Chalcogen bonding and latest application

M1 ZHAI

2021/10/21

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- ◇ Introduction of chalcogen bonding
- ◇ Chalcogen Bonding in Crystal Engineering
- ◇ Anion Binding with Chalcogen Bonds
- ◇ Chalcogen Bonding in Organic Synthesis and Noncovalent Organocatalysis
- ◇ Bis-selenonium Cations as Bidentate Chalcogen Bond Donors in Catalysis
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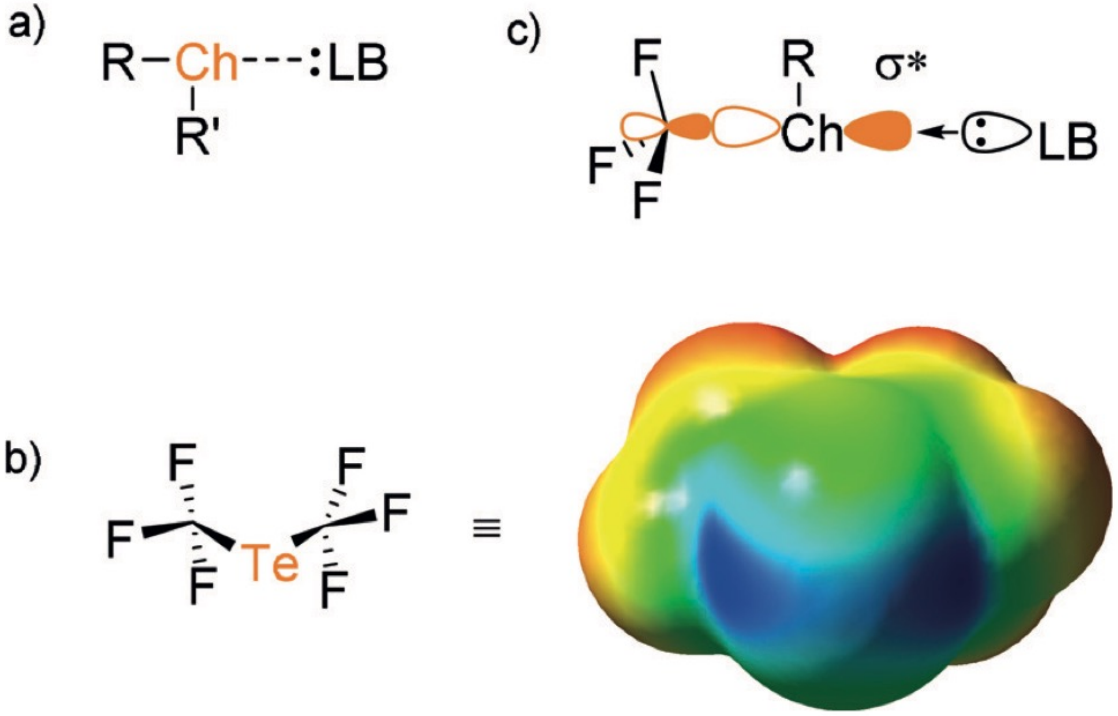
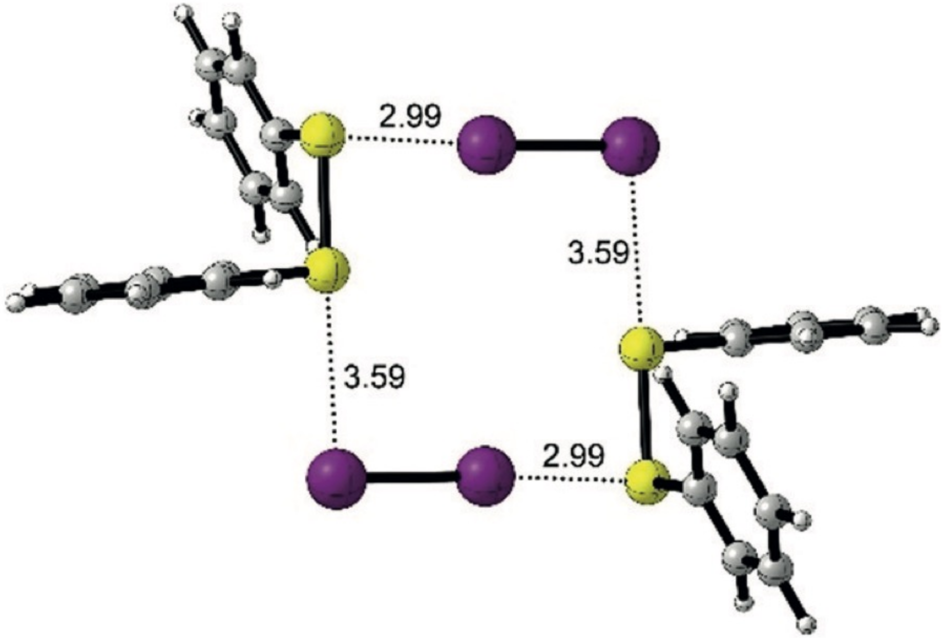
Chalcogen bonding

Chalcogen bonding (ChB) is defined as the interaction between a positively polarized chalcogen atom and a Lewis base (LB) .



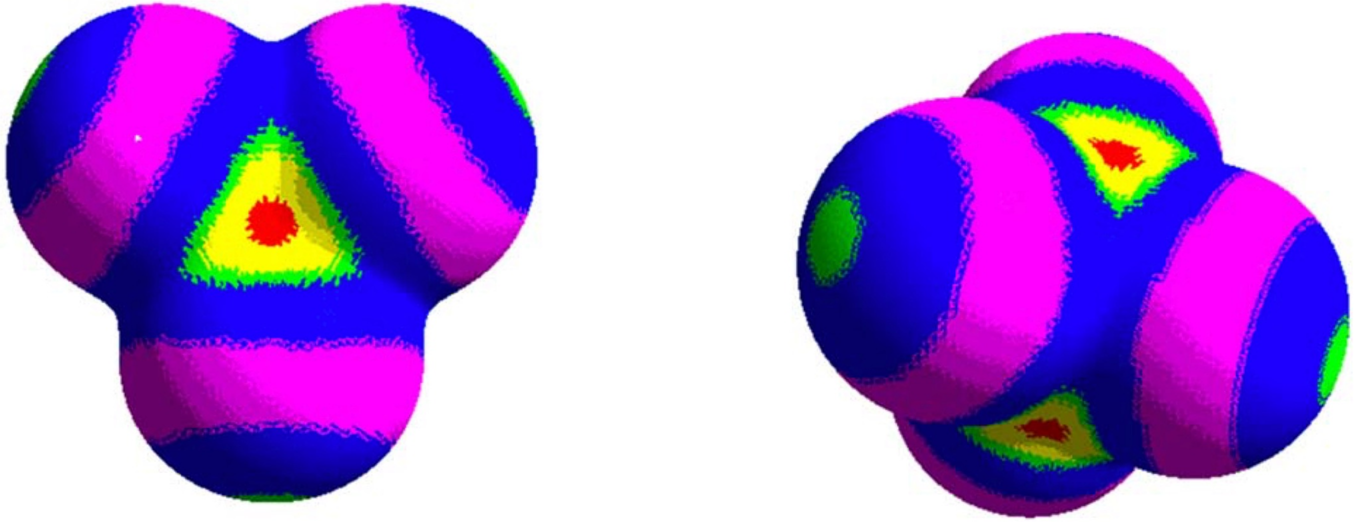


Early example of chalcogen bonding.

Chalcogen bonding：σ-hole

The term “σ-hole” originally referred to the electron-deficient outer lobe of a half-filled p (or nearly p) orbital involved in forming a covalent bond.

