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Transition-metal mediated carbon–sulfur bond activation and transformations

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Liandi Wang,[a] Wei He[a] and Zhengkun Yu*[ab]

C–S bond activation, cleavage and transformations by means of transition metal compounds have recently become more and more important in the petroleum industry and synthetic chemistry. Homogeneous transition metal compounds have been investigated in order to provide the fundamental insight into the C–S bond cleavage in problematic organosulfur compounds such as thiophene, benzo- and dibenzothiophene derivatives. Rendering transition-metal mediated reactions with organosulfur compounds catalytic may provide promising routes to deep hydrodesulfurization of petroleum feedstocks, and offer potentially useful synthetic protocols for cross-couplings and biomimetic organic synthesis. During the last few decades increasing work was documented on C–S bond activation and transformations by means of transition metal compounds. This review summarizes the recent advances in C–S bond cleavage *via* the insertion of transition metals into the inert C–S bonds of these problematic organosulfur compounds, and transition-metal mediated C–S bond transformations *via* C–S activation through cross-couplings of thioesters, ketene dithioacetals, sulfonyl chlorides, and other diverse organosulfur compounds.

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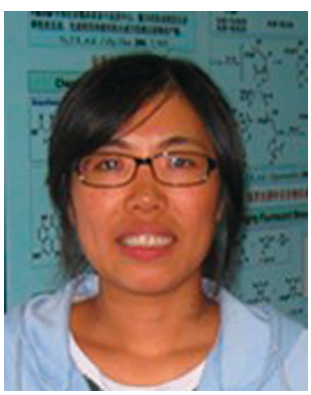
1. Introduction

Carbon–sulfur bond activation by transition metal compounds has been extensively studied for decades due to its importance in the petroleum industry.[1–3] Hydrodesulfurization (HDS) is among one of the two most important steps in the processing of petroleum, by which sulfur is removed from hydrocarbons during the refinement of petroleum. Inefficient removal of sulfur during this process leads to the production of noxious sulfur oxides upon fuel combustion, which has been considered as the major cause for air pollution. Although Ni/Mo and Mo/Co sulfide-based heterogeneous catalysts are effective for the removal of most organosulfur compounds, removing substituted thiophenes, benzothiophenes, dibenzothiophenes, and their derivatives remains a challenge. Improvement in catalyst efficiency requires increased effectiveness towards these problematic compounds,[4–8] and understanding their activation

[a] *Dalian Institute of Chemical Physics, Chinese Academy of Sciences (CAS), 457 Zhongshan Road, Dalian, Liaoning 116023, China. E-mail: zkyu@dicp.ac.cn*

[b] *State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, CAS, 354 Fenglin Road, Shanghai 200032, China*



Liandi Wang

Liandi Wang studied chemistry at Liaoning Normal University and received her BSc degree in July 2004. *She then joined Prof. Zhengkun Yu's group at Dalian Institute of Chemical Physics, CAS, as a research associate to work on synthetic and coordination chemistry. In April* 2012, *she completed her MSc degree thesis under the supervision of Prof. Yu. Her current research interest focuses on homogeneous catalysis with Ru(II) complexes.*

Wei He

Wei He studied chemistry at Lanzhou University and received his BSc degree in July 2003. *In July* 2004, *he joined Prof. Zhengkun Yu's group at Dalian Institute of Chemical Physics, CAS, as a research associate to work on homogeneous catalysis. In April* 2012, *he completed his MSc degree thesis under the supervision of Prof. Yu. His current research interest focuses on heterogenized homogeneous catalysis and green chemical processes.*

models could potentially lead to the discovery of new catalytic systems for HDS. Thus, homogeneous transition metal compounds have been investigated with the goal of providing the fundamental insight into the C–S bond activation and cleavage in these organosulfur compounds. To date, most of the studies have focused on using transition metal compounds to realize the C–H and C–S bond activation of thiophenes, benzothiophenes, dibenzothiophenes, and their derivatives.

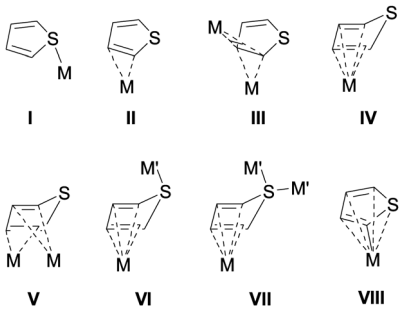
Recently, transition-metal mediated C–S bond activation and cleavage has been applied in diverse bioorganic and synthetic chemistry.[9,10] In particular, as cross-coupling has been paid more and more attention in the construction of new chemical bonds, organosulfur compounds have been shown increasing importance as coupling partners or building blocks and have exhibited potentials for biomimetic organic synthesis. In the presence of a thiophilic metal reagent, transition-metal mediated C–S bond activation of specific organosulfur compounds could be rendered catalytic, leading to C–S bond cleavage and transformation. This review presents a brief overview of C–S bond activation by stoichiometric transition metal compounds and summarizes the recent advances in transition-metal mediated catalytic C–S bond activation and transformations.

2. C–S bond activation by stoichiometric transition metal compounds

It has been well-known that C–S bonds can be activated by transition metals to form novel sulfur compounds or sulfide complexes.[11–13] This transformation allows insight into the mechanistic aspects of two related heterogeneous catalytic HDS processes.[14] Thus, transition-metal mediated bond cleavage reactions have been well investigated and established for various C–S bonds. In this section, only a concise overview of C–S bond cleavage by stoichiometric amounts of transition metal compounds is presented although a variety of reports have been documented in this area.[1–3,15–30] Coordination

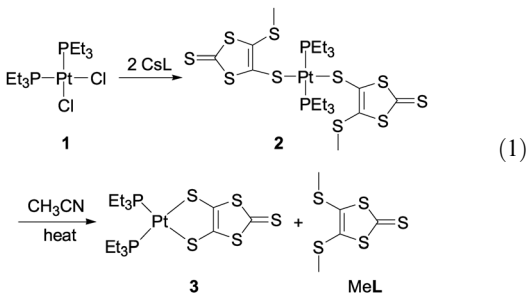
Zhengkun Yu

Prof. Zhengkun Yu obtained his PhD degree at Dalian Institute of Chemical Physics (DICP), CAS in July 1995. *During October* 1995–*January* 2003 *he worked as a post-doctoral fellow or a research associate in the labs of Prof. Rudolf Aumann (University of Münster, Germany), Prof. John G. Verkade (Iowa State University, USA) and Prof. Chuck Winter (Wayne State University, USA) and in Japan Corporation of Science and Technology (Tokyo, Japan). He returned to DICP as a "Hundred Talents Program of CAS" professor in February* 2003. *Since then he has been a full professor at DICP where his research interests are focused on novel organometallic complex catalysts and catalytic C–H and C–X bond activation.*



Scheme 1 Coordination models of thiophene ligands in transition metal complexes.

