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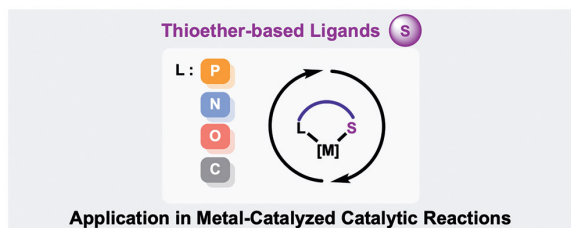
Recent Progress in Developing Thioether-Containing Ligands for Catalysis Applications

Stéphane Bellemin-Laponnaz^a 

Thierry Achard^b 

^a Institut de Physique et Chimie des Matériaux de Strasbourg
UMR 7504 - Université de Strasbourg & CNRS, 23 rue du Loess,
67034 Strasbourg, France
bellemin@unistra.fr

^b Institut des Sciences Moléculaires de Marseille UMR 7313 - Aix
Marseille Université, CNRS, Centrale Marseille, 52 Av. Escadrille
Normandie Niemen, 13013 Marseille, France
thierry.achard@univ-amu.fr



Abstract The ligand that stabilizes the metal center is crucial to its catalytic activity. Historically dominated by phosphorus and nitrogen, sulfur has long been little considered as a hetero element for stabilizing a potentially active metal center. However, this situation is changing and we are seeing more and more examples that incorporate this element. This review provides an overview of recent transition-metal-catalyzed reactions with ligands containing neutral sulfur groups, i.e. thioethers. A selection of examples published since 2013 illustrates the diversity of applications of thioether-containing ligands and shows that sulfur should be more widely used in the development of homogeneous catalysis.

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Key words Homogeneous catalysis, S,N ligands, S,P ligands, S,NHC ligand, S,O ligands, thioether ligands

1 Introduction

Many homogeneous catalytic reactions rely on an active species combining the right metal with a carefully designed or serendipitously found organic ligand. It became clear early on in the development of this field that the molecular architecture and the choice of the heteroatoms that will interact with the metal are crucial for the catalytic activity of the metal. In 1966, Wilkinson's seminal paper demonstrated the feasibility of homogeneous hydrogenation of alkenes using $\text{RhCl}(\text{PPh}_3)_3$ as a catalyst precursor.¹ The mechanism of the Rh catalyst was reasonably well-understood, showing



Stéphane Bellemin-Laponnaz is CNRS Research Director at IPCMS (CNRS – University of Strasbourg). His research focuses on fundamental and applied aspects of transition metal chemistry for catalysis, materials chemistry, and medicinal chemistry.

Thierry Achard is CNRS Researcher at ISm2 (CNRS – University of Aix-Marseille). His research focuses on the development of new synthetic methodologies via ligand synthesis and transition metal catalysis, as well as bioorganic and medicinal chemistry.

the importance of the phosphine ligands binding the metal and its ability of stabilizing a variety of metal oxidation states. This step has been crucial to the development of homogeneous catalysis in general and enantioselective catalysis in particular, particularly through the development of bidentate ligands.² Researchers rushed to develop ligands with atoms from the 5th column of the periodic table (N,P) because they form metal–ligand bonds that are sufficiently stable to generate well-defined catalysts.

Sulfur-based ligands have always been much less considered because they have much less donor and acceptor character compared to phosphorus. In addition, the presence of two lone pairs induces the formation of diastereomeric thioether complexes, which can interconvert and disrupt catalytic processes. One exception is sulfur in a higher

oxidation state, i.e. sulfoxide, which has undergone a period of steady development since the pioneering work of James et al.³ and has been recently reviewed.⁴

Despite these unfavorable points, ligands containing sulfur with a low degree of oxidation, generally in combination with another heteroatom, are proving capable of generating interesting catalysts and reviews have covered this field in the past few decades,⁵ with a particular focus on asymmetric catalysis.^{6,7} One of the advantages of combining a sulfur atom with another heteroatom is to give a class of ligand, potentially bidentate, that combines a strong and a weak donor. Merging the different electronic and steric properties of these heteroatoms is a powerful way of controlling reactivity and stereoselectivity, if required.

The aim of this article is to illustrate recent examples in which the presence of a thioether group has been shown to be crucial in the ligand scaffold. This paper is not intended to be exhaustive, but to give examples of enantioselective and non-enantioselective reactions reported since 2013, in order to demonstrate the remarkable progress made with this type of scaffold. We will not discuss here systems containing thiols as ligands, which have also been of particular interest in recent years.⁸

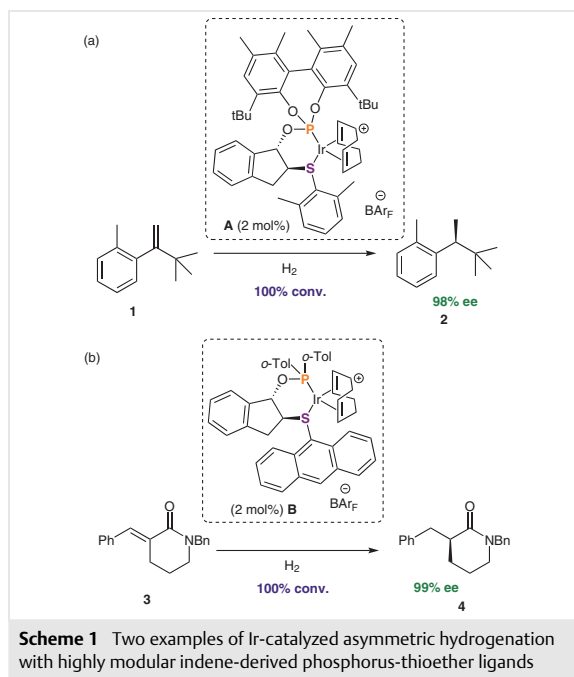
The paper is organized according to the type of heteroatom (or atom) that accompanies the thioether function. Here, we present catalytic reactions supported by P-S, N-S, O-S, and C-S ligands, where the sulfur is neutral (i.e. thioether function), which may lead to some lability.

2 Phosphorus-Thioether Ligands

The development of ligands combining phosphorus with another heteroatom began with the undeniable success of the P-oxazoline ligands, first reported in 1993.^{6,9} As early as 1996, Pregosin,¹⁰ followed by Evans a few years later,¹¹ demonstrated the benefits of combining phosphorus and sulfur in palladium-catalyzed alkylation reactions. In asymmetric catalysis, these ligands have proved most interesting for alkylation and hydrogenation reactions. This area has been reviewed recently by Diéguez and co-workers.^{7f} The most remarkable scaffolds used recently in these systems often involve chiral diphenyl-atropisomers with a chiral amino-thioether.