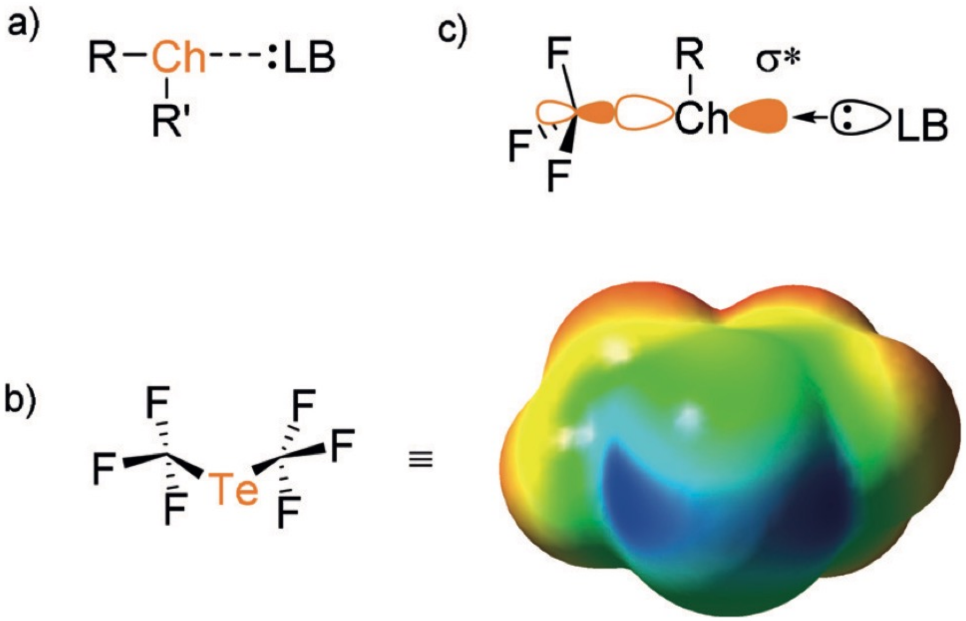
A region of positive electrostatic potential which can interact attractively (noncovalently) with negative sites on other molecules (σ-hole bonding).



Two views of the calculated electrostatic potential on the 0.001 au molecular surface of SiCl4.

Jane S. Murrary et al, *J Mol Model,* **2009**, 723, 15

Chalcogen bonding



Chalcogen bonding

Electrostatics

anisotropic distribution of electron density

Charge-transfer

electron donation

Dispersion

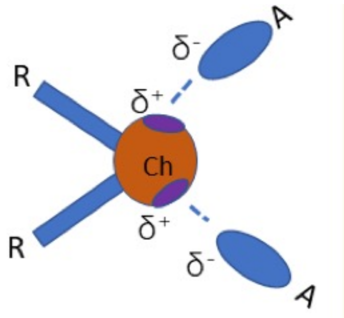
(particularly relevant for weak complexes)

Chalcogen bonding

The strength of a chalcogen bond depends on:

1. the Lewis basicity of the interacting partner
2. the nature of the chalcogen atom (Te > Se > O > S)
3. the polarization of the chalcogen atom
4. the R-Ch···LB interaction angle: strong ChBs require angles close to 180°

$\mathrm{R{-}\underset{\displaystyle R'}{\underset{|}{Ch}}{-}{-}{-}{:}LB}$



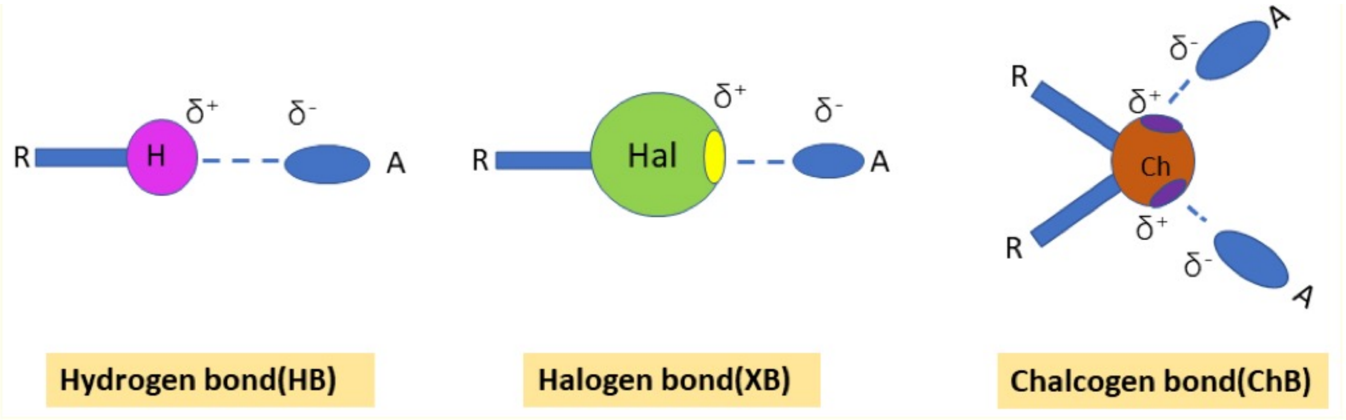
Chalcogen bond(ChB)

De Silva et al., *Molecules*, **2021**, 26, 4125

Chalcogen bonding

ChB vs HB:

1. Hydrogen bonding is limited to one atom, several alternatives are available for ChB, with Se and Te certainly being the most promising candidates for strong ChBs.
2. Hydrogen bonding is markedly less directional than chalcogen bonding, with much stronger deviations of the R-H···LB angle from 180° being tolerated.



De Silva et al., *Molecules*, **2021**, 26, 4125

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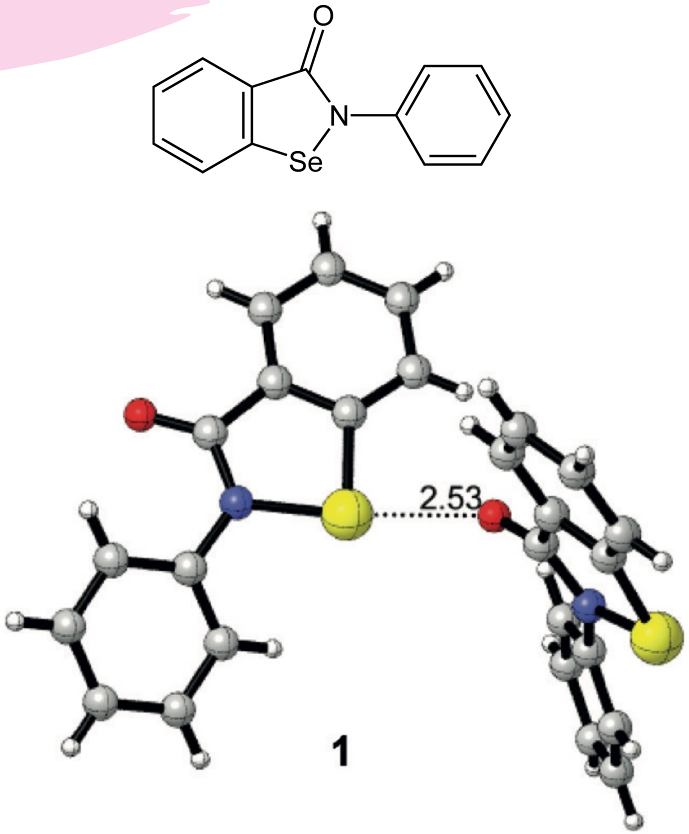
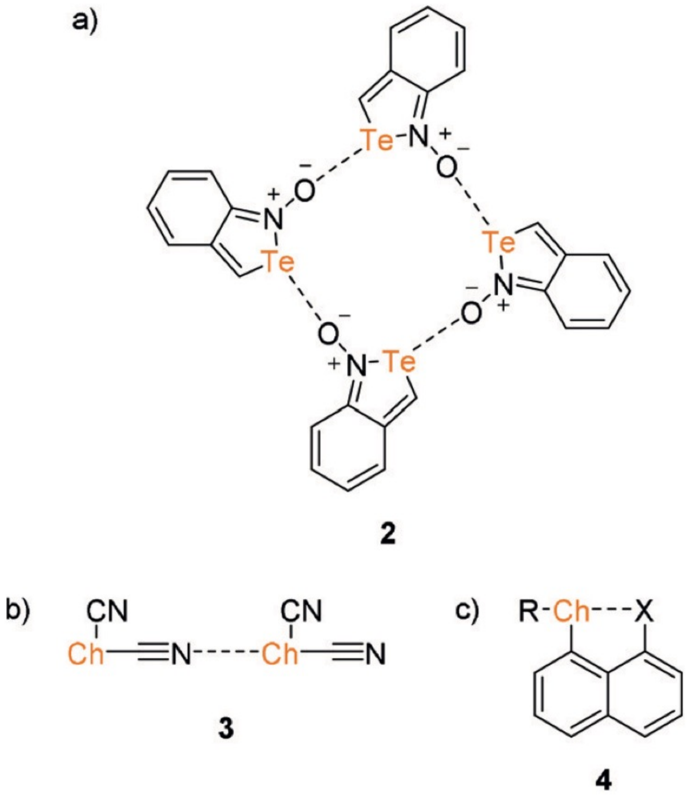
Chalcogen Bonding in Crystal Engineering