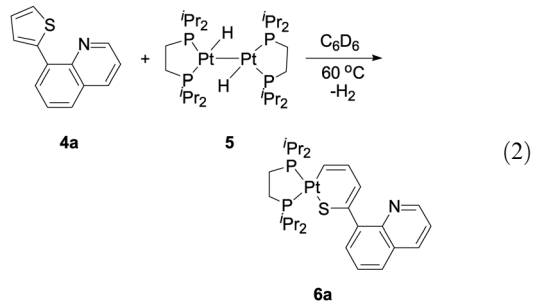
models of thiophene rings to transition metals have been reported, demonstrating diverse C–S bond activation in the complexes (Scheme 1).[31] In particular, the insertion reactions of metal atoms to C–S bonds in thiophenes and other organosulfur compounds have been extensively studied in order to get better understanding of the heterogeneous HDS mechanisms. Dibenzothiophene, benzothiophene, thiophene and their methyl-substituted derivatives as well as heteroatom-containing functional group-substituted thiophene derivatives can be used as the substrates. The low-valent complexes of transition metals such as platinum, ruthenium and rhodium, *etc.* have usually been utilized for this purpose.



(1)

Substitution of the chloro ligands in *cis*-[Pt(PEt$_3$)$_2$Cl$_2$] (**1**) by 4-methylthio-2-thioxo-1,3-dithiole-5-thiolate (**L**) led to the thiolate complex *trans*-[Pt(PEt$_3$)$_2$L$_2$] (**2**). *S*-Demethylation occurred when **2** was heated in acetonitrile, yielding the dithiolene complex [Pt(PEt$_3$)$_2$(2-thioxo-1,3-dithiole-4,5-dithiolate)] (**3**) and Me**L** (eqn (1)).[32] 2-(Quinolin-8-yl)thiophene (**4a**) and 3-(quinolin-8-yl)thiophene (**4b**) reacted with [Pt(dippe)H]$_2$ (dippe = ^{i}Pr$_2$P(CH$_2$)$_2$P^{i}Pr$_2$) (**5**) to selectively undergo C–S bond cleavage of the thiophene substrates (eqn (2) and (3)).[1] Pt(H)$_2$(dippe) was proved to be formed during the reaction. However, no reaction took place between **4** and Pt(H)$_2$(dippe) under 4 atm of H$_2$ at up to 85 °C, implying that the loss of hydrogen from this species has to occur prior to C–S activation. Platinum hydride [Pt$_2$H$_3$(dppp)]ClO$_4$ (dppp = Ph$_2$P-(CH$_2$)$_3$PPh$_2$) (**7**) was found to activate the C–S bond and cause partial hydrogenation of free thiophene, and the reaction at reflux temperature resulted in [(dppp)Pt(SC$_4$H$_4$-C,S)] (**8**) and [(dppp)$_2$Pt$_2$(μ-C$_4$H$_5$-C,S)]ClO$_4$ (**9**) at a 2 : 3 molar ratio (eqn (4)).[33] Treatment of dithiodiphenolate (**10**) with 3 equivalents of [Pt(η^2-nb)(PPh$_3$)$_2$] (nb = norbornene) in toluene, the activation of both benzylic C–S and phenolic O–H bonds happened to give novel 1,2-oxaplatinacyclo- and *cis*-

(dithiolato)Pt(II) complexes (**11** and **12**) in 72% and 69% yields (eqn (5)), respectively.[14] Substituted thiophene such as 2-cyanothiophene reacted with $[Pt(dippe)]_2(cod)]_2$ (**13**) at elevated temperature afforded Pt(dippe)(κ^2-C,S-C_4H_3S) (**14**) and the [Pt(dippe)] fragment *via* dissociation of cyclooctadiene (eqn (6)).[15] Two isomers, *i.e.*, **14a** (major) and **14b** were generated. The kinetic product was formed from the cleavage of the unsubstituted C–S bond. Further heating resulted in its conversion to the thermodynamically preferred product generated from the cleavage of the substituted C–S bond.



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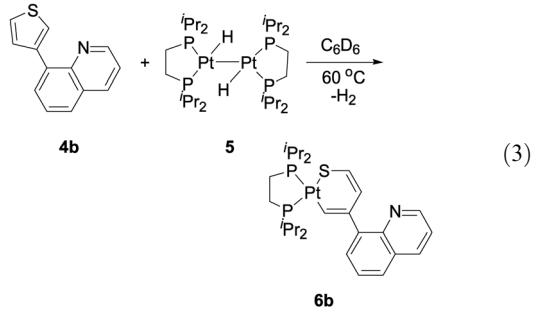

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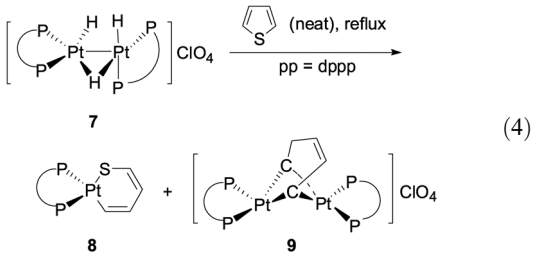

