Cluster Preface: Organosulfur and Organoselenium Compounds in Catalysis

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Received: 01.08.2019
Accepted: 01.08.2019
Published online:

Sulfur and selenium are group 16 elements (chalco-
gen). While organosulfur and organoselenium compounds have been recognized as useful reagents in synthetic organ-
ic chemistry since the 1970s, the use of organosulfur/sele-
nium in catalysis has emerged in recent years. Catalysis plays a central role in modern synthetic chemistry. Thus, significant efforts have been devoted to the development of various catalytic protocols in the past decades. For catalyst structure design, oxygen, nitrogen and phosphorus are employed as the constitutional elements in many circumstanc-
es. For example, amines are frequently used as Lewis bases in organocatalysis and as ligands in transition-metal catal-
ysis. Chalcogenides, including sulfides and selenides, are a separate class of Lewis base. The relatively soft Lewis basic nature of organosulfur and organoselenium compounds leads to interesting catalytic performance as compared with hard Lewis bases such as amines. As a result, research efforts to explore the chemistry of organosulfur and organoselenium compounds as organocatalysts and ligands for transition metals in various catalytic processes have received considerable attention from the scientific community.

Unlike oxygen, which is also a group 16 element, sulfur and selenium are multivalent in nature. As a result, they have fruitful chemistry in catalytic oxidation reactions. Other than applications as Lewis bases, using organochalco-
gen as soft Lewis acids through chalcogen bond interaction has been studied in biological systems and in crystal engineering. This interaction has emerged as a new tool in catalytic organic reactions in the past few years.

Despite the usefulness of organosulfur/selenium compo-
unds as catalysts, the odor of sulfur and selenium re-
agents and inefficient classical preparation procedures are obstructions in this research field. As a result, the develop-
ment of more efficient and preferentially odorless method-
ologies to introduce C–S and C–Se bonds is highly relevant to boosting the progress of organochalcogen catalysis.

In this SYNLETT Cluster, we are delighted to feature 11 important contributions dedicated toward different themes and concepts related to organosulfur/selenium catalysis. These endeavors include the development of new reactions and efficient methods for the preparation of chalcogen compounds, as well as a mechanistic study.

Lewis basic chalcogen-catalyzed electrophilic functional-
izations of olefinic substrates are very useful reactions which allow the rapid construction of structurally complex cyclic molecules in a single chemical operation. Halogen and chalcogen electrophilic reagents have been widely uti-
лизов. The resulting cyclized products are valuable building blocks of biologically relevant molecules. In addition, the halogen/chalcogen functionalities can easily be manipul-
ed to give various derivatives. Some new catalytic protocols for electrophilic cyclizations are reported in this Cluster, in-
cluding catalyst-controlled regio- and stereoselective bromo-
laconitzation of stilbene-type carboxylic acids with chi-
ral bifunctional sulfides (S. Shirakawa)1 and enantioselect-
ive halo-/selenocyclization of olefinic acids with C2-
symmetric sulfur-based catalysts, which gave rise to
a range of normal- and medium-sized cyclic lactones (S. Kumar). A detailed study of the kinetic profiles for polyene sulfenocyclizations catalyzed by Lewis basic selenides has provided very useful information on the mechanistic aspects of such transformations (S. E. Denmark).

Organoselenium compounds are stable at various oxidation states and have been utilized as catalysts in several oxidation reactions. Benzene selenenic acid, which is generated in situ from diphenyl diselenide, was found to be effective in catalyzing the oxidative degradation of benzoins into benzoic acids with hydrogen peroxide as the stoichiometric oxidant (H. Cao and X. Zhang). Diphenyl diselenide could also be oxidized by NFSI to generate phenylselenyl fluoride in situ, which effectively catalyzed aza-Wacker reactions of olefinic hydrazones and oximes to give isoquinolinium imides and an isoquinoline N-oxide, respectively (X. Zhao).

Other than small molecules, the synthesis of polyanilines through the organoselenium-catalyzed oxidation of anilines is reported (L. Yu and Q. Xu).

Compared to Lewis base catalysis, using organochalcogens as acid catalysts (π-acids and σ-hole catalysts) are less studied. Nonetheless, the use of chiral organoselenium compounds as π-acid catalysts for enantioselective iminolactonization is reported (K. Maruoka and T. Hashimoto). The use of sulfur- and selenium-based bidentate cationic chalcogen bond donors to catalyze the reduction of quinolines (through σ-hole interactions) is also described (S. M. Huber).

Other than being organocatalysts, organosulfur compounds can serve as ligands for transition-metal catalysis. A report on using chiral-sulfonamide-based olefin ligands for the rhodium-catalyzed enantioselective addition of glyoxylate with arylboronic acids is reported (M.-H. Xu).

Some efficient methods to introduce sulfur and selenium to build catalyst scaffolds are also presented in this Cluster. Dialkyl diselenides are useful catalysts for various oxidation reactions. However, classical preparation methods often rely on malodorous starting materials such as selenols. The odorless reagent sodium selenosulfate, which can readily be synthesized from sodium sulfite and elemental selenium, has been utilized in the synthesis of various dialkyl diselenides (L. Yu and X. Jiang). The formation of C-S bonds typically requires harsh conditions and an elevated temperature. Alternatively, photocatalytic electrophilic benzothialation to give benzothiazoles and direct C-H selenylation of indoles are reported (J. L. Gustafson).

The important contributions clearly showcase that the research field of organosulfur and organoselenium catalysis is dynamic and ever-growing. I am very grateful to all the distinguished scientists who have contributed to this SYNLETT Cluster.

Y.-Y. Yeung, Hong Kong, June 2019

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