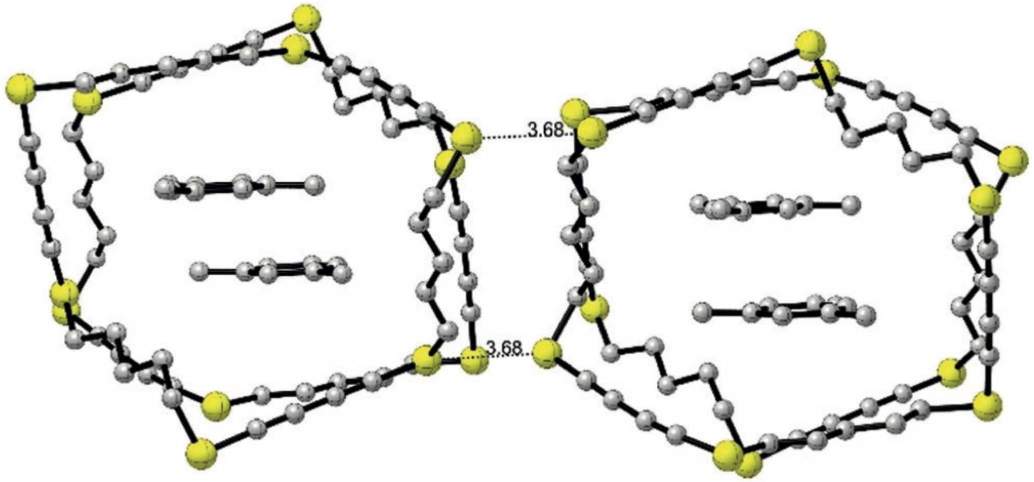
1

Crystal structure of Ebselen highlighting the short chalcogen bond

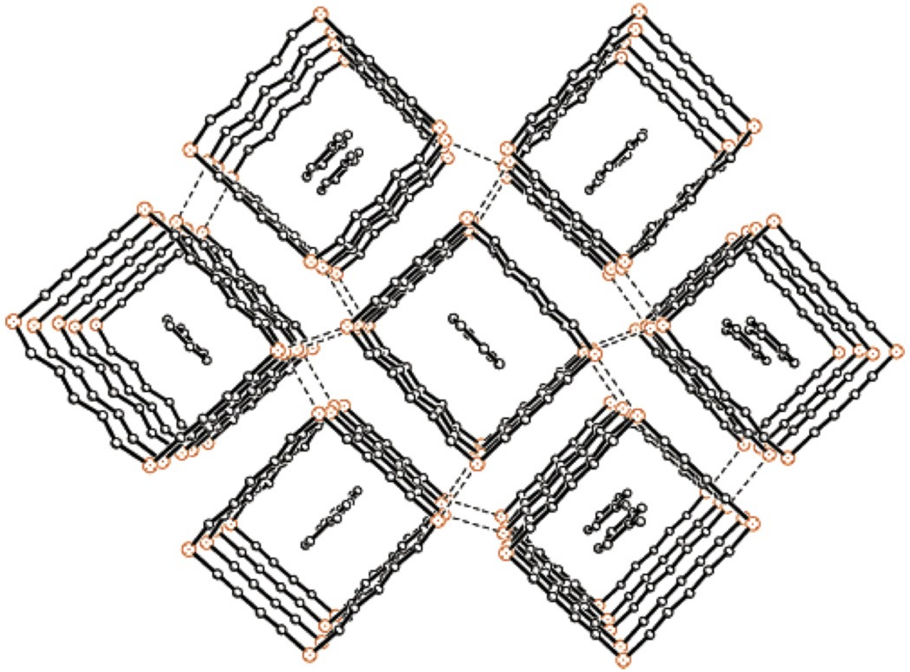


a) Supramolecular assembly of iso-tellurazole oxides (2); b) linear assembly of chalcogenodicyanides 3; c) intramolecular chalcogen bond in a 1-chalcogeno-8-halogeno-naphthalene 4.

Applications of Chalcogen-Bonded Structures



Crystal structure of nanotubes formed by cyclic hexaselenides, , which incorporate mesitylene molecules as guests.



Columnar structure of 1,6,12,17-tetrathiacyclodocosa-2,4,13,15tetrayne in the solid state with included toluene guest molecules. H atoms are omitted for the sake of clarity.

C. Bleiholder, D. B. Werz, H. Koppel, R. Gleiter, J. Am. Chem.Soc. **2006,** 128, 2666

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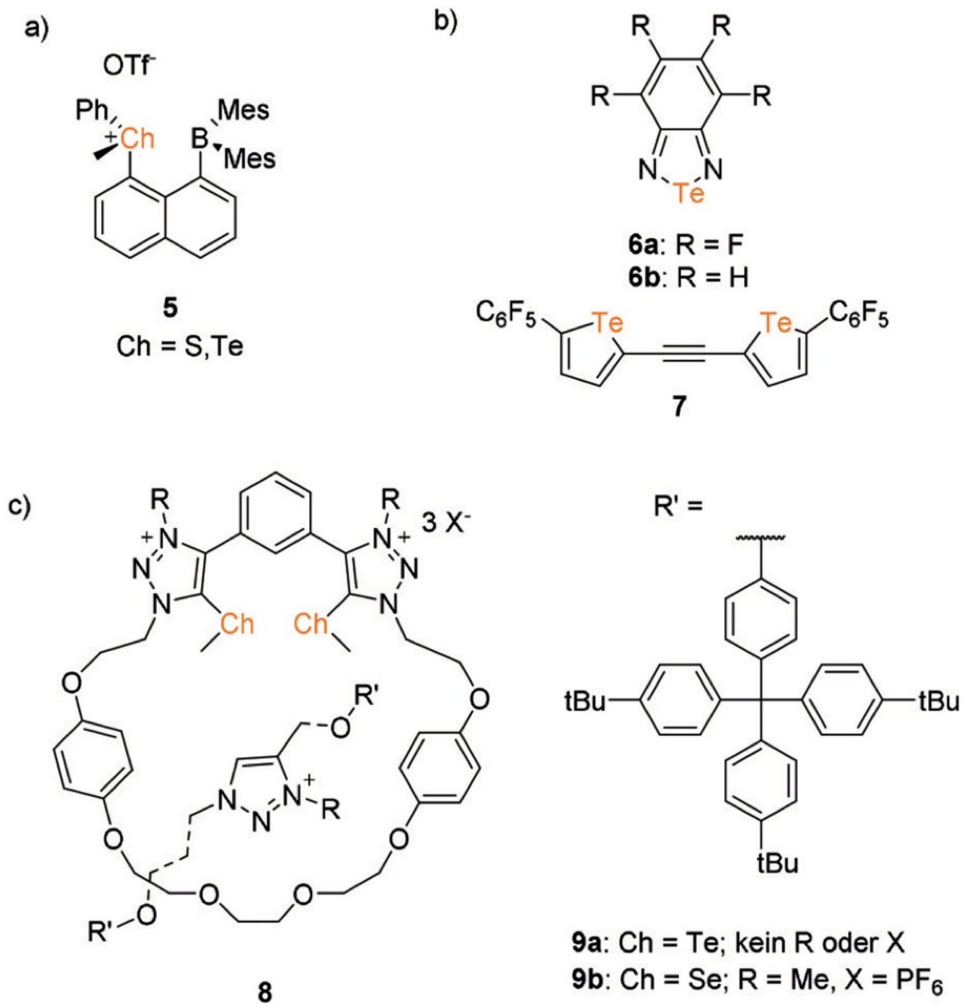
Anion Binding with Chalcogen Bonds