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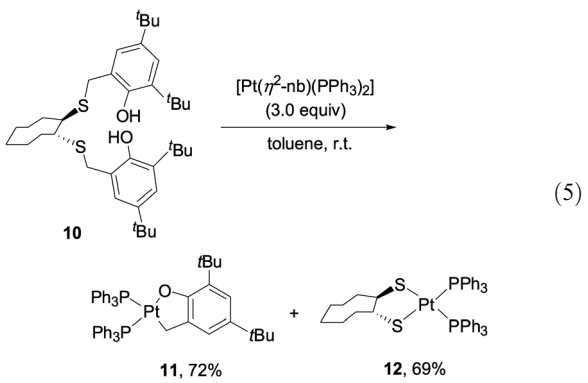
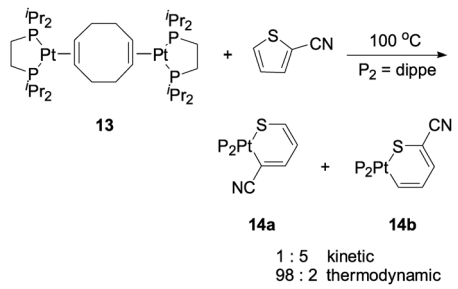


(5)

The moderate reactivity of α,β-unsaturated thioesters ArSC(O)C(R) = CHR′ towards the Pt(0) complex, $Pt(PPh_3)_2(C_2H_4)$, has been utilized to explore the oxidative addition of α,β-unsaturated acid halide derivatives to low-valent transition-metal complexes.[34] The results demonstrate that the acyl platinum complexes can be formed by direct C–S bond cleavage or by attack of coordinated $Pt(PPh_3)_2$ on the β-carbon. Thus, temperature-dependent formation of the C–S activation product was realized from the reaction of thioester **15** and the Pt(0) complex. Complex *cis*-**17** was then formed in 3% yield at −40 °C after 10 min, whereas *trans*-**17** was quantitatively produced at 25 °C (eqn (7)). Thiaplatinacycles derived from dibenzothiophene-containing phosphites were successfully applied in homogeneous desulfurization reactions.[35] Pt(0) complexes such as [(dippe)-Pt(nb)] (nb = norbornene) can also be used to cleave the C–S bonds of both cyclic and acyclic thioesters.[2] In the cases of *S*-methyl and *S*-ethyl thioacetates, [(dippe)Pt(COMe)(SR)] (R = Me, Et) formed initially. Further heating in the presence of a thioester generated $[(dippe)Pt(SR)_2]$ as well as acetone and RSMe as the side products. The reactions of $[Pt(PEt_3)_4]$ with 2,2′-bithiophene and 1-methyl-2-(2-thienyl)pyrrole afforded two types of products, *i.e.*, thiaplatinacycles resulting from C–S insertion, and Pt(II) hydride arising from C–H insertion.[36] Remote activation of C–S bonds in alkylated benzothiophenes and dibenzothiophenes by metal coordination to a carbocyclic ring was achieved (eqn (8)).[37] For the C–S bond cleavage reactions of benzothiophenes, the metal of a highly coordinatively unsaturated nucleophilic metal fragment usually inserts into the C(vinyl)–S bond instead of inserting into the stronger C(aryl)–S bond of the free benzothiophene. Sweigart *et al.* used an alternative method instead of using highly reactive transition metal fragments to cleave C–S bonds in benzo-thiophene and dibenzothiophene systems, that is, to activate the heterocyclic rings by precoordination of a metal to a carbocyclic ring. Thus, the addition of $[Pt(PPh_3)_2(C_2H_4)]$ to complexes **18** at room temperature in CH_2Cl_2 resulted in rapid insertion of $Pt(PPh_3)_2$ into the C(vinyl)–S bond or C(aryl)–S bond, or both.[37]



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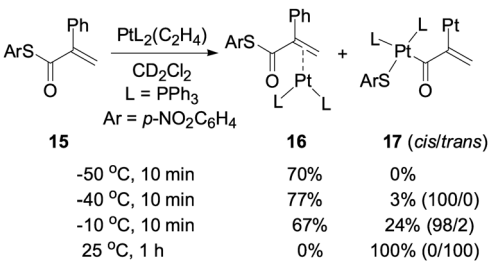
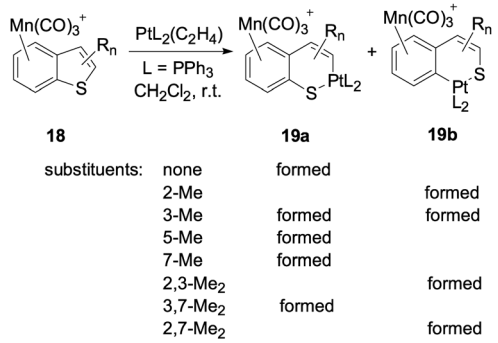


(7)

Ruthenium complexes have also been employed for C–S bond activation and cleavage. The neutral silylene ruthenium complex Cp*(CO)(H)Ru = Si(H)C($SiMe_3$)$_3$ (**20**) reacted with

isothiocyanate MesNCS (Mes = mesityl) in hexane at room temperature to instantaneously cleave the C=S bond, giving the isocyanide complex Cp*(CO)Ru(CNMes){$SSiH_2C(SiMe_3)_3$} (**21**) (eqn (9)).[38]



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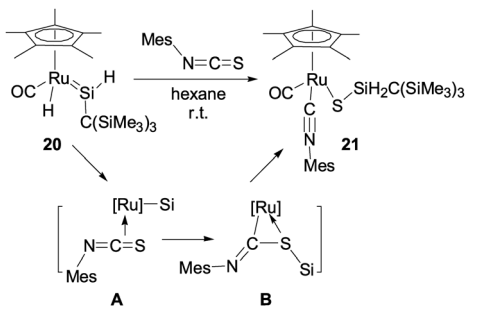
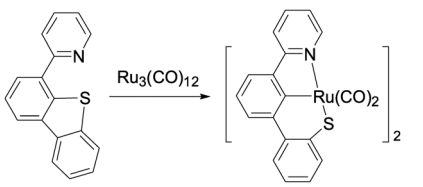


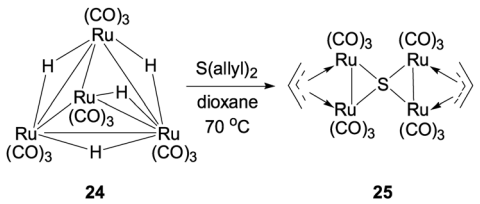
(9)

Activation of the C=S bond by its coordination to the ruthenium center forms species **A**, and subsequent silyl migration to the sulfur atom in **A** produces intermediate **B** in which the weak C–S bond easily cleaves to complex **21**. Treatment of 4-(2′-pyridyl)dibenzothiophene (**22**) with ruthenium carbonyl cluster $Ru_3(CO)_{12}$ formed dimeric Ru(II) complex **23** (eqn (10)), where the ligand donates a dianion of 3′-(2″-pyridyl)-1,1′-biphenyl-2-thiol.[17]