Phosphite/phosphinite thioether ligands can be synthesized very easily in just a few steps and are stable solids in air. They offer a highly modular architecture that makes it easy to optimize performance for a given substrate. Compared to functionalized olefins, the hydrogenation of unfunctionalized substrates is more challenging. Diéguez and co-workers showed that chiral phosphite/phosphinite thioether/iridium systems are excellent systems for such challenging substrates.¹² Scheme 1 displays two selected examples.¹³ In Scheme 1a, the unfunctionalized trisubstituted substrate **1** is fully converted into the corresponding alkane

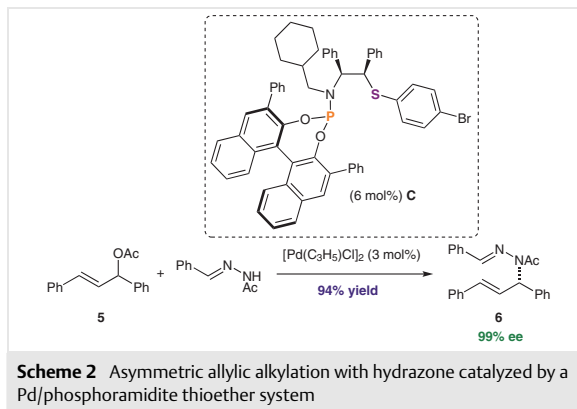
2 in 98% ee using 2 mol% of Ir catalyst **A**. The excellent enantioselectivity is the result of the judicious combination of a chiral biphenyl moiety and an indene-based chiral thioether. Scheme 1b displays the hydrogenation of cyclic α,β -unsaturated enone **3** which gave the expected product **4** in quantitative yield with 99% ee. The iridium catalyst **B** is a phosphinite-indene-based thioether ligand with no chirality at the phosphorus moiety. The design of modular ligands that are easy to assemble is an effective strategy for optimizing the desired result. The most interesting phosphite/phosphinite thioether ligands are often based on binaphthyl, biphenyl, mannitol, or tartaric acid derivatives as the chiral entities.¹⁴



Scheme 1 Two examples of Ir-catalyzed asymmetric hydrogenation with highly modular indene-derived phosphorus-thioether ligands

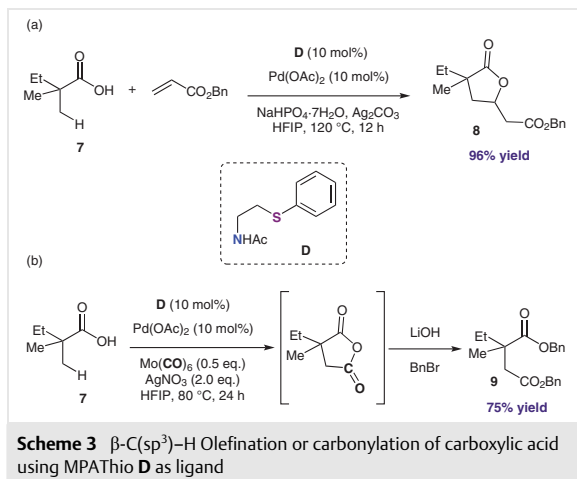
Scheme 2 displays an example of a phosphoramidite thioether palladium complex **C** that has been applied to the asymmetric *N*-allylic alkylation of hydrazone with success.¹⁵ The P,S ligand was also built on a strategy of a rational combination of two well-established scaffolds into one molecule. This protocol constitutes a general and efficient approach for several important *N*-allylated hydrazones. The use of this type of ligand is still very popular for Pd-catalyzed alkylation reactions, as recent references show.¹⁶

Spiro PNS chiral tridentate ligands (SpiroSAP) were also developed by Q. L. Zhou's group for the iridium-catalyzed asymmetric hydrogenation of β -alkyl- β -keto esters.¹⁷ SpiroSAP ligands containing an aryl thioether group gave the product β -alkyl- β -hydroxy esters with a good 84% ee, however the highest enantioselectivities (95–99.9% ee) were obtained with the 1,3-dithiane sulfur group.



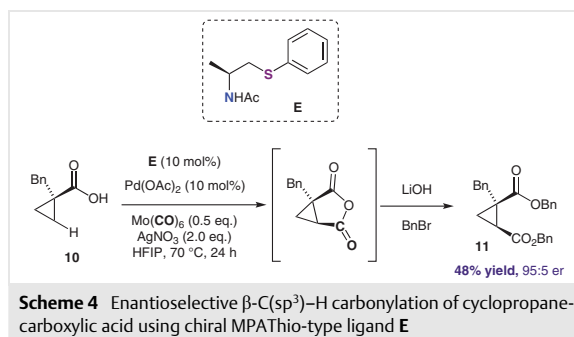
3 Nitrogen-Thioether Ligands

Among all the recent developments involving nitrogen-thioether ligands, monoprotected aminoalkyl thioethers (MPATHio) have demonstrated their usefulness and versatility in C(sp³)-H activation reactions. In 2018, Yu and co-workers developed a new family of thioether ligand that effectively promotes β -C(sp³)-H olefination of free carboxylic acids.¹⁸ The strategy relies on the combination of a monodentate directing group and a bidentate ligand to enable the activation reaction. Scheme 3a displays the direct reaction of 2,2-dimethylbutyric acid (**7**) with benzyl acrylate to give the corresponding γ -lactone **8**. The screening of ligands showed that bidentate ligands combining the NHAc and thioether functions exhibit good activity, with ligand **D** being the ligand of choice. The scope of the reaction in the presence of **D** was established on a large number of substrates and the synthetic utility was also demonstrated by

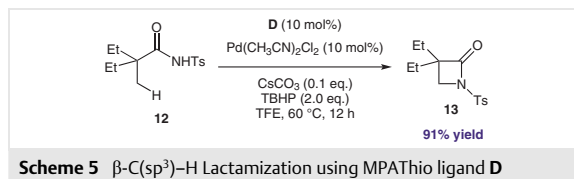


converting the γ -lactone into synthons of interest. The replacement of the acrylate by Mo(CO)₆, which is a convenient solid source of CO, offers the opportunity to induce a direct carbonylation of the substrate (Scheme 3b).¹⁹ After hydrolysis and protection with benzyl, the corresponding diester **9** was obtained in 75% yield from substrate **7**.