- Chalcogen-Bonding-Based Anion Recognition
- Chalcogen-Bond-Based Anion Transport

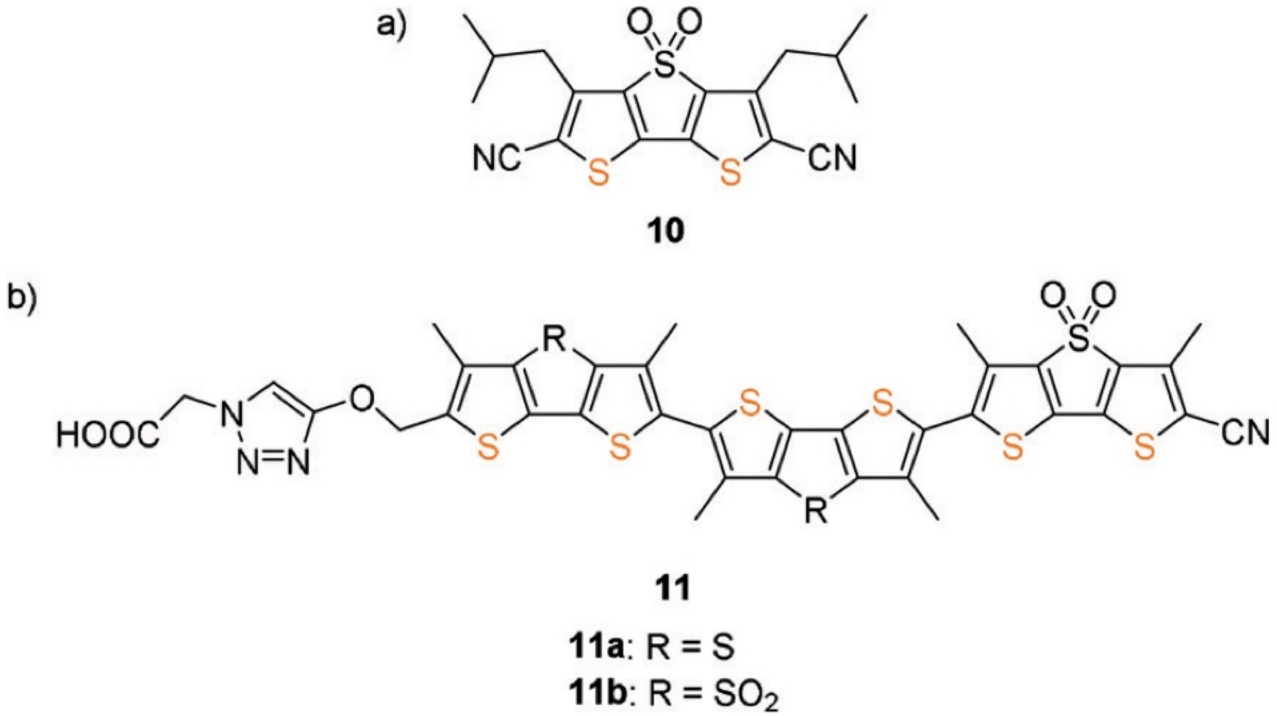
Chalcogen-Bonding-Based Anion Recognition



Chalcogen bonding anion-receptors from
a) Gabba and Zhao,
b) Taylor et al.
c) Beer et al.

H. Y. Zhao, F. P. Gabbai, *Nat. Chem.*, **2010**, 2, 984

Chalcogen-Bond-Based Anion Transport



10

11

11a: R = S
11b: R = SO_2

Anion transporters 10 and 11 by Matile et al.

S. Benz et al., *J. Am. Chem. Soc,* **2016**, 138, 9093
M. Macchione et al., *Helv. Chim. Acta*, **2018**, 101, e1800014

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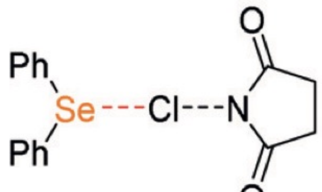
Chalcogen Bonding in Organic Synthesis and Noncovalent Organocatalysis

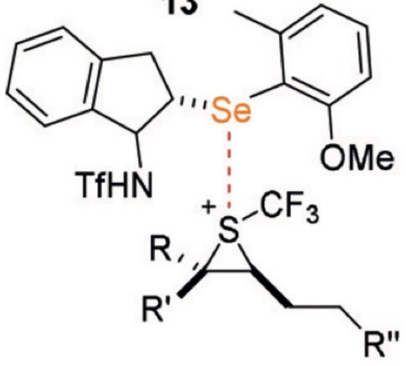
- Organochalcogen Compounds as Lewis Bases and Transient Chalcogen Bonding
- Intramolecular Chalcogen Bonding in Synthesis: Rigidification of Chiral Structures
- Intermolecular Chalcogen Bonding in Synthesis and Organocatalysis

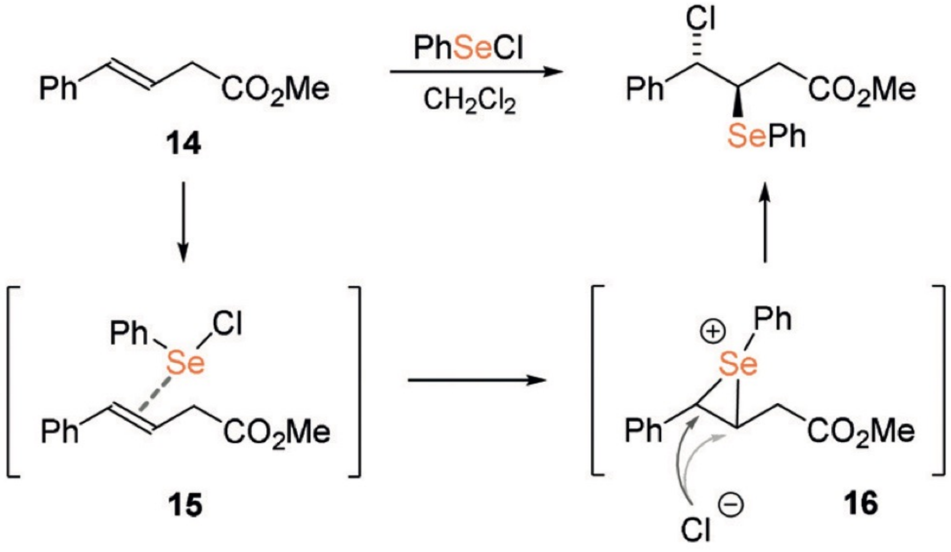
Organochalcogen Compounds as Lewis Bases and Transient Chalcogen Bonding