(10)

The tridentate-N,C,S ligand provides a pincer structure consisting of a six-membered thiaruthenacycle and a five-membered azaruthenacycle. The reaction of cluster complex $H_4Ru_4(CO)_{12}$ (**24**) with allyl disulfide in dioxane at 70 °C yielded $Ru_4(\mu_4\text{-}S)(\mu,\eta^3\text{-}C_3H_5)_2(CO)_{12}$ (**25**) as the major product (eqn (11)).[39] In the complex product, two Ru-fragments are bonded by μ_4-bridging sulfur, affording a rare metal-containing structural unit $Ru_4(\mu_4\text{-}S)_4$. Insertion of ruthenium into the thianthrene ring by C–S activation was accomplished in the reaction of $Ru_3(CO)_{12}$ with thianthrene in refluxing toluene, forming versatile cluster complexes containing unusual μ_5-sulfido-, μ_4-benzyne-, and thianthrene-derived ligands.[40] Reaction of [TpRu(CO)(NCMe)Ph] (Tp = hydridotris(pyra-zolyl)borate) (**26**) with electron-rich olefins such as ethyl vinyl sulfide (neat) at 100 °C resulted in C–S cleavage product $[TpRu(CO)(\mu\text{-}SEt)]_2$ (**27**) as well as styrene as the side product (eqn (12)).[41] The X-ray single crystal structure of **27** reveals two *pseudo*-octahedral Ru(II) fragments bridged by two symmetrically equivalent μ-SEt moieties. However, a different reaction occurred between [Ru(cod)(cot)] (cod = 1,5-cyclooctadiene; cot = 1,3,5-cyclooctatriene) (**28**) and vinyl sulfide, and displacement of ligands in **29** with PMe_3 followed by C–S bond cleavage with MeI formed complex **30** as the final product (eqn (13)).[42] The hydrochloride of levamisole (lvms), *i.e.*, (−)-2,3,5,6-tetrahydro-6-2,3,5,6-tetrahydro-6-phenylimidazo[2,1-*b*]thiazole hydrochloride (Hlvms)Cl (**31**) reacted with $Ru_3(CO)_{12}$ to generate a new cluster complex $[Ru_3(\mu\text{-}Cl)(\mu\text{-}\eta^2\text{-}C_{11}H_{13}N_2S\text{-}C,S)(CO)_9]$ (**32**) (eqn (14)).[43] It is proposed that $Ru_3(CO)_{12}$ was attacked by the chloride anion to form $[Ru_3(\mu\text{-}Cl)(CO)_{10}]^-$ anion, and a subsequent coupling of this cluster anion with $[Hlvms]^+$ cation led to a complex bearing an intact [Hlvms] group attached to a ruthenium atom through the sulfur atom. This neutral complex easily underwent C–S bond activation/cleavage to produce **32**. α-Oxoketene dithioacetal (**33**) was treated with $Ru_3(CO)_{12}$ in THF to yield the C–S cleavage product **34** (eqn (15)), and varying the reaction conditions produced a tetranuclear cluster complex.[44]



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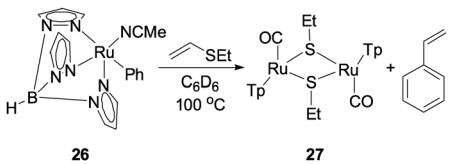

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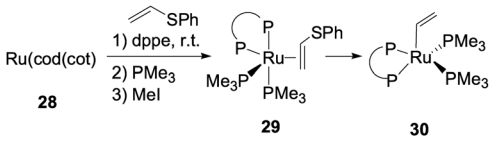

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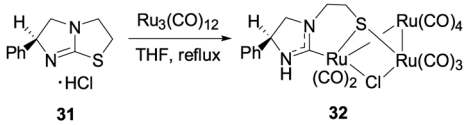

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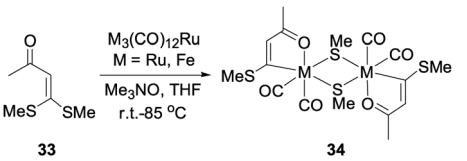

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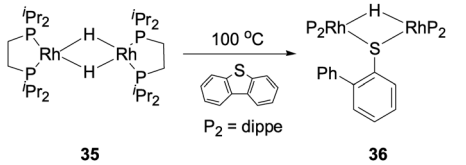
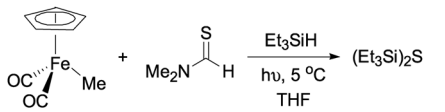


(16)

Dimeric rhodium(I) complex $[Rh(dippe)(\mu\text{-}H)]_2$ (**35**) reacted with dibenzothiophene in benzene at 100 °C to exclusively form