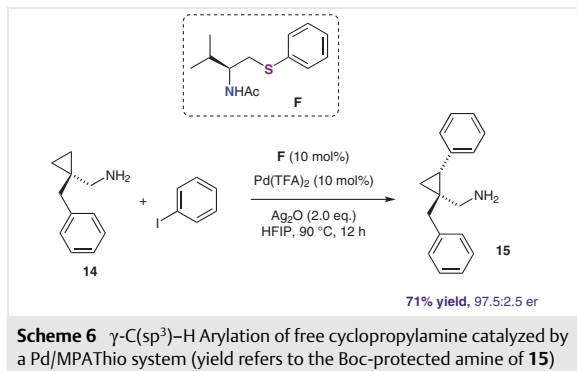
The protocol was also extended to the enantioselective carbonylation of cyclopropanecarboxylic acids (Scheme 4). The ligand of choice was the alanine-derived MPATHio ligand **E**, where a range of cyclopropane derivatives were tested affording good enantioselectivities (up to 96:4 er) with moderate yields.¹⁹



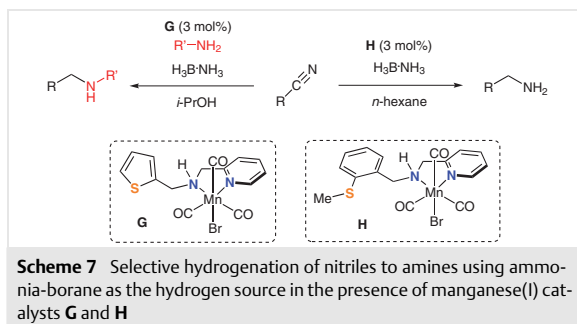
The same group also investigated the direct β -lactamization of aliphatic amides using the same catalytic system Pd/MPATHio system (Scheme 5).²⁰ The authors pointed out that this reaction offers many advantages over other C-H activation protocols, low cost of the oxidant, air and humidity tolerance, and reliable scalability in particular, which makes this reaction highly practical.



Such Pd(II) catalysts bearing a chiral thioether ligand also enable the direct functionalization of free aliphatic amines, which are challenging substrates for metal-catalyzed C-H functionalization reactions.²¹ Here, the bidentate coordination mode of the ligand and the thioether motif favors the formation of a mono(amine)-Pd(II) intermediate, thus enabling the enantioselective C-H functionalization. Addition of an aryl iodide engages the intermediate in a Pd(II)/Pd(IV) catalytic cycle giving the arylated product **15** (Scheme 6). The mechanism has been confirmed by DFT and experimental investigations.²² Alternatively, enantioselective carbonylation or olefination of the free aliphatic amine may be possible via a Pd(II)/Pd(0) catalytic cycle.

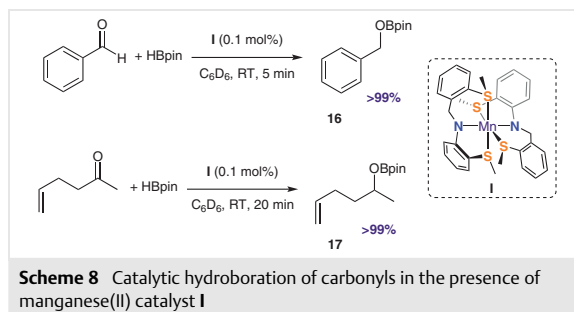


The Maji group reported, in 2021, a manganese(I) catalyst for the transfer hydrogenation of nitriles where ammonia-borane is used as the source of hydrogen. A thioether moieties in the ligand provides a hemilabile donor which may stabilize coordinatively unsaturated intermediates in the catalytic cycle. The final amine is either primary or secondary amine, the selectivity can be controlled by the ligand structure and the experimental conditions (Scheme 7).²³ A mechanistic study revealed that the dehydrogenation of ammonia-borane probably took place via an outer-sphere pathway, whereas the hydrogenation of nitrile adopted an inner-sphere hydrogen transfer.

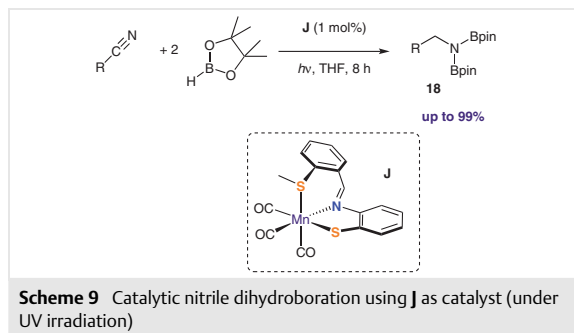


[SNS] Pincer-type ligands were used to stabilize manganese(II) that were tested in the hydroboration reaction. It was found that the paramagnetic Mn complex **I** is an efficient catalyst for the hydroboration of aldehydes and ketones with pinacolborane (HBpin) as reagent, at low catalyst loading and reaction times.²⁴ As shown in Scheme 8, the products **16** and **17** were obtained in quantitative yield under these conditions. Several mechanistic studies were carried out on the system, highlighting the importance of the hemilability of the thioether groups in ensuring catalytic activity and the stability of intermediates during the catalytic cycle. Interestingly, the active species does not involve a Mn-H intermediate but an inner-sphere pathway with coordination of the carbonyl to the Mn center and amido activation of the B-H function.

Pincer ligand [SNS] have also been used with zinc to produce valuable catalysts for the same hydroboration reactions, in which the active species is a zinc alkoxide complex.²⁵

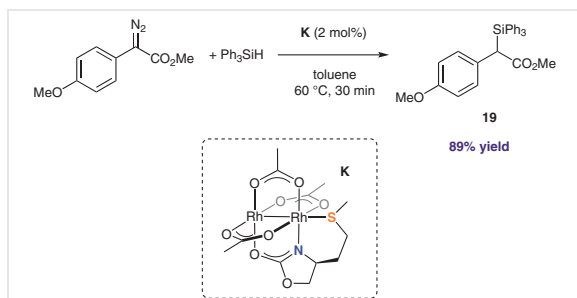


Such metal-ligand cooperativity was next extended to manganese(I) complexes with a ligand that combines thioether, imine, and thiolate donors (complex **J**, Scheme 9). The Mn complex catalyzes the dihydroboration of nitrile under UV irradiation and quantitatively yields the corresponding *N,N*-diborylamine product **18**.^{24b,26} Mechanistic studies and DFT calculations revealed the crucial role of the ligand in this exceptional activity: the weak field donor properties of the ligand allow the metal to access a low-energy (high spin) intermediate, the thiolate allows activation of the borane and the hemilability of the thioether enables facile rearrangement of the ligand around the metal. The same ligand was coordinated to copper(I) together with an *N*-heterocyclic carbene ligand, and this system proved effective in hydrosilylation and hydroboration of aldehydes or ketones.²⁷ However, a recent mechanistic study shows that the sulfur ligand is rapidly released during catalysis, generating [CuH(NHC)]₂ as the active species.²⁸



Dirhodium(II) complexes are well-established to generate reactive carbenoid species from α -diazo carbonyl reagents, which can then promote a large variety of organic