12

13





Organochalcogens **12** and **13** as Lewis basic organocatalysts

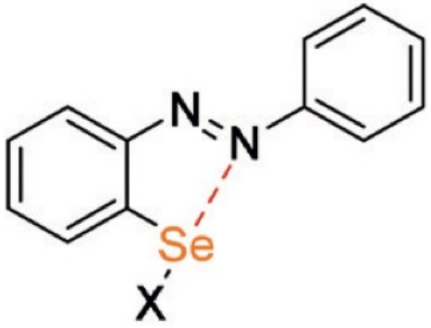
Selenenylation of alkenes **14** involving transient chalcogen bonding

D. W. Tay et al, *Org. Lett.*, **2013**, 15, 1310.

X. Liu et al., *J. Am. Chem. Soc.*,**2018**, 140, 4782

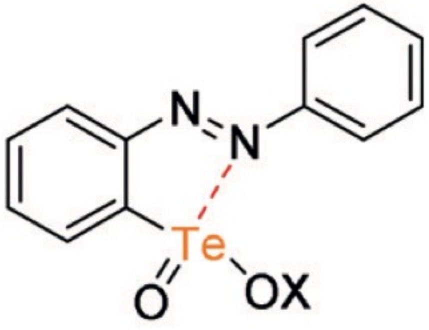
M. G. Edwards et al., *J. Org. Chem.,* **2006**, 71, 7293

Intramolecular Chalcogen Bonding in Synthesis: Rigidification of Chiral Structures



X = Cl, Br, I, PhN$_2$Ph

17



X = H, Na

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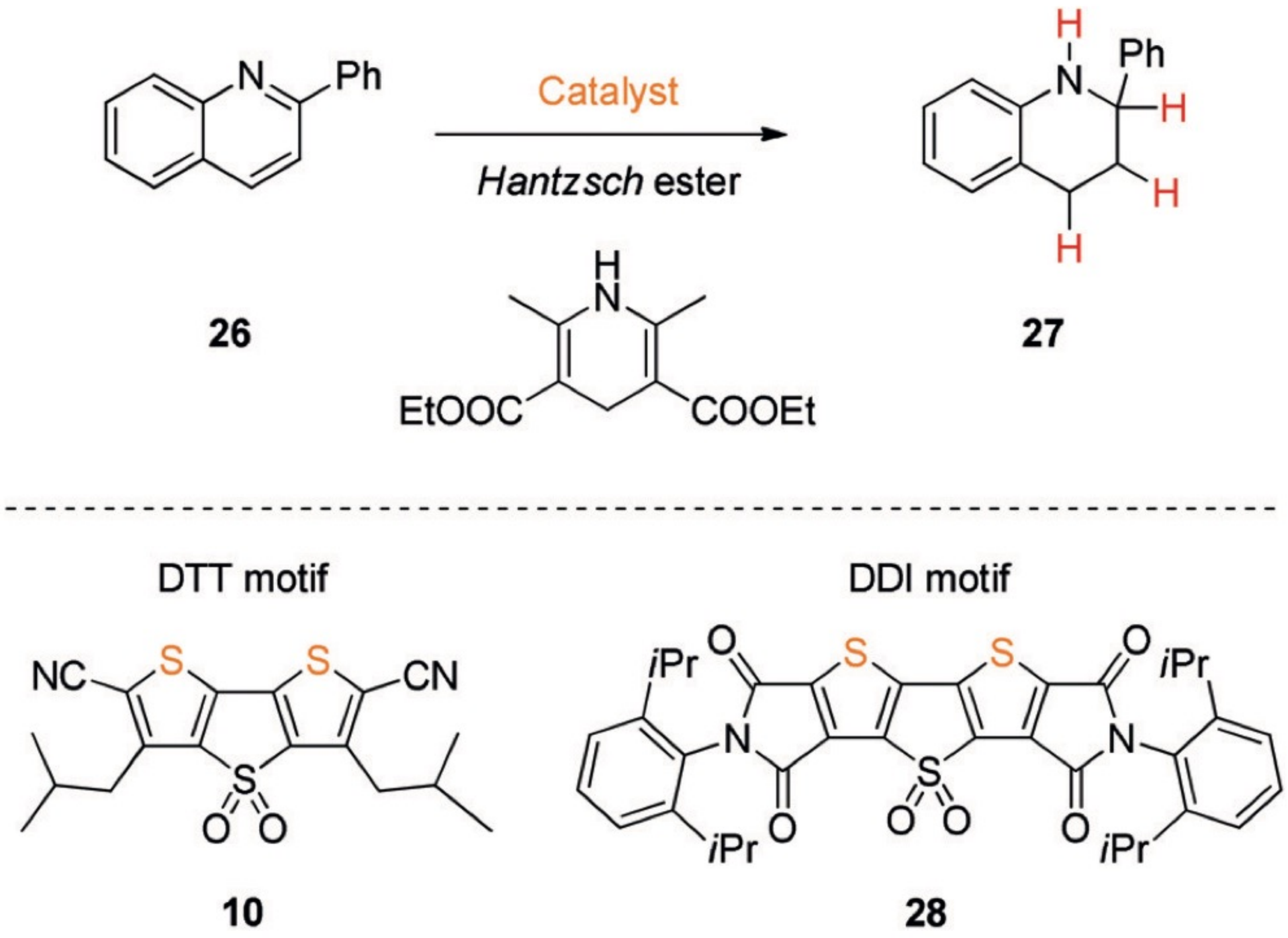
Intramolecular chalcogen bonding as a tool to rigidify and stabilize