the C–S cleavage complex $[Rh_2(dippe)_2(\mu\text{-}SC_{12}H_9)(\mu\text{-}H)]$ (**36**) (eqn (16)).[16] Activation of only one C–S bond of the organosulfur substrate was observed, despite the presence of a second metal and a hydride ligand in the product. Increasing temperature to 135 °C, complex **35** also efficiently reacted with 4-methyldibenzothiophene and 4,6-dimethylthiophene to produce products of type **36**. Theoretical studies were carried out on the C–S activation reactions of 2/3-cyanothiophene, 2/3-methoxythiophene, and 2/3-methylthiophene with the $[Cp^*Rh(PMe_3)]$ fragment to compare with selectivity of these reactions observed in the experimental study.[45] Thus, treatment of $[Cp^*Rh(PMe_3)(Ph)H]$ (**37**) with the above-mentioned thiophene derivatives led to selective formation of products resulting from insertion of the Rh atom into the less or more hindered C–S bonds (Scheme 2). Relevant density functional theory (DFT) calculations on the C–S bond activation reaction of thiophene with the $[Cp^*Rh(PMe_3)]$ fragment have also been performed, giving two new isomeric C–S bond activation transition states, in which the coordinated thiophene molecule tilts towards either the Cp* ligand or the PMe_3 ligand.[46] By means of the multitude of alkyne coupling transformations, the α,ω-diyne 4,7,10-trithiatrideca-2,11-diyne (**38**) was reacted with the Wilkinson catalyst and other transition-metal complexes to form C–S cleavage product **39** and polythiamacrocyclic complexes **40** and **41** (Scheme 3), respectively.[47–49] In the presence of an excessive amount of hydrosilane and with the help of an iron complex, *i.e.*, $[Cp(CO)_2FeMe]$ (**42**), desulfurization of *N,N*-dimethylthioformamide was achieved (eqn (17)).[50] In the reaction sequence, silyl migration from Fe to S of thioformamide triggered the cleavage of a C=S bond to generate a carbene–iron complex which was isolated and characterized by X-ray crystallographic determination (eqn (18)). Reaction of the iron(II) complex (**45**) bearing the bulky *N,N′*-dimesityl-2,2′-diamidophenyl sulfide ligand with 3 equivalents of isocyanide afforded the low-spin complex $[(^{mes}NSN)Fe(CNR)_3]$ (R = Ph-2,6-Me_2) (**46**).[51] Recrystallization of **46** led to isolation of the carbon–sulfur bond cleavage product $[(^{mes}NS)Fe(CNPh\text{-}2,6\text{-}Me_2)_3]$ (**47**) (Scheme 4). Photolysis of a hexane solution containing $Fe(CO)_5$ and CS_2 led to desulfurization and formation of a novel cluster $[\{Fe_2(CO)_6\}_2(\mu\text{-}C_2S_3)]$ (**48**) (eqn (19)).[18] Activation of the C=S bond is selective for the reaction of CS_2 with $Fe(CO)_5$, and the unique C_2S_3 ligand acts as a bridge between the two $Fe_2(CO)_6$ units and forms an unusual ferrathiacyclobutene ring. Azoketene dithioacetals (**49**) were treated with $Fe_2(CO)_9$ in anhydrous ethyl ether at room temperature to produce complex **50** as the major product by cleaving one of the C–S bonds in **49** (eqn (20)).[52]



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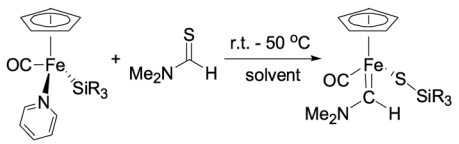

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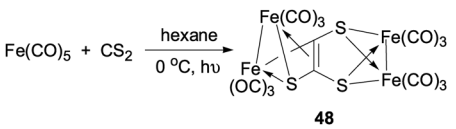

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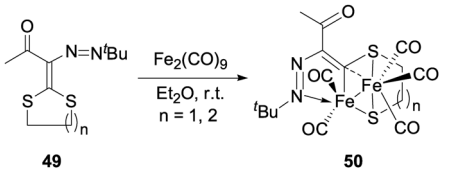
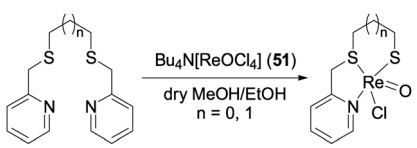
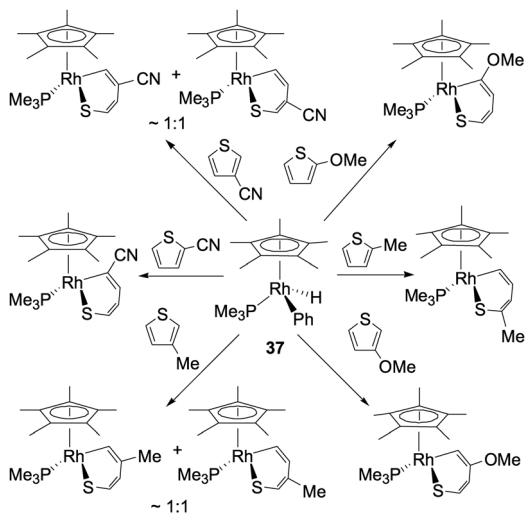


49 50 (20)

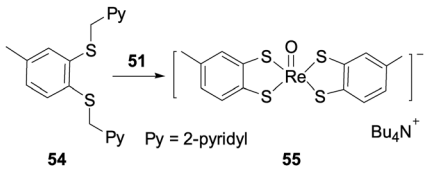
C–S bond cleavage can also be realized by means of the reaction of an oxorhenium(V) ion, *i.e.*, $Bu_4N[ReOCl_4]$ (**51**), with pyridylmethylthioether (**52**) (eqn (21)). The structural results for **53** evidenced the unexpected cleavage of one C–S bond within **52** during the metal complexation. However, treatment of 3,4-bis(2-pyridylmethylthio)-5-methyltoluene (**54**) with **51** under the same conditions led to the formation of a binary oxorhenium(V) complex of 3,4-dimercapto-toluene (**55**) (eqn (22)). Rhenium(V) complexes **56** reacted with excess of PPh_3 in benzene at ambient temperature to undergo C–S cleavage, forming metallacyclic Re(V) complexes **57** with a Re≡S core (eqn (23) and (24)).[53] In the course of the reaction, the Re–O bond was broken, a terminal Re–S bond was made at the expense of breaking C–S–Re bonds, and a C–Re bond was formed. Nucleophilic attack of PPh_3 on the oxo group of the Re^VO core appears to be the rate-determining step.



52 53 (21)



Scheme 2 Observed reactivity of Cp*Rh(PMe3)] with substituted thiophenes.



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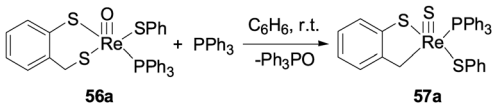

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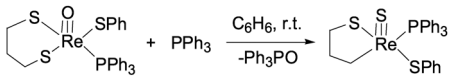
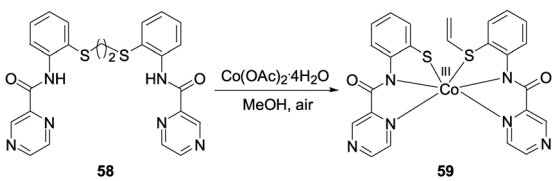


