 in the Supporting Information). This result indicates substantially higher reactivity for aziridination from silver(III), compared to the initially formed silver(II) products.

Further evidence for aziridination proceeding via a silver(III) intermediate was obtained from double labeling studies using two different $PhINSO_2Ar$ derivatives (PhINTs and $PhINSO_2Ph$). In these studies, one derivative was used to generate the initial silver(II) products, and then styrene was added, along with the second oxidant derivative. Prior work has established that, in the case of an active metal−iminoiodane intermediate that forms subsequent to the initial (unreactive) metal nitrenoid, the nitrene fragment from the second equivalent of $PhINSO_2Ar$ is expected to be transferred selectively to the alkene substrate.[16a] On the other hand, if further oxidation with the second equivalent of $PhINSO_2Ar$ occurs, one would expect unselective transfer of either nitrene fragment (Figure 9a). GC analysis of the product mixture confirms that both NTs and NSO_2Ph groups are incorporated into the aziridine product in significant amounts, regardless of the order of addition (see Figure 9b, as well as Figure S12 in the Supporting Information). Total aziridine production was ∼60%, relative to **1** (Figure S11 in the Supporting Information). We do observe a slight preference for incorporation of the second equivalent of $PhINSO_2Ar$ (∼3:1 across the average of replicate trials), which we attribute to partial decomposition of the initially formed silver(II) products prior to addition of the second equivalent of oxidant and styrene. In comparison, catalysts that proceed via metal−iminoiodane intermediates typically display at least 10:1 selectivity for incorporation of the second equivalent of oxidant into the aziridine product.[16a]

Overall, our results indicate that both silver(II) and silver(III) products can be formed between silver(I) catalyst **1** and $PhINSO_2Ar$, and that sequential reaction of **1** with 2 equiv of oxidant generates the active silver(III) group transfer species for alkene aziridination. A summary of the reactivity pathways observed in our studies is shown in Figure 10. At this point, we are unable to fully assign the structure of the silver(III) intermediate, although the double labeling studies are suggestive of a complex with two reactive nitrenoid groups. The hypothesis of a high-valent silver complex bearing two nitrenoid groups is also consistent with the observed generation of complex **3**, via coupling of two NSO_2Ar fragments. It is possible that the dinuclear structure of **1** facilitates the formation of such an intermediate, in which each Ag center bears a nitrene; however, a pathway that proceeds through mononuclear silver(III) nitrene intermediates could also account for the currently available data (see Figure S15 and the accompanying discussion in the Supporting Information). We also note that the data reported here for the formally silver(III) complex cannot distinguish between a "true" d^8 silver(III) center or a more subtle electronic structure description involving ligand orbital involvement in the oxidation process;[18] further structural and spectroscopic characterization will be necessary to explore such distinctions.

■ CONCLUSIONS

In this study, we have presented a detailed experimental investigation of high-valent species derived from a silver(I) nitrene transfer catalyst and commonly used hypervalent iodine oxidants. We have provided the first examples of isolated and structurally characterized silver(II) complexes generated under catalytically relevant conditions, as well as the first direct observation of a silver(III) intermediate. Reactivity studies indicate that nitrene transfer for alkene aziridination occurs from silver(III). Our results suggest that silver(III) intermediates may be more readily accessible than typically assumed, even for silver catalysts with relatively weak ligand fields. Future efforts in our laboratory will aim to explore the potential generality of silver(III) intermediates in homogeneous catalysis, as well as to structurally characterize silver(III) complexes with relevance to catalysis in order to better understand group transfer reactivity from high-valent silver.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acscatal.0c00065.

Experimental procedures and spectroscopic data (PDF)
Crystallographic data of **2** (CIF)
Crystallographic data of **3** (CIF)

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Notes

The authors declare no competing financial interest.

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