K. Srivastava et al., *Dalton Trans.*, **2011**, 40, 4489

Intermolecular Chalcogen Bonding in Synthesis and Organocatalysis



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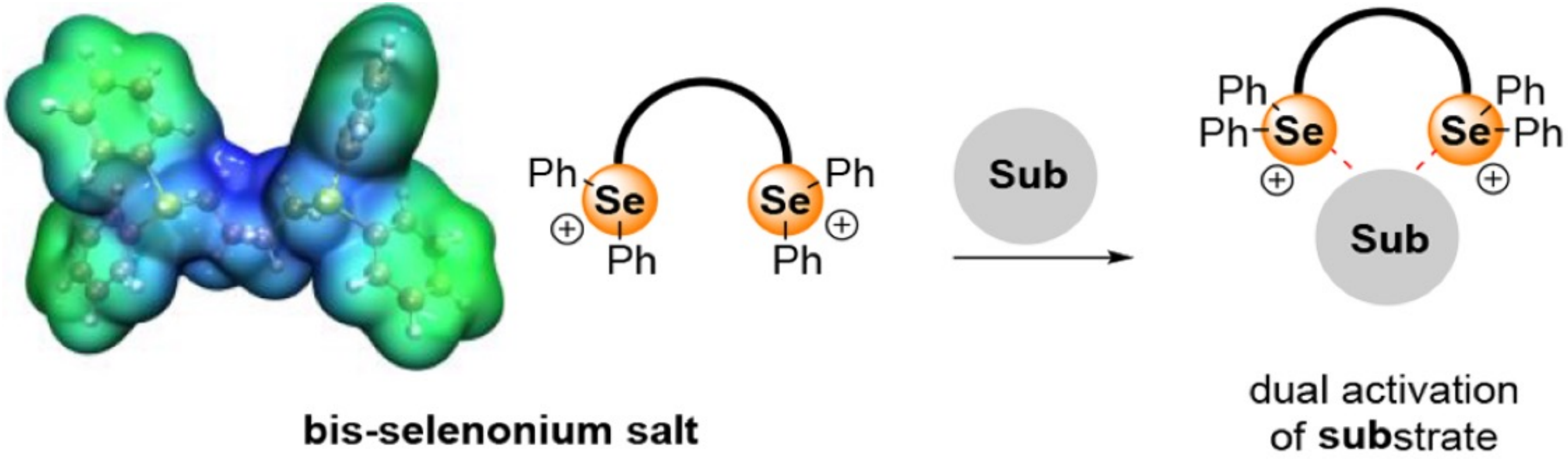
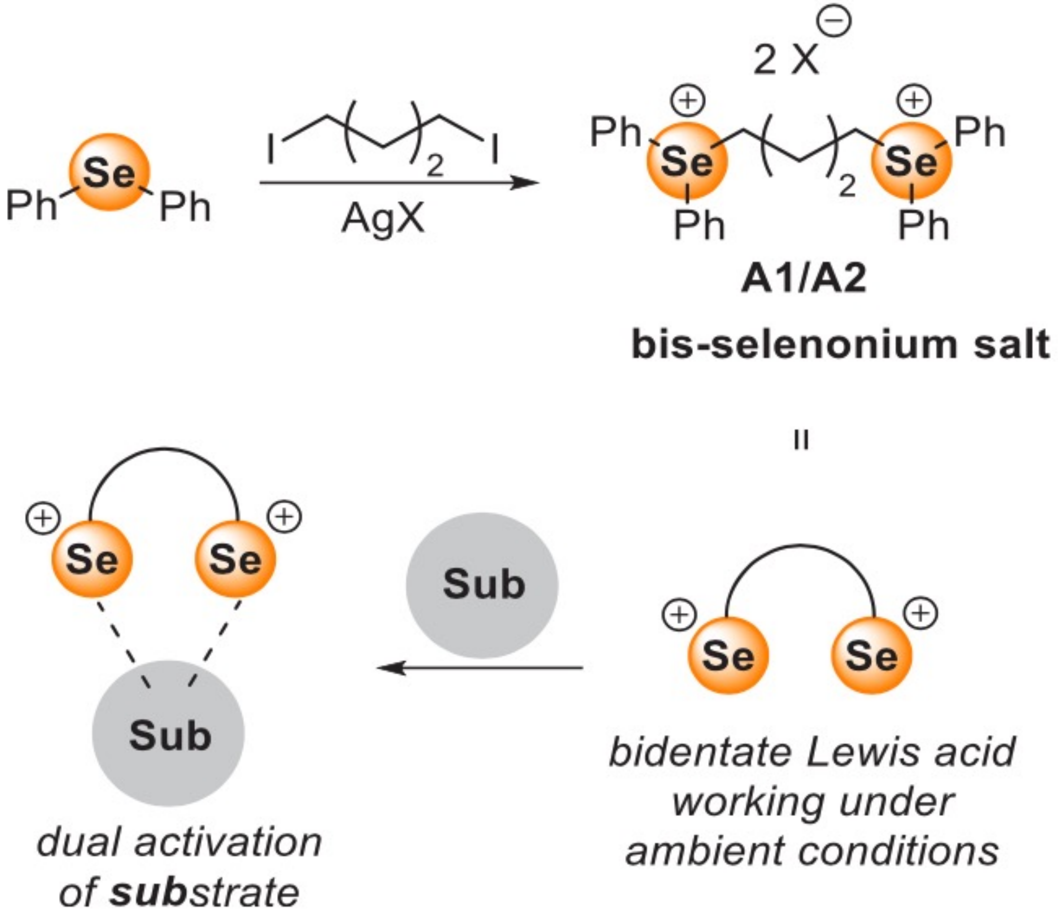
Bis-selenonium Cations as Bidentate Chalcogen Bond Donors in Catalysis



Applications: aza-Diels Alder reaction, Diels-Alder reaction, aromatic halogenation, halolactonization, haloetherification

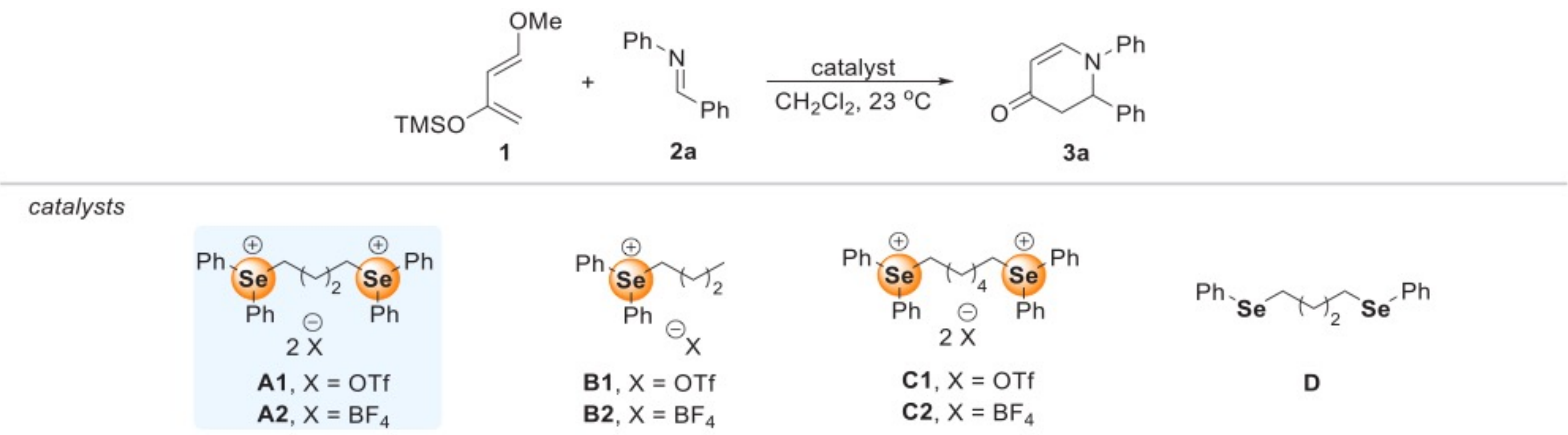
Xinxin H.; Xinyan W. et al., *ACS Catal.,* **2021**, 11, 12632

Bis-selenonium Cations as Bidentate Chalcogen Bond Donors in Catalysis



Xinxin H.; Xinyan W. et al., *ACS Catal.*, **2021**, 11, 12632

Analysis of the bis-selenonium catalyst in aza-Diels–Alder reaction



1 + **2a** → **3a**

A1, X = OTf
A2, X = BF_4

B1, X = OTf
B2, X = BF_4

C1, X = OTf
C2, X = BF_4

D

catalyst comparison

entry	catalyst	time (h)	yield (%)
1	**A1** (2 mol%)	1	99[a]
2	**A1** (1 mol%)	3	99
3[b]	**A1** (2 mol%)	1	90
4	**B1** (4 mol%)	1	37
5	**C1** (2 mol%)	1	77
6	**A2** (2 mol%)	1	11
7	**B2** (4 mol%)	1	<2
8	**C2** (2 mol%)	1	8
9	**D** (2 mol%)	3	0
10	$n\text{Bu}_4\text{N}^+\text{TfO}^-$ (4 mol%)	1	0

effect of pyridine inhibitor

entry	catalyst	pyridine	time (h)	yield (%)
11	**A1** (2 mol%)	-	1	99
12	**A1** (2 mol%)	4 mol%	1	60
13	**A1** (2 mol%)	4 mol%	3	86
14	**A1** (2 mol%)	4 mol%	5	90
15	$BF_3 \cdot OEt_2$ (10 mol%)	-	1	73
16	$BF_3 \cdot OEt_2$ (10 mol%)	10 mol%	1	24
17	$BF_3 \cdot OEt_2$ (10 mol%)	10 mol%	3	24
18	$BF_3 \cdot OEt_2$ (10 mol%)	10 mol%	5	25