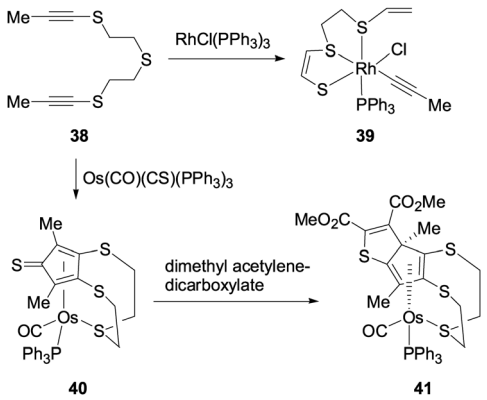
(24)

The aerobic reaction of $Co(O_2CMe)_2{\cdot}4H_2O$ with thioether-containing acyclic pyrazine amide hexadentate ligand 1,4-bis[*o*-(pyrazine-2-carboxamidophenyl)]-1,4-dithiobutane (**58**) in air furnished complex **59**, resulting from a C–S bond cleavage reaction triggered by an acetate ion as a base, having CoN_2(pyrazine)N'_2(amide)-S(thioether)S(thiolate) coordination (eqn (25)).[20] Similar results were also obtained from the reaction of 1,2-di-(*o*-salicylaldiminophenylthio)ethane (**60**) with Co(II) salts in the presence of oxygen (eqn (26)).[54] A Co(III) complex (**62**) of the cleaved ligands was produced by oxidative cleavage of one of the C–S bonds. By monitoring the reaction in solution with UV-Vis spectra, it was noticed that the product (**61**) was stable under an argon atmosphere, while it was changed quickly when the reaction mixture was bubbled with oxygen.

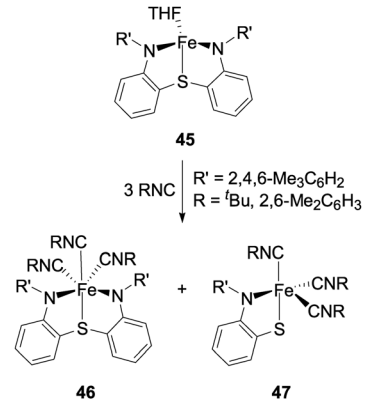


(25)

The tridentate ligands $S(CH_2CH_2NHP^iPr_2)_2$ (**63a**) and $S(CH_2CH_2OP^iPr_2)_2$ (**63b**) underwent C–S oxidative addition to the Ni(0) complex, *i.e.*, $Ni(COD)_2$, to form complexes $(SCH_2CH_2E\text{-}P^iPr_2)Ni(CH_2CH_2EP^iPr_2)$ (E = NH, O) (**64**) (eqn (27)).[55] The $^{31}P\{^1H\}$NMR spectrum of **64a** (E = NH) exhibited two doublets at 121.8 and 80.3 ppm with a P–P coupling constant of 270.0 Hz, suggesting a *trans* disposition of inequivalent P atoms. X-ray methods also confirmed the pseudo-square-planar geometry around the nickel atom. Nickel-mediated C–S cleavage of sulfoxides containing sp^2- and sp^3-hybridized carbon bonds attached to the sulfur atom was reported.[21] The reaction of dinuclear complex $[Ni(NHC)]_2(COD)$ (NHC = *N*-heterocyclic carbene) (**65**) with two equivalents of dimethyl sulfoxides (DMSO) or phenyl methyl sulfoxide (PMSO) in toluene smoothly yielded products **66** from the sp^3-C–S(O) bond cleavage of DMSO and sp^2-C–S(O) bond cleavage of PMSO (eqn (28)). Interestingly, diphenyl sulfoxide (DPSO) could also be activated by $Ni(COD)_2$, but its reaction afforded product **67** in which the phenyl sulfinyl ligand is bound *via* the oxygen atom to the nickel atom.

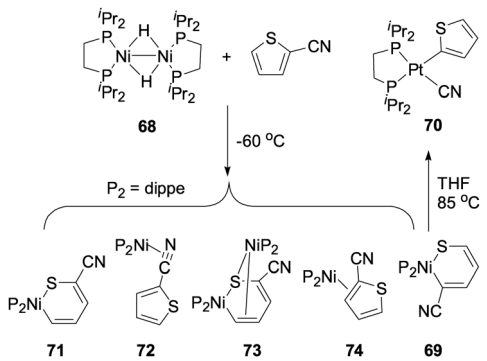


Scheme 3 Rh(I) and Os(I)-mediated sp C–S cleavage.



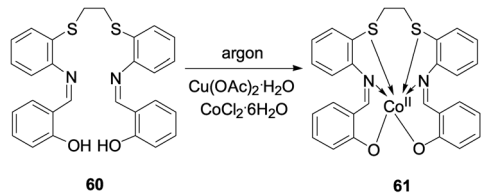
Scheme 4 Iron-mediated sp^2 C–S cleavage.

Competitive C–S *vs.* C–C bond activation of 2-cyanothiophene with $[Ni(dippe)H]_2$ (**68**) was observed.[3] When **68** was reacted with 2-cyanothiophene at room temperature, cleavage of the nitrile-substituted C–S bond occurred, forming the Ni-metallacycle complex **69** which could be converted to the C–CN cleavage product **70** when heated in solution. A kinetic product (dippe)-$Ni(\kappa^2\text{-}S,C\text{-}SC(CN){=}CHCH{=}CH)$ (**71**) was formed from cleaving the nonsubstituted C–S bond as well as a Ni(0) η^2-nitrile intermediate **72** and a dinuclear mixed Ni(0)–Ni(II) product **73**

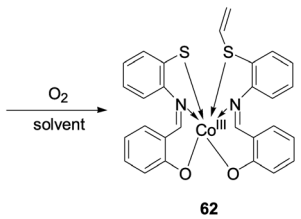


Scheme 5 NiH-activated C–S bonds of 2-cyanothiophene.

(Scheme 5). Complex **74** was a short-lived Ni(0) intermediate that disappeared after 10 minutes at −60 °C.



