Cooperative chalcogen bonding interactions in confined sites activate aziridines

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The activation of aziridines typically involves the use of strong Lewis acids or transition metals, and methods relying on weak interactions are rare. Herein, we report that cooperative chalcogen bonding interactions in confined sites can activate sulfonyl-protected aziridines. Among the several possible distinct bonding modes, our experiments and computational studies suggest that an activation mode involving the cooperative Se···O and Se···N interactions is in operation. The catalytic reactions between weakly bonded supramolecular species and nonactivated alkenes are considered as unfavorable approaches. However, here we show that the activation of aziridines by cooperative Se···O and Se···N interactions enables the cycloaddition of weakly bonded aziridine-selenide complex with nonactivated alkenes in a catalytic manner. Thus, weak interactions can indeed enable these transformations and are an alternative to methods relying on strong Lewis acids.
Weak interactions are among the significant evolutionary forces that are smartly exploited by nature to modulate the conformation of proteins and to drive cellular reactions. The simulation of this biomimetic strategy in supramolecular catalysis has gained fruitful achievements in promoting chemical reactions. Amongst these interactions, catalysis with hydrogen bond plays a dominant role while halogen−4, as well as chalcogen bonding catalysis,5−9, has lately attracted ever-increasing research interest. Since the weak interactions restrict both the reactivity and the concentration of equilibrating supramolecular complex, this catalysis discipline has its constraint boundary considering the limitations of the activation targets and reaction patterns. Even though weak interactions can activate a range of molecules such as carbonyl compounds, imines, nitro olefins, etc., it is a challenging task for these interactions to activate target molecules like aziridines which were conventionally handled by strong Lewis acids or transition metals. (Fig. 1a)9. Furthermore, the reactants suitable for trapping these weakly bonded supramolecular species have specific requirements, thus partly restricting the reaction patterns. For instance, the reactions between weakly bonded supramolecular species and nonactivated alkenes are considered unfavorable approaches in supramolecular catalysis. To develop this field, research toward expanding the activation targets and establishing distinct reaction patterns is of vital importance.

Chalcogen bonding11, the noncovalent interaction between an electron donor and a chalcogen atom incorporated in a specific molecular entity, has recently found application in drug design, material chemistry,13, intramolecularly conformational control,14−18 anion recognition and transport processes. The theoretical investigation suggests that charge transfer, disperse force, and electrostatic potential are significant contributors to the formation of chalcogen bonding interactions. As the chalcogen bond, in general, is weak, catalysis with chalcogen bonding interactions based on divalent chalcoster is thus a rarely explored concept and a limited number of examples were introduced.28−37. Herein, we report the chalcogen bonding mode of the aziridine-selenide complex and the catalytic reactions between these supramolecular complexes and nonactivated alkenes. We show that weak interactions enable catalytic transformations, in contrast with methods relying on stoichiometric strong Lewis acid-mediated organic transformations (Fig. 1b).

Results and discussion

Bonding property. We recently developed a class of phosphonium selenide-based chalcogen bonding catalysts, which showed catalytic activity in the activation of carbonyl groups and vinylindoles. Since there are multiple Lewis basic sites in sulfonyle-protected aziridine like (Fig. 2a), the binding modes for activating aziridines with such phosphonium selenides are much more complicated and the interactions with proper sites are crucial to the generation of catalytic capability. To understand the distinct bonding behavior of monodentate and bidentate chalcogen bonding donors and aziridine gives short-life supramolecular species with very low concentration.

Upon forming intermolecular interaction with 1a/1a’s, the distinct structure of 1b reveals that the variation of the 77Se signal is of vital importance. Even though weak interactions restrict both the reactivity and the concentration of equilibrating supramolecular complex, this catalysis discipline has its constraint boundary considering the limitations of the activation targets and reaction patterns. Even though weak interactions can activate a range of molecules such as carbonyl compounds, imines, nitro olefins, etc., it is a challenging task for these interactions to activate target molecules like aziridines which were conventionally handled by strong Lewis acids or transition metals. (Fig. 1a)9. Furthermore, the reactants suitable for trapping these weakly bonded supramolecular species have specific requirements, thus partly restricting the reaction patterns. For instance, the reactions between weakly bonded supramolecular species and nonactivated alkenes are considered unfavorable approaches in supramolecular catalysis. To develop this field, research toward expanding the activation targets and establishing distinct reaction patterns is of vital importance.

