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Mechanistic Insights into Transition Metal Catalysis Mediated by Functionalized Organochalcogen Compounds

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Abstract: *Functionalized organ chalcogen compounds containing sulfur (S), selenium (Se), and tellurium (Te) have emerged as highly important substrates, ligands, intermediates, and catalytic modifiers in modern transition-metal-mediated organic synthesis. Their distinctive electronic properties, variable oxidation states, soft donor characteristics, and ability to form strong yet reactive metal–chalcogen bonds provide unique opportunities for controlling catalytic activity and selectivity.*

Keywords: Organ chalcogen compounds; transition-metal catalysis; organosulfur; organ selenium; organotellurium; oxidative addition; reductive elimination.

I. INTRODUCTION

Transition-metal catalysis has revolutionized synthetic organic chemistry by providing efficient pathways for the formation of carbon–carbon and carbon–heteroatom bonds. Among heteroatom-containing molecules, organochalcogen compounds occupy a particularly important position because sulfur, selenium, and tellurium exhibit distinctive electronic and coordination properties. Functionalized organochalcogen compounds are widely encountered in pharmaceuticals, biologically active molecules, advanced materials, ligands, and synthetic intermediates. Their application in catalysis has expanded considerably because transition metals can activate C–S, C–Se, Se–Se, S–S, and C–Te bonds under comparatively mild reaction conditions.

The chemistry of organochalcogen compounds is strongly influenced by the soft and polarizable nature of the heavier chalcogen atoms. Sulfur, selenium, and tellurium can coordinate effectively with soft transition metals, including Pd, Pt, Rh, Ru, Cu, Ag, Au, and Ni. Such coordination can either promote catalytic transformations or inhibit them. This dual behavior represents one of the central mechanistic characteristics of organochalcogen-mediated catalysis.

The development of transition-metal-catalyzed C–S, C–Se, and C–Te bond-forming reactions has provided efficient alternatives to traditional multistep synthesis. Cross-coupling and atom-economic addition reactions are two major approaches in this area, while mechanistic studies have become essential for improving catalyst efficiency, selectivity, sustainability, and substrate compatibility.

Recent research has also demonstrated the importance of direct C–H chalcogenylation. Transition-metal-promoted conversion of relatively inert Csp^3–H bonds into C–S and C–Se bonds provides a valuable strategy for late-stage functionalization and molecular diversification. However, the low polarity and high bond strength of unactivated Csp^3–H bonds make mechanistic control particularly challenging. Thus, understanding the interaction between the transition-metal center and functionalized organochalcogen compounds is essential for the rational design of improved catalytic systems.

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II. FUNDAMENTAL TRANSITION-METAL–CHALCOGEN INTERACTIONS

The interaction between a transition metal and a chalcogen atom is governed by orbital overlap, electron donation, back-donation, and the soft–soft affinity between the metal and chalcogen donor. Organosulfur, organoselenium, and organotellurium ligands can donate electron density from the lone pair of the chalcogen atom to an electron-deficient metal center.

In many catalytic systems, coordination is the first stage of substrate activation. The coordinated organochalcogen compound becomes electronically polarized, thereby weakening a C–E or E–E bond and facilitating further transformation. In other cases, strong coordination produces stable metal–chalcogen species that act as catalyst resting states or even deactivate the catalyst.

Oxidative addition of organochalcogen bonds to low-valent transition-metal centers is frequently a key mechanistic step. Metal complexes can cleave E–E or C–E bonds to generate metal–chalcogen intermediates that subsequently participate in transmetalation or reductive elimination. Mechanistic evidence has demonstrated the formation of dinuclear palladium complexes containing bridging sulfur or selenium ligands, illustrating the strong structural influence of chalcogen coordination.

III. OXIDATIVE ADDITION AS A KEY MECHANISTIC STEP

Oxidative addition is one of the most important elementary processes in transition-metal catalysis. In a typical catalytic cycle, a low-valent metal center, such as Pd(0), interacts with an organochalcogen substrate and undergoes cleavage of a C–X or E–E bond.

A simplified representation is:

$LnM^{0} + R–E–E–R \rightarrow LnMII(E–R)_2$

where E = S, Se, or Te.

The oxidative addition step generally increases the oxidation state and coordination number of the metal. The resulting metal–chalcogen complex may undergo transmetalation with an organoboron or organometallic reagent, followed by reductive elimination to generate the desired functionalized organochalcogen product.