Xinxin H.; Xinyan W. et al., *ACS Catal.*, **2021**, 11, 12632

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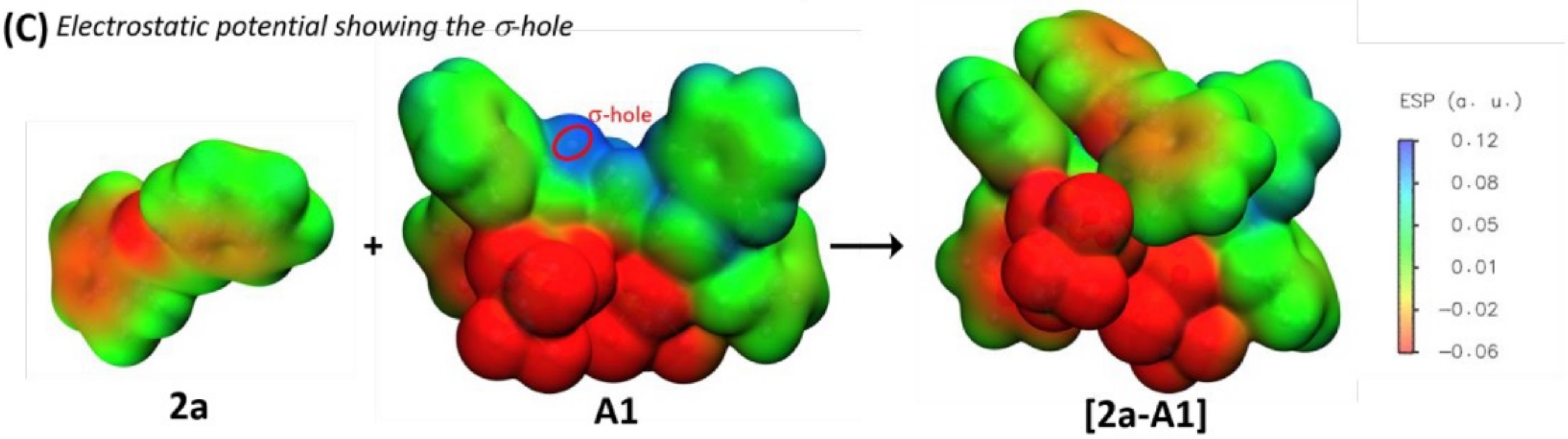

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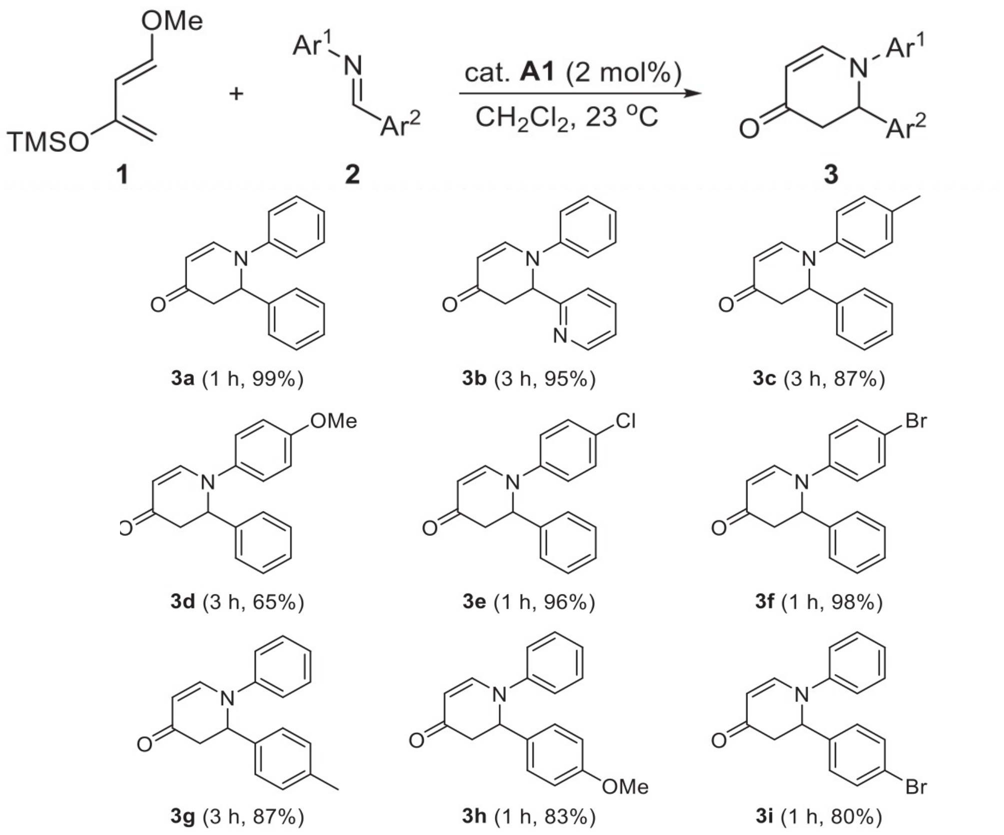

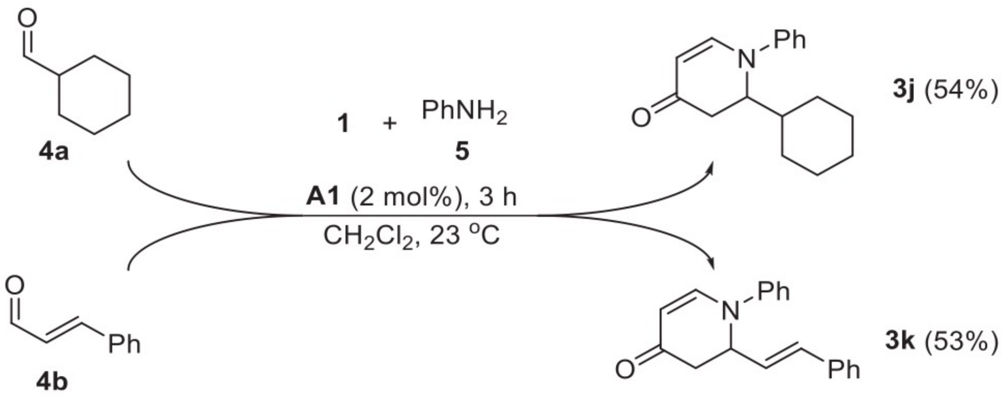

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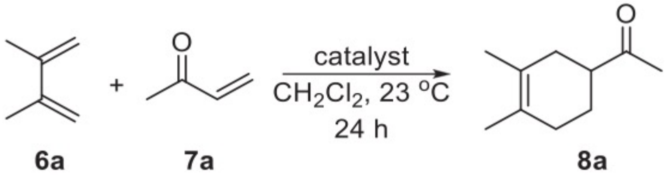
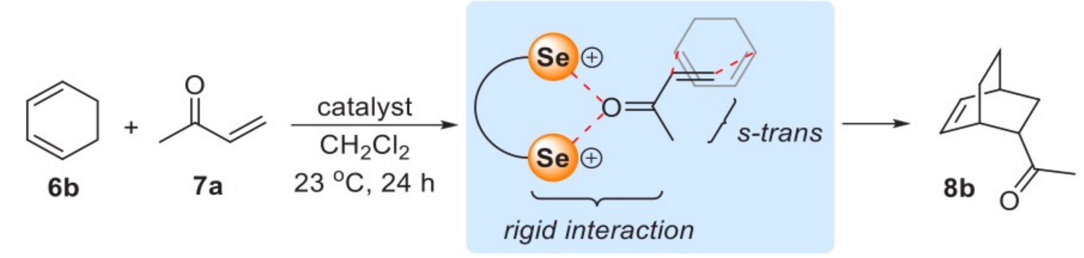
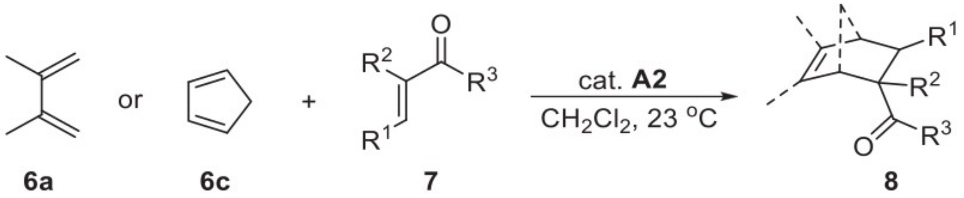
Analysis of the bis-selenonium catalyst in Diels–Alder reaction



entry	catalyst	yield (%)
1	-	0
2	**A1** (2 mol%)	30
3	**A2** (2 mol%)	50
4	**A2** (5 mol%)	84
5	**D** (2 mol%)	0
6	**B2** (2 mol%)	10
7	**B2** (4 mol%)	21



catalyst	yield	endo:exo
nil	0%	NA
A2 (5 mol%)	67%	20:1
B2 (40 mol%)	11%	1:1
C2 (20 mol%)	39%	3:1