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**Fig. 1 Distinct approaches to the activation of aziridines. a** Activation of aziridines: the state of the art. **b** This work: chalcogen bonding activation and catalysis approach.
**Fig. 2** Chalcogen bonding interactions between Ch1-6 and aziridines (77Se NMR in CD2Cl2, 76 MHz, and 298 K). a Chalcogen bonding between monodentate catalysts Ch1-2 and aziridine 1a. b Chalcogen bonding between bidentate catalysts Ch3-6 and aziridine 1a/1a’.

**Fig. 3** Relationship between bonding and structure. a X-ray crystal structures of Ch3-6 (hydrogens and counteranions were omitted for clarity; the selenium atoms are disordered and no chalcogen bonding interaction in Ch6). b Equilibrium between intramolecular chalcogen bonding and non-bonding status of catalysts Ch3-5 and catalyst Ch6.
similar to the previously observed structure of Ch4 associated with a TfO counterion\(^2\), which also shows two intramolecular Se···O bonding interactions. These observations indicate the counterion can pronouncedly affect the bonding interactions. The crystal structure of Ch5 exhibits the Se··· \(\pi\) bonding interactions between the selenium and the phenyl ring in the other unit. In contrast, no intramolecular chalcogen bonding interaction was observed in the crystal structure of Ch6. While X-ray crystallographic data of Ch5 and Ch6 indicate solvent in the crystals, powder X-ray diffraction (PXRD) data of Ch3-6 are in agreement with the simulated results from corresponding single crystal diffraction data (see Supplementary Figs. 28–31).

Owing to the presence of the intramolecular Se···O interaction in Ch3 as well as both Se···O and Se···Se interactions in Ch4 (Fig. 3b), the addition of aziridine \(1a/1a'\) competitively generates the intermolecular Se···O and Se···N interactions which are the similar type relative to the intramolecular interactions, thus resulting in less variation of the \(^{77}\)Se signals as shown in Fig. 2. In contrast, in the case of Ch5 or Ch6 which does not have an intramolecular Se···O or Se···Se interaction, the intermolecular Se···O and Se···N interactions with \(1a/1a'\) would substantially change the bonding status of Ch5 and Ch6, thus inducing more marked variation of the \(^{77}\)Se signals.

**Bonding mode.** To investigate the active bonding modes (Fig. 4a), a range of molecular control experiments were carried out as depicted in Fig. 4b–e (see Supplementary Figs. 7–22).
Using aziridine m1 as a model Lewis base, the control $^{13}$C NMR experiments reveal that the chemical shift of C$_\alpha$ (attached to S) almost remains unchanged while the chemical shift of the more remote C$_\beta$ (two bonds from S) varies dramatically when comparing the bonding performance of monodentate catalyst Ch2 (Ch2:m1 2:1) and their counterparts, bidentate catalysts Ch5 and Ch6 (Ch:m1 1:1) (Fig. 4b). For a bidentate catalyst, it is unlikely that the shifting from a single interaction mode (i.e., SC0 or SC1) to a mode of double interaction with oxygen (i.e., SC4 or SC5) would lead to almost no perturbation of the chemical shift of C$_\alpha$ while resulting in a marked variation of C$_\beta$. Instead, the dramatic change of C$_\beta$ attached to nitrogen indicates that a double interaction mode involving the direct interaction with nitrogen (i.e., SC6) is a reasonable binding mode to explain the experimental results. For a much sharper contrast, the formation of the complexes between Ch5/6 and m1 led to a negligible variation of C$_\alpha$ (0.07 and 0.06 ppm) while resulting in a much more pronounced change of C$_\beta$ (0.65 and 0.55 ppm), which also suggests the direct interaction with nitrogen (i.e., SC6) to be the active complex. To give a more direct comparison, twofold Ch7 (Ch7:m1 2:1) was used, i.e., monodentate version of Ch5 and Ch6, and similar results were obtained. Further using m2 as a model Lewis base gave similar observations.