The efficiency of oxidative addition depends on:

1. The oxidation state of the metal.
2. The electron-donating ability of ancillary ligands.
3. The strength of the C–E or E–E bond.
4. Steric properties of the substrate.
5. Solvent and temperature.
6. Electronic effects of functional groups.

Palladium-catalyzed transformations frequently rely on oxidative addition, particularly in cross-coupling chemistry. Nickel can also activate relatively strong bonds and offers an attractive alternative because of its lower cost and diverse oxidation-state chemistry.

IV. TRANSMETALATION AND CHALCOGEN TRANSFER

After oxidative addition, the catalytic cycle may involve transmetalation. This process transfers an organic group from one reagent to the transition-metal center. Organoboron compounds are particularly useful because boronic acids and boronic esters are relatively stable and compatible with many catalytic systems.

The general sequence can be represented as:

$$Ar–B(OH)_2 + LnM(E–R)X \rightarrow LnM(Ar)(E–R) + \text{Boron by-product}$$

The resulting mixed aryl–chalcogen metal intermediate then undergoes reductive elimination to form a new carbon–chalcogen bond.

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Transition-metal-catalyzed reactions involving organoboron reagents have been widely developed for the synthesis of sulfides, selenides, and tellurides. Metals including Cu, Ag, Pd, Fe, In, Rh, and Ni have been reported for such C–S, C–Se, and C–Te bond-forming reactions.

The mechanism of transmetalation is influenced by the nature of the chalcogen ligand. Strongly coordinating thiolate or selenolate species may stabilize the metal center but can also slow ligand exchange. Therefore, the rate of transmetalation frequently determines the overall catalytic efficiency.

V. REDUCTIVE ELIMINATION AND PRODUCT FORMATION

Reductive elimination is generally the product-forming step in many transition-metal-catalyzed cross-coupling reactions. Two ligands attached to the metal center combine to form a new covalent bond, while the metal undergoes reduction.

For example:

$$LnMII(Ar)(SeR) \rightarrow Ar–SeR + LnM^{0}$$

The reductive elimination process regenerates the active low-valent catalyst. The rate of this step depends on the relative orientation of the organic and chalcogen ligands, steric congestion, metal oxidation state, and ancillary ligand properties.

Electron-rich ligands may accelerate reductive elimination in some catalytic systems by destabilizing high-coordinate intermediates. Conversely, excessively strong metal–chalcogen interactions can inhibit product release and generate inactive species.

Therefore, successful catalyst design requires a balance between sufficient metal–chalcogen interaction for substrate activation and sufficiently weak interaction to allow catalyst turnover.

Table 2. Major Mechanistic Steps in Transition-Metal-Catalyzed Organochalcogen Reactions

Mechanistic Step	Description	Role of Functionalized Organochalcogen Compound	Catalytic Consequence
Coordination	Chalcogen atom binds to metal	Acts as substrate or ligand	Activates substrate or modifies catalyst
Oxidative addition	C–E or E–E bond cleavage	Generates metal–chalcogen intermediate	Initiates catalytic transformation
C–H activation	Metal activates a C–H bond	Chalcogen may stabilize intermediate	Enables direct chalcogenylation
Transmetalation	Organic group transfers to metal	Metal–chalcogen complex undergoes ligand exchange	Forms coupling intermediate
Migratory insertion	Unsaturated molecule inserts into metal–ligand bond	Chalcogen-containing ligand migrates	Produces new C–C or C–E framework
Radical transfer	Single-electron pathway forms radical intermediate	Chalcogen-centered radical participates	Enables alternative reactivity
Reductive elimination	New bond forms and catalyst is regenerated	Releases organochalcogen product	Completes catalytic cycle
Catalyst poisoning	Stable metal–chalcogen species forms	Excessively strong coordination	Reduces catalytic turnover

VI. C–H ACTIVATION AND DIRECT CHALCOGENYLATION

Direct C–H functionalization represents an important advancement in organochalcogen synthesis because it reduces the need for prefunctionalized starting materials. Transition metals can activate aromatic or aliphatic C–H bonds and subsequently introduce sulfur or selenium-containing groups.

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A general catalytic pathway involves:

C–H activation → Metal–carbon intermediate → Chalcogen transfer → Reductive elimination

The first stage may proceed through concerted metalation–deprotonation, oxidative addition, electrophilic metalation, or radical hydrogen abstraction depending on the catalyst and reaction conditions.