60 **61**



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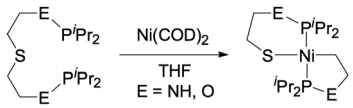
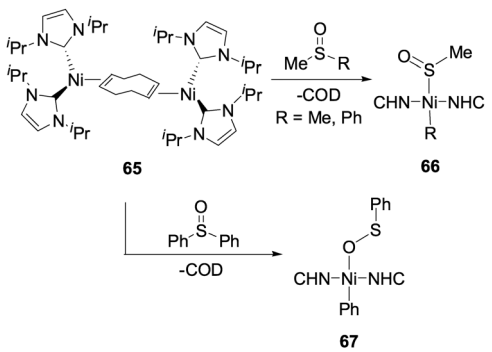


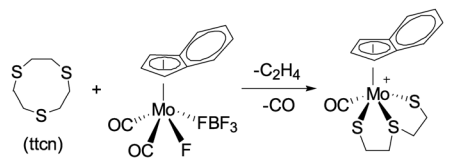
63 **64** (27)



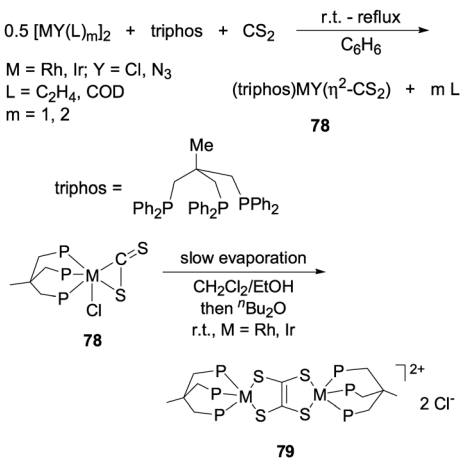
65 **66** **67** (28)

The macrocycle 1,4,7-trithiacyclononane (ttcn, **75**) interacted with $[(\eta^5\text{-Ind})Mo(CO)_2(C_3H_6)(FBF_3)]$ (Ind = indenyl) (**76**) to give the C–S bond cleavage product $[(\eta^5\text{-Ind})Mo(CO)(\kappa^3\text{-1,4,7-trithiaheptanate})]BF_4$ (**77**) by losing ethylene (eqn (29)).[56] DFT calculations showed that the η^5-Ind coordination mode is always the most stable, and the conversion to **77** proceeds stepwise, with loss of ethylene followed by loss of CO. Reaction of trithiolato-bridged complex $[Mo_2Cp_2(\mu\text{-SMe})_3(MeCN)_2](BF_4)$ with acyclic (*e.g.*, Et_2S) or cyclic (*e.g.*, thiirane, thietane, tetrahydrothiophene, 1,4-dithiane and 1,4-thioxane) thioethers and chalcogenophenes (benzothiophene and dibenzothiophene) in dihaloalkanes led to either (di)thioether- and halide-bridged compounds or μ-sulfido complexes.[22]

CS_2 can undergo many reactions with transition metals and activations of CS_2 have been paid much attention from catalytic



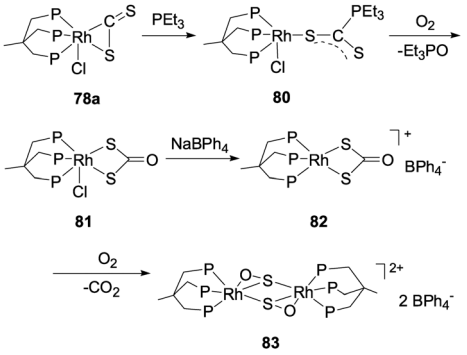
75 **76** **77** (29)



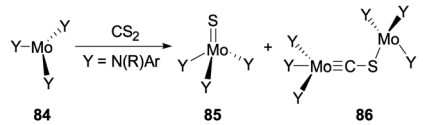
78 (30)

78 **79** (31)

and biological points of view. Rhodium(I) and iridium(I) compounds have been known to activate CS_2 by forming η^2-CS_2 complexes of the metals (eqn (30)).[57,58] Binuclear complexes of the general formula $[(triphos)M(\mu\text{-}C_2S_4)M(triphos)Y_2$ (triphos = $MeC(CH_2PPh_2)_3$; M = Rh, Ir; Y = Cl, N_3)] (**79**) were obtained from the η^2-CS_2 complexes **78** after elimination of the Y ligands and addition of suitable anions (eqn (31)). Nucleophilic attack by PEt_3 at the carbon atom of the η^2-CS_2 ligand in **78a** yielded the η^1-phosphoniodithiocarboxylate complex $[(triphos)RhCl(S_2CPEt_3)]$ (**80**), which reacted with O_2 in the presence of $NaBPh_4$ to produce the μ-SO complex **83** *via* intermediates **81** and **82** (eqn (32)).[59] Further treatment of complex $[(triphos)Rh(S_2C{=}O)]$ (**82**) with CS_2 afforded complex $[(triphos)Rh(S_2C{=}S)]$ with release of COS.[60] A similar nickel(II) complex of type **78**, *i.e.*, $[(triphos)Ni(\eta^2\text{-}CS_2)]$, was used for the same purpose.[61] Recent experimental results have demonstrated that only one bond in CS_2 can be cleaved by a transition metal, and that the remaining CS can also be activated but the bond is not broken.[62] Thus, the addition of 1 equiv. of CS_2 to $Mo[N(R)Ar]_3$ (R = $C(CD_3)_2CH_3$, Ar = 3,5-$Me_2C_6H_3$) (**84**) resulted in complexes Mo(S)$[N(R)Ar]_3$ (**85**) and $(\mu\text{-CS})(Mo[N(R)Ar]_3)_2$ (**86**) (eqn (33)), demonstrating that, although complex **84** was able to break one of the C–S bonds of CS_2, the cleavage of C–S bond of the CS moiety was unfeasible. However, DFT calculations show that the combination of Re and Ta in the $(NH_2)_3Re/CS_2/Ta(NH_2)_3$ complex would be the most promising system for the cleavage of both C–S bonds of CS_2.[63] Because breakage of the C–S bond in CS is strongly endothermic, the reaction has not been observed.