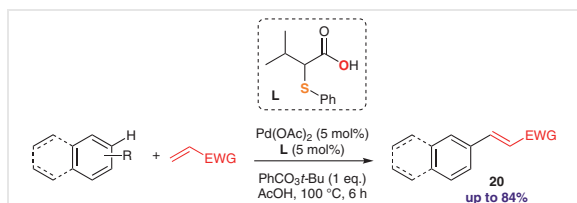
transformations.²⁹ Recently, Darko and co-workers investigated the incorporation of a thioether moiety into carboxylate or carboxamidate ligands used to stabilize such dinuclear species and found that the yields were improved in cyclopropanation reactions.³⁰ They next extended the concept to develop more efficient catalysts for silyl-hydrogen insertion into carbenoids, such as Scheme 10, achieving yields up to 89% for compounds such as **19**.³¹



Scheme 10 Rhodium-catalyzed Si-H insertion to carbene

4 Oxygen-Thioether Ligands

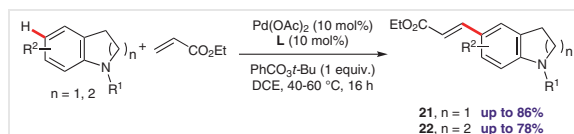
Oxygen-thioether ligands have also shown their effectiveness in catalysis either through neutral or anionic oxygen donor functions. Fernández-Ibáñez and co-workers have recently developed a new class of thioether carboxylates, to overcome the deactivation of the palladium catalyst by too strong coordination of its two picolinic acid ligands during C-H acetoxylation reactions.³² Combined with Pd(OAc)₂, S,O-ligands are able to promote nondirected C-H functionalization reactions of electron-rich and electron-poor arenes by olefins with high yields (ligand **L**, Scheme 11). The optimization of the ligands showed that the bidentate ligands carrying an aliphatic chain in the α -position and a thioether function S-Ph present the best activity, the ligand **L** being the most effective. One of the main advantages of these ligands is that they can be easily prepared at the gram scale in just two steps from commercial carboxylic acids. The authors point out that the olefination reaction occurs preferentially at the most electron-rich position of the arene (product **20**). A mechanistic study revealed that the C-H cleavage is the RDS in both cases with and without



Scheme 11 Palladium-catalyzed C-H olefination of arene

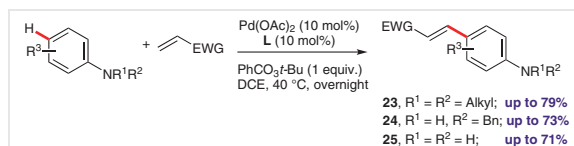
S,O-ligand. Several monomeric Pd/S,O complexes were isolated before and after the C-H activation step, and mass spectroscopy studies suggest that the S,O-ligand triggers the formation of more active Pd cationic species.³³

Subsequently, indoline and tetrahydroquinoline substrates were also found to be suitable and they were efficiently olefinated in products **21** and **22** under mild reaction conditions in the presence of ligand **L**.³⁴ Remarkably, olefination occurs at position C5 for indoline and C6 for tetrahydroquinoline with high selectivity >20:1 for both substrates (ligand **L**, Scheme 12).



Scheme 12 Selective palladium-catalyzed C-H olefination of indoline and tetrahydroquinoline

In 2019, Fernández-Ibáñez and co-workers described the first efficient *para*-selective C-H olefination of aniline derivatives promoted by a Pd/**L** ligand.³⁵ The reaction proceeds smoothly with high efficiency, selectivity, and wide substrate scope (ligand **L**, Scheme 13). Mono-, di-, and tri-substitution of tertiary, secondary, or primary anilines has been shown to be highly compatible with this catalytic system, even with electron-withdrawing groups. The primary and secondary anilines lead almost exclusively to the *para* products **23–25** and only a few traces of *ortho* product are observed. The authors mentioned that the lack of reactivity observed for *ortho*-substituted *N,N*-dialkylanilines is due to a loss of nucleophilicity of aniline caused by steric repulsion between the *ortho*-substituent and the *N*-methyl group of *N,N*-dimethylaniline which forces the nitrogen to twist out of plane with the aromatic ring.

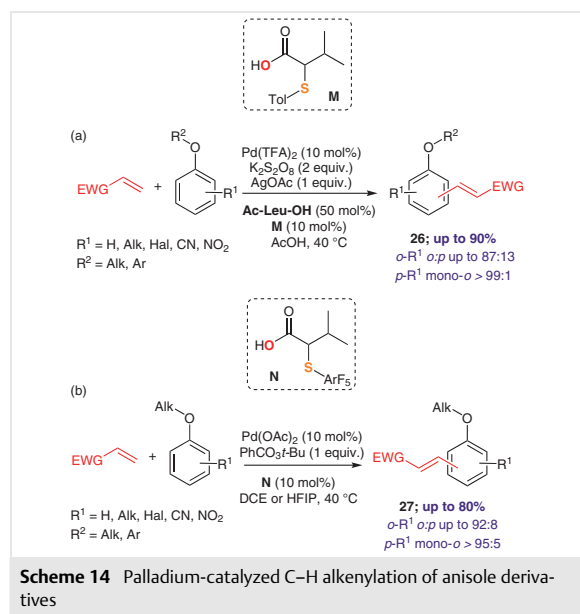


Scheme 13 *para*-Selective Pd-catalyzed C-H olefination of anilines

This catalytic system was also found to promote the C-H acetoxylation and allylation reaction of benzene with moderate yields and low selectivity of β -hydride elimination.^{32,36}

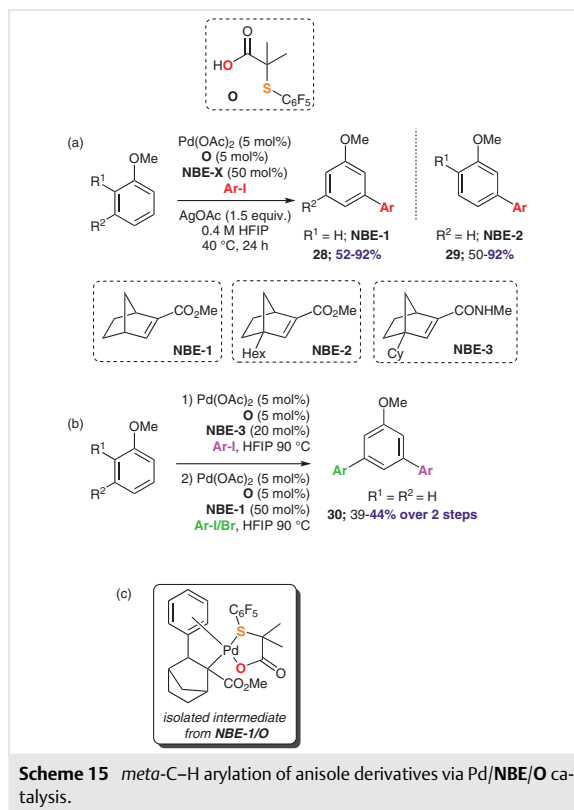
In 2020, the group of Qing Zhu reported a Pd/dual ligand catalytic system for the C-H alkenylation of aryl ethers.³⁷ The best combination involved the presence of a monoprotected amino acid *N*-acetyl-leucine **Ac-Leu-OH** and the S,O ligand **M** (Scheme 14a). This system allows the formation of alkenylated products **26** in good yields and with a wide