Recent studies have highlighted transition-metal-promoted direct Csp^3–H chalcogenylation as an important route for the formation of C–S and C–Se bonds. However, achieving high chemo-, site-, and enantioselectivity remains difficult because unactivated Csp^3–H bonds are relatively inert.

Direct C–H chalcogenylation offers important advantages, including atom economy, reduced synthetic steps, late-stage functionalization, and rapid molecular diversification.

VII. MIGRATORY INSERTION AND ADDITION TO UNSATURATED BONDS

Transition metals can catalyze the addition of organochalcogen compounds across carbon–carbon double and triple bonds. In these reactions, a metal–chalcogen or metal–carbon intermediate undergoes migratory insertion with an alkene or alkyne.

The simplified pathway may be represented as:

M–E + C≡C → M–C–C–E

Subsequent protonation, reductive elimination, or reaction with another coupling partner yields the final organochalcogen product.

Such reactions are potentially atom-efficient because both components can be incorporated directly into the final molecule. Historically, sulfur- and selenium-containing compounds were often considered catalyst poisons because of their strong coordination with transition metals. Nevertheless, mechanistic studies have shown that carefully designed catalytic systems can convert these interactions from inhibitory processes into productive catalytic pathways.

This change in mechanistic understanding has significantly expanded the use of organosulfur and organoselenium compounds in transition-metal-mediated addition reactions.

VIII. CATALYST POISONING AND METAL–CHALCOGEN DEACTIVATION

Catalyst poisoning is a major challenge in organochalcogen chemistry. Sulfur, selenium, and tellurium are capable of binding strongly to many transition-metal centers. If the resulting metal–chalcogen complex is excessively stable, it can remove the active catalyst from the catalytic cycle.

Common poisoning pathways include:

1. Formation of stable metal thiolates.
2. Generation of metal selenolates.
3. Bridging chalcogen ligands between two metal centers.
4. Formation of insoluble metal sulfides or selenides.
5. Aggregation of metal nanoparticles.
6. Irreversible occupation of active coordination sites.

However, not all strong metal–chalcogen interactions are detrimental. Some represent catalytically competent intermediates or resting states. A major objective of mechanistic research is therefore to distinguish between productive and nonproductive metal–chalcogen species.

Modern analytical techniques such as NMR spectroscopy, X-ray crystallography, mass spectrometry, kinetic analysis, and computational chemistry are increasingly used to identify catalyst resting states and determine the actual active catalytic species.

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IX. ROLE OF FUNCTIONALIZED ORGANOCHALCOGEN LIGANDS

Functionalized organosulfur, organoselenium, and organotellurium compounds can act as ligands rather than merely substrates. These ligands influence catalytic activity by altering the electron density, coordination geometry, steric environment, and stability of the transition-metal center.

Selenium-containing ligands have been incorporated into complexes of Pd, Ru, Rh, Ir, Ni, Cu, Ag, Au, Bi, and Fe and have been investigated in numerous catalytic transformations. Their coordination properties make them useful for tuning catalyst structure and reactivity.

Similarly, molecular complexes containing organosulfur, organoselenium, and organotellurium ligands have been investigated as homogeneous catalysts for Suzuki coupling. The identity of the chalcogen donor, ligand-binding mode, temperature, substrate structure, and metal center can significantly influence catalytic performance.

Table 3. Influence of Organochalcogen Ligands on Catalytic Performance

Ligand Property	Mechanistic Effect	Expected Catalytic Outcome
Strong σ-donation	Increases electron density at metal	Facilitates oxidative addition in some systems
Soft donor ability	Stabilizes soft metal centers	Improves catalyst stability
Steric bulk	Controls coordination environment	Enhances selectivity and reduces aggregation
Hemilabile coordination	Allows reversible metal binding	Promotes ligand exchange
Chelation	Stabilizes catalytic intermediates	May improve turnover frequency
Excessively strong binding	Produces inactive metal complexes	Causes catalyst poisoning
Redox-active functionality	Enables electron-transfer processes	Facilitates radical pathways

X. RADICAL AND SINGLE-ELECTRON MECHANISMS

Not all transition-metal-mediated organochalcogen reactions proceed through classical two-electron mechanisms. Copper, iron, cobalt, nickel, and photocatalytic systems can participate in single-electron-transfer pathways.

A possible sequence includes:

1. Oxidation or reduction of the organochalcogen precursor.
2. Formation of a chalcogen-centered radical.
3. Addition of the radical to an alkene, alkyne, or aromatic system.
4. Formation of a carbon-centered radical intermediate.
5. Metal-mediated oxidation, reduction, or coupling.
6. Product formation.