The subsequent molecular control experiments further support SC6 as the active binding species. As shown in Fig. 4c, in contrast to aziridine 1a, its ring-opening counterpart m3 almost gave no change in the chemical shift of C$_\alpha$ regardless of in the presence of a monodentate or a bidentate catalyst. These observations

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**Fig. 5 DFT calculations.** a The optimized structures of the complexes SC3 and SC6 between Ch5 and 1-(phenylsulfonyl)aziridine. b The key intermolecular donor-acceptor orbital interactions between Ch5 and 1-(phenylsulfonyl)aziridine in SC3 (I) and SC6 (II-IV); BD*(1) denotes the $\sigma^*$ antibonding orbital; LP(1) and LP(3) denote the first and third lone-pair orbitals, respectively.
Chalcogen bonding catalysis. The reactions between weakly bonded supramolecular species and nonactivated alkenes are considered unfavorable transformations.\textsuperscript{1–10} Therefore, to apply the bonding property of the aziridine-selenide complex, the cycloaddition of aziridines with nonactivated alkenes was selected as a target reaction as literature reports indicate that it would be a tough challenge for a weak interaction to promote this reaction (Fig. 6).\textsuperscript{40–43} To generate reactivity, the reported precedent used strong Lewis acid BF\textsubscript{3}\cdot\text{OEt}$_2$ to promote this reaction (Fig. 6a).\textsuperscript{40,41} Moreover, in order to generate a proper concentration of intermediate suitable for trapping with nonactivated alkenes, a stoichiometric amount of BF\textsubscript{3}\cdot\text{OEt}$_2$ was used. Otherwise, the reaction has to be carried out under a thermal-driven condition (100 °C) to give reactivity in the presence of a transition-metal catalyst.\textsuperscript{42,43} To achieve this reaction by a weak interaction, there are two challenging problems (Fig. 6b). As the weak interaction provides much less activation than the strong Lewis acid counterpart, one problem is thus how a weak interaction with aziridine can give rise to activation ability. Furthermore, in contrast to the strong Lewis acid counterpart, the weak interaction always results in the generation of an unstable supramolecular complex with low concentration. Therefore, the other glaring problem is how to increase the concentration of aziridine-mediated supramolecular species to a reactive level by only using a catalytic amount of noncovalent activator. In this context, the chalcogen bonding approach was applied to address these problems.

Initially, to evaluate the reactivity of this cycloaddition process towards activation by noncovalent interactions, the well-established hydrogen-bonding donors H1–H3 were employed as references (Fig. 7a). There was no background reaction even after 24 h in the absence of a catalyst. In the presence of 10 mol % of a typical hydrogen-bonding donor (H1–3), the reaction did not work. Furthermore, only a trace amount of product 3a (<5%) was obtained using a stoichiometric amount of a hydrogen-bonding catalyst H1 (1.0 equiv), indicating inertness of this reaction under activation by weak interactions. Considering the poor reactivity of this cycloaddition reaction, we envisioned that cooperative chalcogen–bonding interactions with aziridine would enhance the activation ability and provide more stabilization of the supramolecular species, thus improving the reactivity. However, to match the confined Lewis basic binding sites in phenylsulfonyl protected aziridines, the judicious use of bidentate chalcogen bonding donors that are capable of precisely recognizing the proper Lewis basic sites of aziridine is critically important to give catalytic activity (Fig. 7b).

In consistence with the results in Figs. 2, 4, upon using monodentate chalcogen bonding donors Ch1–2 as catalysts, the reaction did not work. Nonetheless, these experiments revealed neither the phosphonium unit nor the BArF$_4$ counterion is catalytically active (Fig. 7c). To implement the idea as depicted in Fig. 7b, two sets of bidentate catalysts were investigated. One set is catalyst Ch3 with a free rotation linker and its rigidified counterpart Ch4. The other set is catalysts Ch5–7 with different lengths of linkers. The comprehensive control experiments (see Supplementary Figs. 15–22) indicate Ch3 bearing a long linker with free rotation between two chalcogen bonding sites operates like a monodentate catalyst. In consistence with these observations, the experimental results revealed that catalyst Ch3 with a
**Fig. 7** Noncovalent catalysis approach to cycloaddition of aziridine 1a with nonactivated alkene 2a. 

**a** Catalysis with typical hydrogen-bonding donors. 

**b** The interactions between bidentate chalcogen bonding donors and phenylsulfonyl protected aziridines. 

**c** Chalcogen bonding catalysis approach to cycloaddition of aziridines with nonactivated alkenes. 

**d** Inhibition experiment. DCE 1, 2-dichloroethane.
long and free rotation linker gave no catalytic activity. Then the free rotation linker of catalyst Ch3 was rigidified. Upon changing catalyst Ch3 to catalyst Ch4 with a rigid backbone, the reaction began to work and catalyst Ch4 showed high catalytic activity to give a 77% yield of product 3a at room temperature. Analysis of the mixture of Ch4 and olefin 2a by $^{77}$Se and $^{31}$P NMR indicated that there was no detectable variation of the $^{77}$Se and $^{31}$P signals, indicating there is no competitive bonding between catalysts Ch4 and 2a (see Supplementary Fig. 23).