range of substrates, including alkyl aryl ethers and cyclic aryl ethers (2,3-dihydrobenzofuran). Interestingly, *para*-substituted anisole leads to functionalization of only one *ortho* position. Immediately after, Fernández-Ibáñez and co-workers improved this procedure by a small modification of the S,O ligand (a pentafluorobenzyl group is attached to the sulfur atom, ligand **N**) which made it possible to carry out this reaction without Ag oxidant and extra ligand, at low temperature and with an extended scope (Scheme 14b).³⁸ *ortho*-Substituted anisoles gave the olefin products **27** in good yields and with site selectivities favoring the *para*-product, the HFIP solvent was crucial in obtaining high *para* selectivity with electron-withdrawing groups.

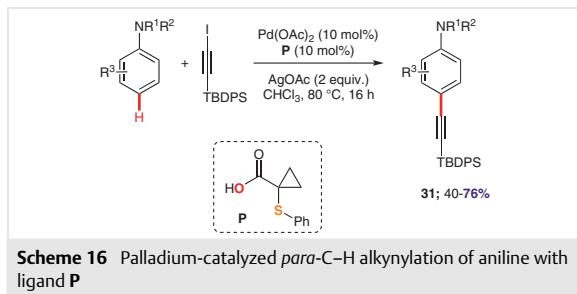


This electron-depleted sulfur trick was also found to be crucial in promoting the *meta*-C–H arylation reaction of anisole derivatives which is highly challenging.³⁹ This result is quite remarkable due to the high challenge of functionalizing an electron-deficient position. The system involves a cooperative palladium/norbornene/SO catalysis in a Catellani-like reaction,⁴⁰ using only a catalytic amount of modified norbornene (NBE-X). 3-Substituted alkoxyarenes provide high yields of the desired *meta*-arylated products **28** even with electron-withdrawing substituents, but in this case **NBE-CONHMe** (bearing an amide group), was used instead of **NBE-1** (ligand **O**, Scheme 15a). By simple steric tuning of norbornene partner, *ortho*-substituted alkoxyarenes are fully arylated in **29** bypassing the standard *ortho* constraint by using **NBE-2**. Unsymmetrical terphenyls **30** have been successfully synthesized via unprecedented se-

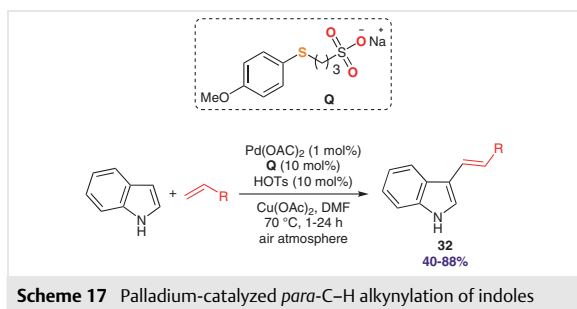
quential double monoarylation of alkoxyarenes, in a one-pot procedure (ligand **O**, Scheme 15b) using appropriate modified **NBEs**. Mechanistic investigations point out that C–H activation and NBE insertion are not rate-limiting steps. The authors were able to isolate and fully characterize both neutral and anionic palladium intermediate **NBE-1/O** (Scheme 15c for the neutral intermediate).



Once again, fine tuning of the thioether carboxylic acids structure enable the nondirected *para*-selective C–H alkylation of aniline derivatives.⁴¹ In the presence of Pd(OAc)₂ and ligand **P**, the products **31** were obtained with moderate yields but with complete *para*-selectivity, the other regioisomers were not observed (Scheme 16). Fernández-Ibáñez and co-workers showed that *meta*-substituted *N,N*-dibenzylanilines lead to the same reactivity as the unsubstituted tertiary aniline. *ortho*- and Disubstituted *N*-benzylanilines are also suitable substrates and better results were obtained for anilines bearing electron-withdrawing groups. This procedure was successfully applied to pyrrolidine, morpholine derivatives, and to bioactive spiro-tetrahydroquinoline substrates.

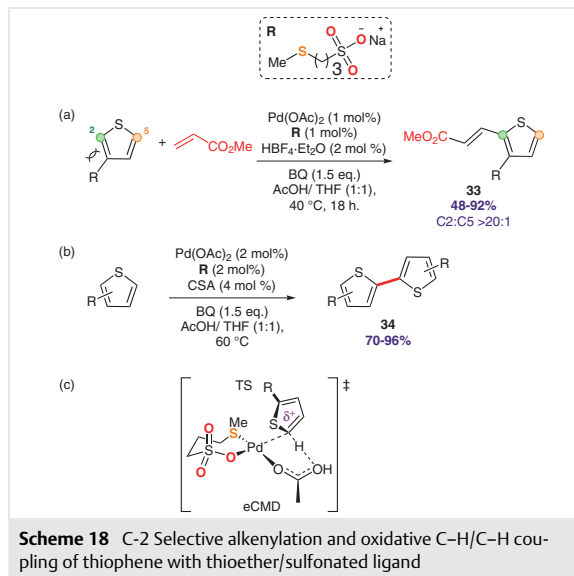


The Carrow group reported an anionic thioether ligand, that contains a sulfonate group as a second anchor, in the Pd-catalyzed C–H alkenylation of indoles (ligand **Q**, Scheme 17).⁴² With indole substrates, C–H alkenylation proceeds easily and takes place at the C3 position, giving 3-alkenylin-dole product **32** in good yields. The use of ligand **Q** strongly accelerated the reaction compared to ligand-free system and this was attributed to the change from a neutral to a cationic pathway induced by the coordination of thioether to Pd.



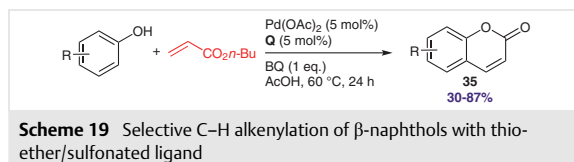
More interestingly, this catalytic system allows an uncommon highly C2-selective alkenylation of thiophene providing **33** products in good yields (ligand **R**, Scheme 18a).⁴² The Carrow group performed extensive mechanistic studies suggesting that *contra*-steric selectivity depends on both the electrophilic nature of Pd(II) (thioether) catalysts and a highly polarized electrophilic concerted metalation–deprotonation (eCMD) transition state that is crucial for cleavage of C–H which favors the more π -basic C2 site (Scheme 18c).^{42,43} C2-Functionalization of 3-substituted thiophenes has also been performed, with good selectivity, by Fernández-Ibáñez using ligand **L**, however this system requires a large amount of AgOAc.⁴⁴

The reactivity of thioether/sulfonated ligand was then extended to the synthesis of oligothiophenes **34** by oxidative coupling producing interesting conjugated organic bricks for optoelectronic applications.⁴⁵ These privileged bi-, α -quart-, and α -sexithiophenes (fluorinated, hindered, with EWG) were obtained with low catalyst loading, in the



presence of benzoquinone (BQ) as oxidant and in the absence of stoichiometric metal promoters (Scheme 18b).