The increasing use of visible-light-assisted methods has expanded the mechanistic possibilities available for organochalcogen synthesis. Recent photocatalytic approaches have been developed for constructing C–S and C–Se bonds under comparatively mild conditions, with relevance to sustainable synthesis and reduced dependence on stoichiometric oxidants.

Radical pathways are particularly valuable when conventional oxidative addition is difficult or when highly reactive C–H bonds require activation.

XI. SUSTAINABILITY AND GREEN CATALYTIC APPROACHES

Current research increasingly focuses on sustainable organochalcogen synthesis. Important strategies include:

1. Use of earth-abundant metals.
2. Reduction of precious-metal loading.
3. Direct C–H functionalization.
4. Atom-economic addition reactions.
5. Recyclable heterogeneous catalysts.
6. Nanocatalysis.
7. Photocatalysis.

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8. Mild reaction conditions.
9. Safer chalcogen sources.

Recent reviews of transition-metal-catalyzed C–S, C–Se, and C–Te bond formation emphasize the importance of catalyst efficiency, reduced catalyst loading, cost reduction, environmental considerations, and mechanistic understanding in the development of improved catalytic systems.

The mechanistic knowledge gained from these studies allows the design of catalysts that minimize inactive metal–chalcogen species while maximizing productive turnover.

X. APPLICATIONS IN ORGANIC SYNTHESIS AND MATERIALS CHEMISTRY

Functionalized organochalcogen compounds produced through transition-metal catalysis have broad applications in medicinal chemistry, materials science, and molecular electronics.

Organoselenium compounds are important because selenium-containing structures can exhibit significant biological activity and can also serve as intermediates for further functionalization. Organosulfur compounds occur extensively in pharmaceuticals and biologically active molecules. Organotellurium compounds, although less widely used, possess distinctive reactivity and electronic properties that make them useful in advanced synthesis.

Transition-metal-mediated methodologies also enable the construction of complex molecular frameworks through cross-coupling, multicomponent reactions, direct C–H functionalization, and late-stage derivatization. Multicomponent strategies incorporating chalcogen atoms provide additional opportunities for rapid generation of molecular complexity.

Table 4. Mechanistic Challenges and Future Opportunities

Challenge	Mechanistic Cause	Future Opportunity
Catalyst poisoning	Strong metal–chalcogen coordination	Design of hemilabile ligands
Low Csp^3–H reactivity	Strong and nonpolar C–H bonds	Directed activation and radical pathways
Poor selectivity	Multiple reactive sites	Ligand-controlled and asymmetric catalysis
High precious-metal use	Dependence on Pd, Rh and Ru	Fe, Ni, Cu and Co catalysis
Intermediate instability	Reactive metal–chalcogen species	In situ spectroscopic monitoring
Limited mechanistic evidence	Complex catalyst speciation	Combined kinetic and computational studies
Tellurium toxicity concerns	Handling and environmental limitations	Safer tellurium-transfer reagents
Difficult catalyst recycling	Homogeneous catalyst loss	Heterogeneous and nanocatalytic systems

XI. CONCLUSION

Functionalized organochalcogen compounds have become highly valuable components of transition-metal-catalyzed synthetic chemistry. Their catalytic behavior is governed by a complex interplay between metal–chalcogen coordination, oxidative addition, transmetalation, migratory insertion, C–H activation, radical transfer, and reductive elimination. The strong affinity of sulfur, selenium, and tellurium for transition metals represents both an opportunity and a challenge. Productive coordination can activate substrates and stabilize reactive intermediates, whereas excessively strong binding can generate catalyst resting states or irreversible catalyst poisoning.

Mechanistic investigations have demonstrated that efficient organochalcogen catalysis requires careful control of metal oxidation state, ligand properties, substrate electronics, steric effects, and reaction environment. Palladium remains a major catalyst for cross-coupling, while nickel, copper, iron, rhodium, ruthenium, silver, and gold offer complementary mechanistic pathways. Direct C–H chalcogenylation, atom-economic addition reactions, photocatalysis, and earth-abundant metal catalysis represent particularly promising directions for future research.

Overall, mechanistic understanding provides the foundation for rational catalyst design. Continued integration of experimental kinetics, spectroscopy, structural characterization, and computational chemistry will enable the development of more selective, efficient, economical, and sustainable transition-metal catalytic systems based on functionalized organochalcogen compounds.

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