Further investigation of the catalytic performance of the bidentate catalysts Ch5-6 suggests the distance between the two binding sites is critically important. Upon linking the two phosphonium units with one carbon, catalyst Ch5 exhibited good catalytic activity to give a 75% yield of 3a, indicating this distance between the two binding sites can well interact with the proper Lewis basic sites of aziridine. In contrast to Ch5, even only increasing the length of the linker by one carbon, catalyst Ch6 showed poor catalytic activity and only a 13% yield of 3a was obtained. In contrast, monodentate catalyst Ch7 had no catalytic activity. Similar to the case of Ch3, upon linking the two phosphonium units with five carbons, catalyst Ch8 with improperly positioned two binding sites completely lost catalytic activity. Catalyst Ch9 with electron-withdrawing substituents on the aryl ring did not show catalytic activity. For the same selenide, the strength of chalcogen bonding interaction is determined by the electron-donating ability of aziridines. Therefore, toluenesulfonyl-protected aziridine in principle generates stronger and more efficient Ns-protected aziridines in contrast to its counterpart Ch4 or Ch5. On the other hand, comparable results on the interactions of more electron-rich aziridines m1-2 with Ch5 and Ch6 were observed (Fig. 4b), indicating the interaction of Ch6 and aziridine is affected by the electronic effect of aziridines. Based on these observations, the contrast experiments on the catalytic performance of Ch6 in CH$_2$Cl$_2$ using aziridines with different electronic properties were carried out (Fig. 8). The control experiments using p-tBuPh, p-CIPh, and Ph substituted aziridines as substrates showed distinct results (yield: 52% for p-tBuPh; 14% for Ph; 7% for p-CIPh).

As shown in Fig. 9a, the reaction time can be shortened from 10 to 1 h while the yield of product 3a was improved from 77 to 85% upon conducting the reaction at 50 °C. Tracing the reaction system by $^{31}$P NMR reveals that catalyst Ch4 is stable in this reaction process and only the $^{31}$P signal of catalyst Ch4 was observed (see Supplementary Fig. 2). Different protecting groups can be tolerated in this reaction to give products 3b and 3c in 53% and 67% yields, respectively. Terminal olefins, with different chain length showed similar reactivity. Benzylic-substituted olefin was highly reactive to give pyrrolidine 3f in an 82% yield. Cycloalkyl-substituted olefins were used to give different spiro-pyrrolidines 3g-k in good yields. Regardless of the electronic characteristic of the substituents on the aromatic ring as well as the positions where the substitution groups are located, aziridines bearing different aromatic rings were well tolerated to give pyrrolidines 31-u with reasonable yields. Mono-substituted nonactivated alkene was proven to be an effective reactant, and product 3v was obtained in 53% yield (dr: 3:1). Furthermore, alkenes were also effective substrates, and products 5a-5i were obtained in 60-79% yields (Fig. 9b). Upon using ketones as substrates, products 7a and 7b were obtained in 83 and 67% yields, respectively (Fig. 9c).

In summary, this manuscript reports the chalcogen bonding of aziridine-selenide complexes and establishes a type of reaction between weakly bonded supramolecular species and nonactivated alkenes, thus shifting the stoichiometric strong Lewis acid-mediated approach to a noncovalent catalysis manner. Experimental results revealed that the bidentate catalysts with confined binding distance enable the simultaneous formation of Se-O and Se-N interactions with aziridines, which enables their use in catalysis. This research opens up opportunities for addressing problems relative to activation targets and reaction patterns in supramolecular catalysis.