Finally, the **Q**/Pd system was successfully applied to the synthesis of a series of π -expanded coumarins **35** by the selective C–H alkenylation of β -naphthols (Scheme 19). The reaction proceeds under mild reaction conditions, with low catalyst loadings and with high selectivity.⁴⁶

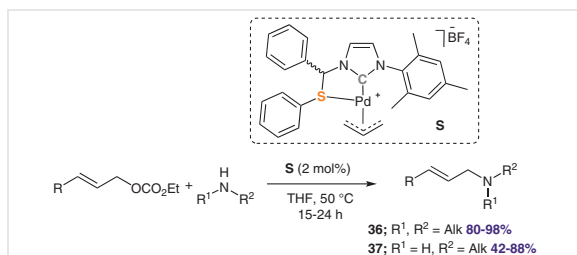


5 NHC-Thioether Ligands

Hybrid N-heterocyclic carbene (NHC) ligands, N-functionalized by a Lewis base, currently constitute a very important class of bidentate ligands.⁴⁷ Although S-functional NHC ligands remain a less exploited family than other heteroelements, they have recently demonstrated their effectiveness in number of metal-catalyzed reactions^{47c,e,48} and in medicinal chemistry.⁴⁹

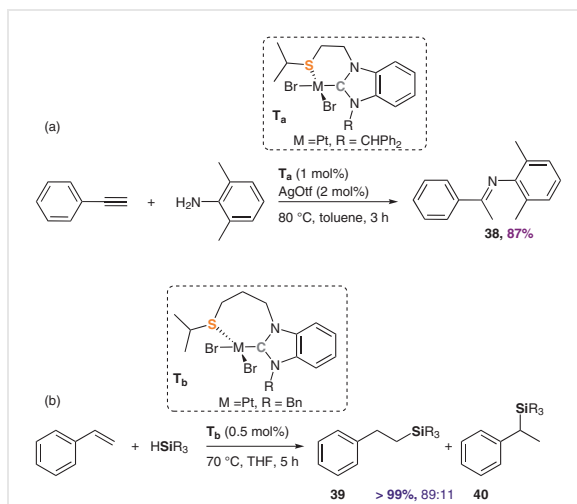
In 2013, Pullarkat and co-workers developed a series of well-defined imidazole-based NHC κ^2 -C,S palladium(II) π -allyl complexes.⁵⁰ They applied the palladium complexes (\pm)-**S** in the allylation reaction of amines with (*E*)-cinnamyl carbonate (Scheme 20). Secondary amines generally give high yields of the corresponding allylated amine products **36**, while primary amines give moderate yields of amines **37**, but high regioselectivity for the *trans*-linear product

was achieved. In the solid state, the sulfur functionalized NHC-Pd π -allyl complex (\pm)-**S** adopts the $\lambda(S_C)$ ring conformation and exists as the single diastereomer (R_S, S_C), in its enantiomerically pure form.



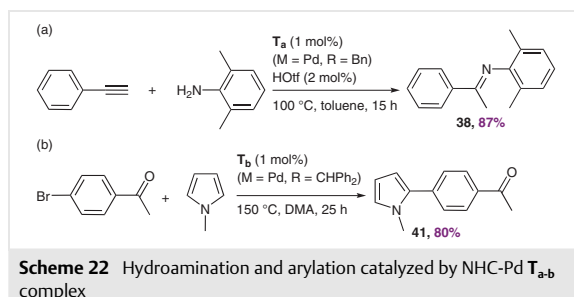
Scheme 20 Allylic amination catalyzed by π -allyl palladium **S** complex

The Huynh group has been very active in the study of the coordination behavior of sulfur-functionalized NHC ligands.⁵¹ Thioether-functionalized benzimidazolium salts are reachable in just three steps and form stable complexes associate to various metals. The hydroamination of phenylacetylene catalyzed by the six-membered κ^2-C,S platynacycle **T_a** proceeds with perfect Markovnikov selectivity, and the enamine formed rapidly tautomerizes to the corresponding imine **38** (Scheme 21a).⁵² The catalytic turnover was enhanced by the presence of a bulky benzhydryl group at the sulfur atom which favors the elimination of the product after the attack of the amine on the activated alkyne. However, for the hydrosilylation of styrene, the seven-membered complex **T_b** proved to be a better catalyst due to, according to the authors, a higher solubility compared to the six-membered catalyst (Scheme 21b).⁵²



Scheme 21 Hydroelementation reactions catalyzed by NHC-Pt **T_{a-b}** complexes

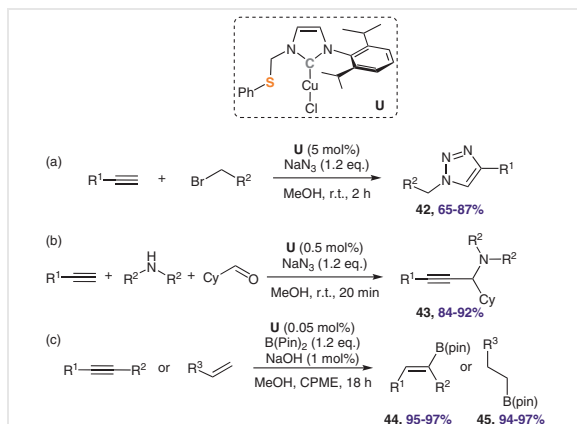
In the presence of a harder palladium center, the thioether group of these NHCs becomes much more hemilabile and these κ^2-C,S complexes exhibit, in solution, a dynamic equilibrium with species involving multiple modes of coordination.⁵³ However, bulkiest group at the N-wing favor the formation, at the solid state, of a dimeric form, in which the thioether moiety and the C_{NHC} coordinate with different metal centers. Complex **T_a** ($R = Bn$) was found to be the best catalyst for the hydroamination of phenylacetylene (Scheme 22a).⁵³ For the direct arylation of 1-methylpyrrole, the highest yields were obtained with complexes containing the bulky benzhydryl group (Scheme 22b). However, the authors mentioned that the slight variation in yield between the different complexes studied is mainly due to the involvement of colloidal palladium via the partial decomposition of the catalyst. We also note that a ligand close to the **T_a** system has been developed for the Suzuki–Miyaura reaction in water.⁵⁴ The heterogenization of the system was also done by immobilizing the catalyst on silica-encapsulated magnetite nanoparticles to develop a filtration-free, magnetically retrievable system.