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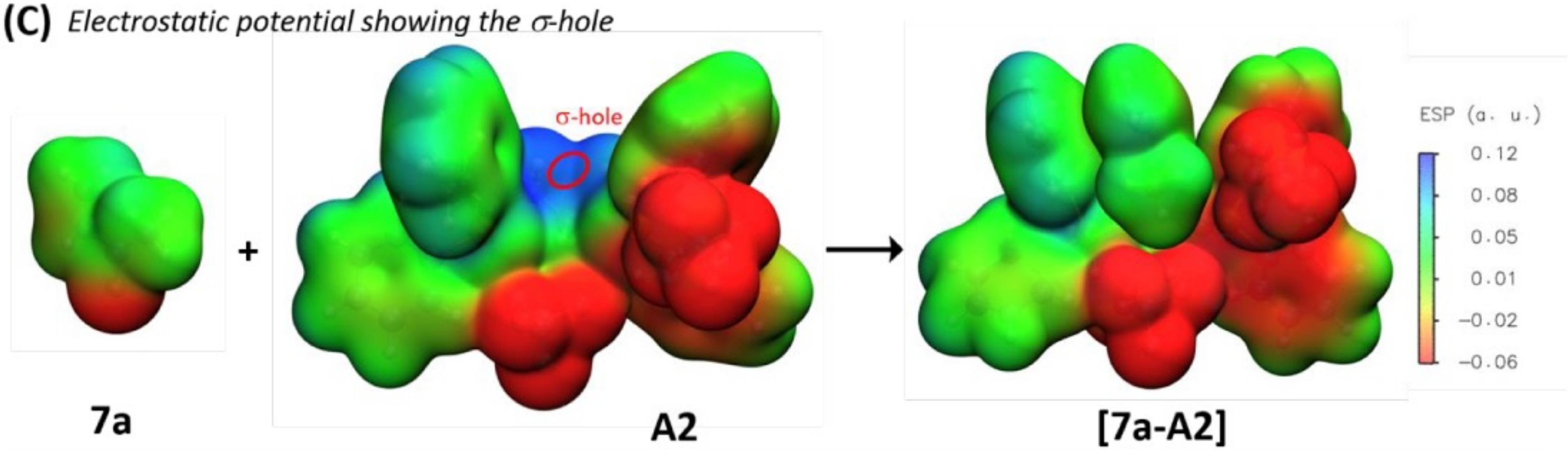
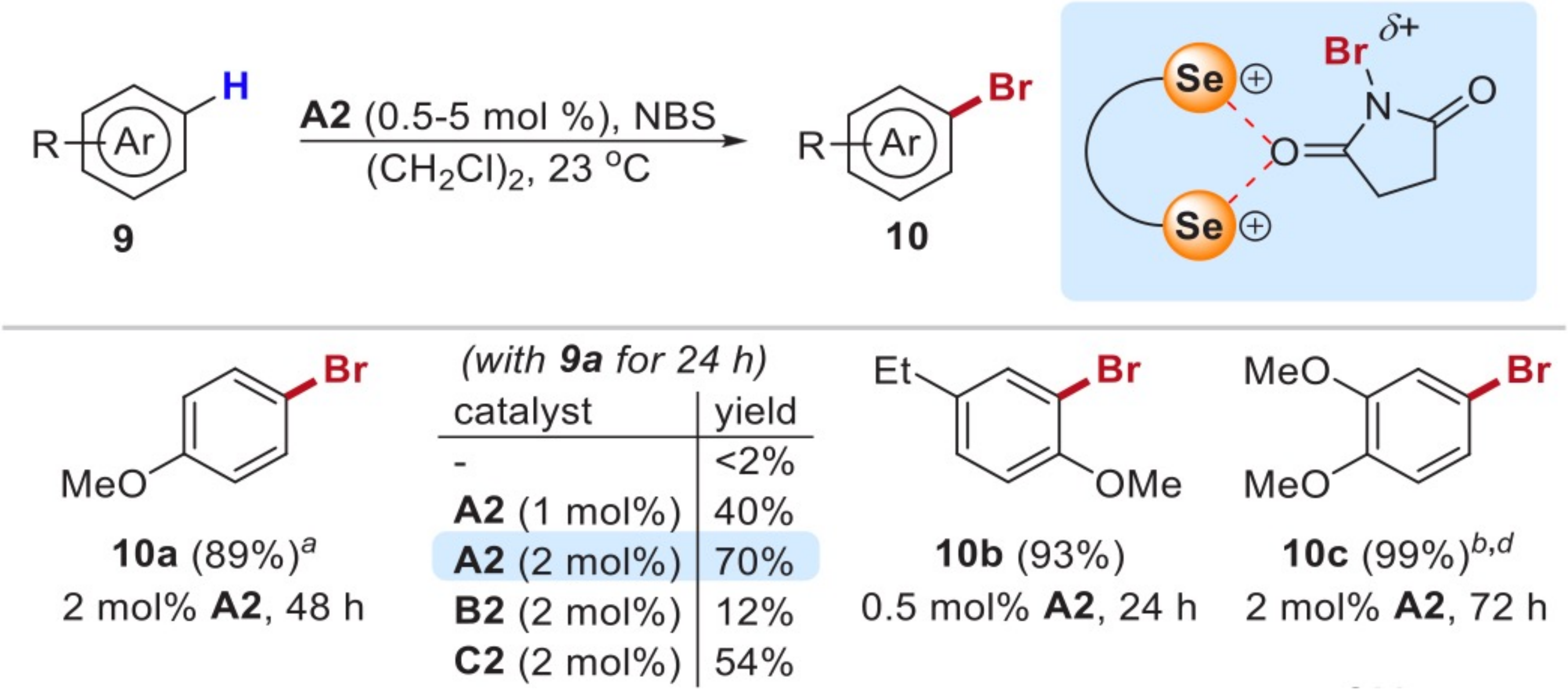
Analysis of the bis-selenonium catalyst in Diels–Alder reaction



Xinxin H.; Xinyan W. et al., *ACS Catal.*, **2021**, 11, 12632

Analysis of the bis-selenonium catalyst in bromination reactions



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10a (89%)^{a}
2 mol% **A2**, 48 h

*(with **9a** for 24 h)*

catalyst	yield
-	<2%
A2 (1 mol%)	40%
A2 (2 mol%)	70%
B2 (2 mol%)	12%
C2 (2 mol%)	54%

10b (93%)
0.5 mol% **A2**, 24 h

10c (99%)^{b,d}
2 mol% **A2**, 72 h

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◇ **Summary**

Summary

- Rational applications of chalcogen bonding have mostly only started to appear in the last two decades or so.
- Chalcogen bonding has by now been used very successfully for the construction of nanoscale materials.
- Chalcogen bonding has been proven to be a powerful tool to rigidify reagents or intermediates and thus to enable highly stereoselective reactions.
- Different monodentate or bidentate neutral or cationic chalcogen-bond donors have now been applied in anion recognition and transport as well as in organic synthesis.