Methods

General procedure for the preparation of bidentate chalcogen bonding catalysts Ch3-6 and Ch8. To a red solution of PhSeCl (383.0 mg, 2.0 mmol) in dry Et$_3$O (6.0 mL) at 0 °C under argon was added TMSOTf (444.5 mg, 2.0 mmol). The reaction mixture was allowed to warm up to room temperature and stirred for 40 min to give a dark orange solution. Then 1.0 mmol phosphate ([oxybis(2,1-phenylene)]bis(diphenylphosphine)) for Ch3; (9,9-dimethyl-9H-xanthene-4,5-diyl)bis(diphenylphosphophine) for Ch4; 1,5-bis(diphenylphosphino)pentane for Ch5; (9,9-dimethyl-9H-xanthene-4,5-diyl)bis(diphenylphosphophine) for Ch6; 1,3-bis(diphenylphosphino)pentane for Ch7) was added in dry CH$_2$Cl$_2$ (4.0 mL) and the reaction mixture was allowed to warm up to room temperature and stand for 30 min at 0 °C. The reaction mixture was filtered and the filtrate was concentrated to give a saturated solid suspension. The white solid suspension was filtered and washed by anhydrous diethyl ether. Then sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (1772.4 mg, 2.0 mmol) was added to a solution of the above white solid (1.0 mmol) in dry CH$_2$Cl$_2$ (10.0 mL) under argon and the reaction mixture was stirred at room temperature for 24 h. Then the reaction mixture was filtered and the filtrate was concentrated to give a saturated solution under reduced pressure and then 10.0 mL n-hexane was slowly added. The two-phase solution was placed at room temperature under argon and the desired product precipitated out as a white solid. Then the precipitated white solid was collected by filtration and recrystallized twice from CH$_2$Cl$_2$ (or ether) and n-hexane to afford the pure catalyst.

![Fig. 8 Control experiments on the catalytic performance of Ch6 by using aziridines with different electronic properties.](image-url)
General procedure for the preparation of monodentate chalcogen bonding catalysts Ch2, Ch7, and Ch9. To a red solution of PhSeCl (191.5 mg, 1.0 mmol for catalysts Ch2 and Ch7) or 3,5-F2C6H3SeCl (227.9 mg, 1.0 mmol for catalyst Ch9) in dry Et2O (6.0 mL) at 0 °C under argon was added TMSOTf (222.3 mg, 1.0 mmol). The reaction mixture was allowed to warm up to room temperature and stirred for 40 min to give a dark orange solution. Then 1.0 mmol phosphine (triphenylphosphine for Ch2 and Ch9; methyldiphenylphosphine for Ch7) dissolved in dry CH2Cl2 (4.0 mL) was added over 5 min at 0 °C. The reaction mixture was allowed to warm up to room temperature and stand for 1 h. Then sodium tetraakis[3,5-bis(trifluoromethyl)phenyl]borate (886.2 mg, 1.0 mmol) was added to the reaction mixture and stirred for 2 h. The reaction mixture was filtered through a pad of silica gel, washed with Et2O, and the filtrate was concentrated in vacuo. The residue was purified by flash chromatography to give the desired product.
above reaction system and stirred at room temperature for 24 h. Then the reaction mixture was filtered and the filtrate was concentrated to give a saturated solution under reduced pressure and then 10.0 mL n-hexane was slowly added. The two-phase solution was placed at room temperature under argon and the desirable product precipitated out as a white solid. Then the precipitated white solid was collected by filtration and recrystallized twice from CH₂Cl₂ and n-hexane to afford the pure catalyst.

General procedures for chalcogen bonding catalysis of cycloaddition reactions. To a reaction mixture of aziridine (0.2 mmol) and catalyst Ch4 (10 mol %, 5.2 mg, 0.02 mmol) in a 10-mL-Schlenk tube was added DCE (1.0 mL) under argon atmosphere. Then the corresponding reactant alkene 2 or alkyne 4 or ketone 6 (0.6 mmol, 3.0 equiv) was added to the above reaction mixture. The reaction was stirred at indicated temperature (50 °C for the reactions to generate products 3 and 7, room temperature for the reactions to generate product 5) until the completion of the reaction as judged by TLC analysis. Then the solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica gel using petroleum ether/ethyl acetate (v/v) = 30:1 to 1:1) as eluent to give the desired products.

Data availability
All the data supporting the findings of this study are available within the article and its Supplementary Information file. The X-ray crystallographic data for structures reported in this study have been deposited in the Cambridge Crystallographic Data Centre under deposition numbers 2069229 (Ch3), 2069224 (Ch5), and 2069228 (Ch6). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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**Author contributions**
Y.W. conceived and directed the project. H.Z. conducted the experiments and prepared the Supplementary Materials. P.-P.Z. performed DFT calculations. Y.W. wrote the manuscript.

**Competing interests**
A patent application naming H.Z. and Y.W as inventors was submitted by Shandong University for this synthetic technology. P.-P.Z. declares no competing interests.

**Additional information**
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