Scheme 22 Hydroamination and arylation catalyzed by NHC-Pd **T_{a-b}** complex

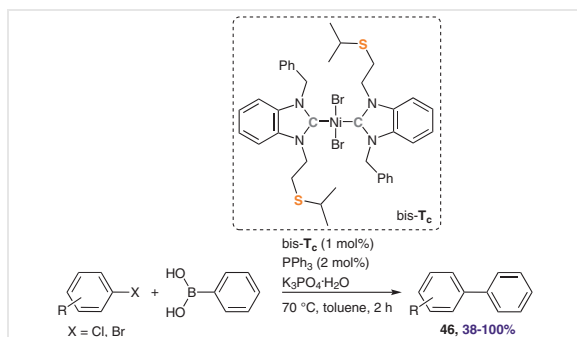
NHC-Thioether ligands were successfully attached, by the Wozniack group, to a copper(I) center but in a κ^1-C coordination mode.⁵⁵ These resulting complexes were then applied in several copper-catalyzed reactions in which the unsaturated **U** complex was found to be the best catalyst (Scheme 23). In Scheme 23a, the three-component click reaction takes place with terminal alkynes, benzyl bromides, and sodium azide, giving almost exclusively the 1,4-disubstituted 1,2,3-triazole products **42**. In contrast, when using substrates with an electron-withdrawing group, perfect regioselectivity was obtained leading to 1,4,5-trisubstituted 1,2,3-triazole products. Complex **U** also promoted the multicomponent A^3 coupling reaction in mild conditions, giving high yields of propargylamine derivatives **43** (Scheme 23b). However, under these conditions, the benzaldehyde substrates failed to generate the expected coupling product. Finally complex **U** was evaluated in the hydroboration reaction of triple and double bonds (Scheme 23c). In cyclopentyl methyl ether (CPME), a selection of alkynes and alkenes provide the desired alkene **44** and alkane **45** products, respectively, in very good yields (93–98%) and with high regi-

oselectivity. Finally, the influence of the hemilability of the thioether group in the mechanism has unfortunately not been addressed for the bis-**Tc** and **U** complexes.



Scheme 23 CuAAC, A³ coupling and hydroboration reactions catalyzed by NHC-Cu **U** complex

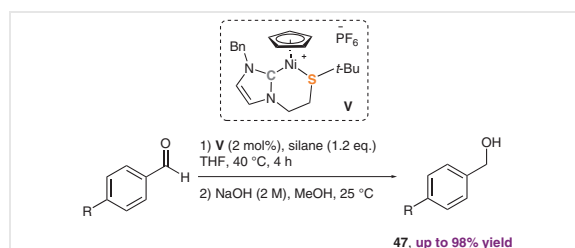
The Suzuki–Miyaura reaction was also successfully promoted by bis-**Tc** (κ^1 -C)-nickel(II) complex (Scheme 24).⁵⁶ In solution, this complex was obtained as an inseparable mixture (1.5:1) of the *trans-syn* and *trans-anti* rotamers. Under optimized conditions, Ar-Br and Ar-Cl were successfully coupled to phenylboronic acid in the presence of triphenylphosphine as an additive. Good yields are obtained for electron-deficient aryl halides, while electron-rich aryl halides are generated with more moderate or even very low yields.



Scheme 24 Suzuki–Miyaura coupling of aryl halides catalyzed by NHC-Ni bis-**Tc** complex

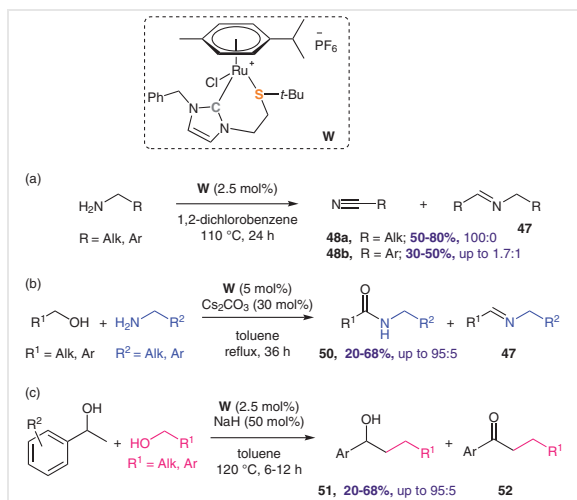
Neutral nickel–N-heterocyclic carbene complexes, (κ^1 -C)-[NiCpBr(NHC-SR)] and cationic (κ^2 -C,S)-[NiCp(NHC-SR)][PF₆]**V** were prepared and well characterized by Rittleing, Achard, Bellemin-Lapponnaz, and co-workers.⁵⁷ These two coordination modes were secured by X-ray diffraction analysis. DFT calculations showed that: (i) for a neutral complex, the coordination of sulfur and the expulsion of bromine atoms is an unfavorable process, (ii) the coordina-

tion of sulfur for cationic complexes is controlled by the coordination power of the solvent, and (iii) a very fast sulfur inversion at room temperature takes place without dissociation for κ^2 -(C,S) complexes. The cationic complex **V** has been identified as the best catalyst for the hydrosilylation of benzaldehydes into benzyl alcohols **47** after hydrolysis (Scheme 25), and it displays a higher reaction rate than its neutral counterpart. The extent of the reaction showed that electron-rich and electron-poor benzaldehydes are well tolerated, giving good to excellent conversions.



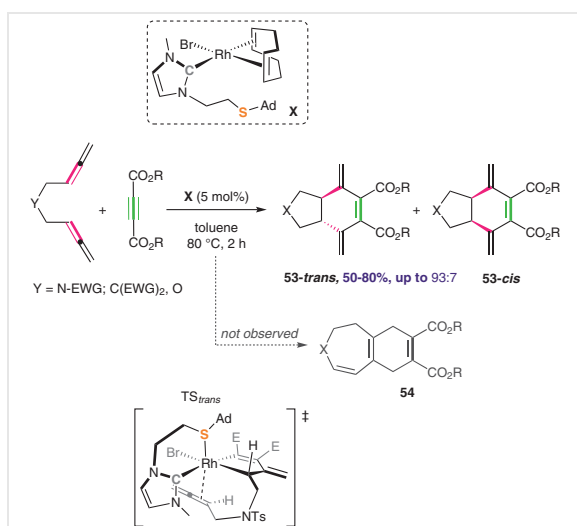
Scheme 25 Hydrosilylation of benzaldehydes catalyzed by Ni-**V** complex

In 2020, Achard, Bellemin-Lapponnaz, and co-workers developed a new class of piano stool cationic ruthenium complexes **W** for acceptorless dehydrogenation reactions (Scheme 26).⁵⁸ These ruthenium complexes displayed a κ^2 -(C,S) coordination mode. Ligand screening showed that imidazolyl-NHC combining the *N*-benzyl wing and the *tert*-butyl thioether group **W** exhibits the highest activity and selectivity towards nitrile **48** for acceptorless double dehydrogenation of primary amine (Scheme 26a).⁵⁸ Remarkably, the reaction proceeds without additional base or oxidant under relatively mild conditions for such transformations. However, this catalyst system only exhibited high selectivity when using aliphatic amines (Scheme 26a). The **W** complex also catalyzed acceptorless dehydrogenative coupling of primary alcohols with primary amines, without an additional ligand, to produce amides **50** (Scheme 26b).⁵⁹ The authors showed that product ratios were sensitive to variations in ligand and substrate structures. Recently, the same catalytic system was successfully applied to the β -alkylation of primary alcohols and secondary alcohols by dehydrogenative coupling (Scheme 26c).⁶⁰ In the presence of sodium hydride, 1° and 2° alcohols generated the coupling products **51** with high selectivity. The scope of the reaction displays full conversions as well as high ratios of the desired β -alcohol (ranging from 90:10 to 97:3) were generally observed, with the exception of benzyl alcohols substituted with electron-withdrawing group (selectivity drop of about 10–15%). Mechanistic studies seem reasonably to involve the classical elimination of β -hydrides to produce carbonyl compounds and thus generate ‘ruthenium hydride species’ followed by a condensation/hydrogen transfer sequence under hydrogen borrowing control.

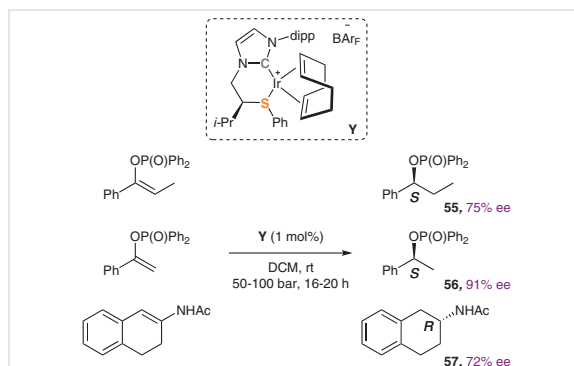


Scheme 26 Acceptorless dehydrogenation and borrowing hydrogen reaction catalyzed by cationic Ru **W** complex

In 2023, within the framework of a collaboration between the Roglans and Bellemin-Laponnaz groups, a Rh(I) complex with hemilabile thioether-functionalized NHC was developed.⁶¹ The rhodium complex **X** catalyzed [2+2+2] cycloaddition of 1,5-bisallenenes and alkynes to form bicyclic *trans*-3,6-dimethylenecyclohex-1-ene *trans*-**53** with high selectivity and good yield (Scheme 27). Noteworthy the cycloisomerization/Diels–Alder cascade product **54** was not observed under these conditions. The reaction scope showed good tolerance for bisallene with $\text{Y} = \text{O, C}$, and N for the latter, the sulfonamide protecting group generated the



Scheme 27 [2+2+2] Cycloaddition between 1,5-bisallenenes and alkynes catalyzed by Rh(I) **X** complex



Scheme 28 Asymmetric hydrogenation of olefins catalyzed by Ir/**Y** thioether

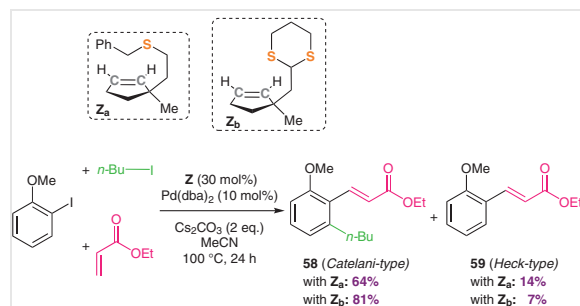
highest cross-selectivity. However, classic terminal alkynes did not react under these conditions. A mechanistic investigation by DFT calculations revealed the pivotal role of the hemilabile character of the sulfur for this remarkable activity and selectivity. The S-adamantyl functionality modulates electron density by facilitating oxidative cyclometallation through its coordination and the final reductive elimination step through its dissociation from the rhodium center.⁶¹ The coordination of the sulfur atom imposes a new geometry for the Rh complex which brings the ligands closer to each other and which will subsequently impose the formation of the *trans*-fused rhodabicyclo intermediate via the transition state TS_{trans} (Scheme 27).

Pàmies, Diéguez, and co-workers developed chiral Ir/thioether-NHC **Y** complexes with a six-membered ($\kappa^2\text{-C,S}$)-chelate and applied them to asymmetric hydrogenation reactions.⁶² Cyclic β -enamides and tri- and disubstituted olefin substrates possessing a good coordination group (enol phosphonate) were totally reduced to give **55–57** with promising ees ranging from 72 to 91% (Scheme 28). However, the high steric constraints imposed by the thioether-carbene backbone are not favorable when considering a more sterically hindered substrate, thus leading to poor asymmetric induction.

6 Cycloolefin-Thioether Ligands

In 2022, Jiao and Zheng describe a new type of thioether-cycloolefin hybrid ligand functioning as a non-innocent ligand in palladium catalysis.⁶³ Hybrid ligands **Z_{a-b}** enable efficient *ipso,ortho*-difunctionalization of iodoarenes via a reversible covalent bond between the substrate and the cycloolefin unit which has been demonstrated by mechanism studies (Scheme 29). Although the alkyl thioether ligand **Z_a** outperformed similar cyclopentene/phosphine ligands, dithiane **Z_b** exhibited the best selectivity, yielding the difunctionalization product **58** in excellent yield and

greatly minimizing Heck product **59**. A wide variety of substituted iodoarene, alkyl electrophile substrate, and terminating reagents have been successfully applied to this catalytic system (up to 40 examples), demonstrating its good tolerance to derivatization.



Scheme 29 ipso,ortho-Difunctionalization of iodoarenes catalyzed by Pd/**Z_s** thioether or Pd/**Z_b** dithiane complex

7 Conclusion

This article discusses the usefulness of the presence of a thioether group in a hybrid ligand for the development of efficient homogeneous metal-catalyzed reactions. Interestingly, despite the fact that the thioether group can generate mixtures of diastereomers upon coordination, S-X (X = P, N, O, C) ligands offer a wide variety of electronic and steric properties that allow them to be adapted to different types of reactions. Here we have presented a selection of recent examples showing that the incorporation of a sulfur into the ligand can produce very interesting homogeneous catalysts. Although the number of examples involving sulfur is still much smaller than its counterparts, interest is clearly growing and we can predict a bright future for sulfur in catalysis.

Conflict of Interest

The authors declare no conflict of interest.

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