78a **80** **81** **82** **83** (32)



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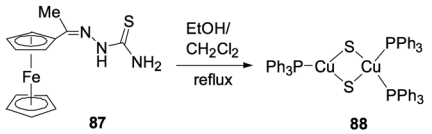
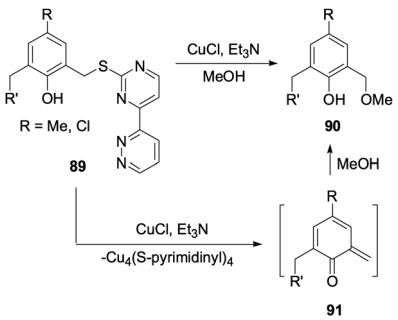


(34)

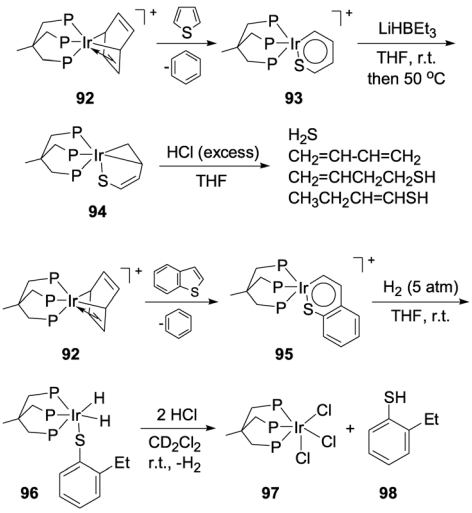
Copper chalcogenide compounds including clusters are of continuing interest in inorganic and materials chemistry. Copper ion mediated selective cleavage of the C–S bond in ferrocenyl-thiosemicarbazone (**87**) to form a rare mixed geometrical $[(PPh_3)Cu(\mu\text{-}S)_2Cu(PPh_3)_2]$ (**88**) with a Cu_2S_2 core (eqn (34)).[64] In this paramagnetic dicopper complex, the copper ions are in the +2 oxidation state with two different geometries. Cu(II) also mediated C–S activation to transform dithiocarbamate into carbamate and thiocarbamate derivatives in the presence of nucleophilic solvent methanol.[65] A Cu(I) reagent such as CuCl was efficiently used to cleave C–S bonds in thiopyrimidine compounds (eqn (35)).[23] Treatment of ligand **89** with cuprous chloride under weak base conditions led to formation of a tetranuclear cluster, *i.e.*, Cu_4(S-pyrimidinyl)$_4$, and the benzylic C–S cleavage product **90** *via* intermediate **91**.



(35)

The complexes of other transition metals such as tantalum,[24] iridium,[25] tungsten,[26] zirconium,[27] manganese,[28] chromium,[29] uranium,[30] and palladium[66] have also been documented to activate or cleave C–S bonds of organosulfur compounds with a stoichiometric amount. All these organometallic systems can be chosen as the models for homogeneous HDS of thiophene and related organosulfur compounds in order to get a deeper insight into the heterogeneous HDS of petroleum feedstocks.

It is noteworthy that transition metal compounds such as iridium(III) complexes have also been investigated for their activation of thiophene and related organosulfur derivatives under HDS conditions.[67–70] The η^4-benzene complex [(triphos)Ir(C_6H_6)] BPh_4 (**92**) reacted with thiophene to give the iridathiabenzene complex (**93**) which could be selectively converted to the butadienethiolate complex **94** by treatment with $LiHBEt_3$ and was then decomposed under acidic conditions (eqn (36)).[67] Benzothiophene was selectively hydrogenated by initial complexation with complex **92** (eqn (37)).[69] Under the HDS conditions, **92** could diversely activate benzothiophene and the reaction parameters such as temperature, H_2 pressure and solvents obviously affected the HDS process.[70]

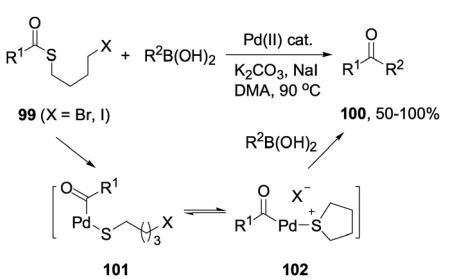


(36)

(37)

3. Catalytic C–S cleavage in thioesters

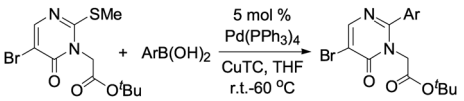
Transition metal-catalyzed carbon–carbon cross-coupling reactions are among the most powerful and flexible transformations in organic synthesis. The cross-coupling procedures usually involve the interaction of a nucleophilic organometallic reagent with an electrophilic organohalide (or related analogues).[71] In this area, organosulfur compounds have also been reported as electrophilic coupling partners.[72–74] Although the oxidative addition of organosulfur compounds to a low-valent transition metal species has been well documented,[14–30] the key to catalytic turnover with organosulfur compounds is activation of the very stable bond that is formed between the catalytically active metal and the soft sulfur atom. The selection of a nucleophilic organometallic reagent for the following transmetalation step is crucial for the reaction to smoothly proceed. In 1997, Liebeskind *et al.* reported that the readily prepared tetramethylenesulfonium salts could be used as the coupling partners in palladium- and nickel-catalyzed cross-coupling reactions with organoboron, -tin, and -zinc reagents under mild conditions.[75] Later in 2000, Liebeskind and Srogl reported the first examples of palladium-catalyzed, copper-mediated cross-coupling between thioesters (thiol esters) and boronic acids under base-free conditions.[76] The feature of this protocol (so-called "Liebeskind–Srogl cross-coupling") is the requirement of a stoichiometric amount of a sacrificial copper(I) carboxylate compound such as copper(I) thiophene-2-carboxylate (CuTC)[77] as a thiophilic metal reagent due to



(38)

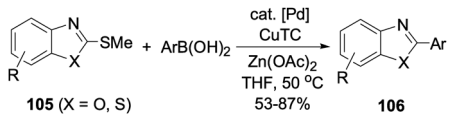
the low thiophilicity of boron and the relatively low nucleophilic reactivity of organoboron compounds.

A sacrificial metal reagent plays a crucial role in facilitating the cross-coupling reactions,[78] and thioesters and boronic acids did not undergo the cross-coupling in the presence of a sole palladium catalyst. However, by means of the principle of "alkylative activation",[79] that is, by using simple alkylating agents the palladium-catalyzed thioester-boronic acid cross-coupling smoothly proceeded (eqn (38)).[80] Alkylative conversion of the very stable palladium–thiolate bond in intermediate **101** to a labile palladium–thioether bond is presumed to be crucial to the catalytic cycle. Such a cross-coupling reaction efficiently afforded ketone **100** as the product. Among the systems investigated, 4-halo-*n*-butylthioesters (**99**) were the most effective for this type of cross-coupling reactions. As a new synthetic methodology, substituted alkynes were also prepared by means of palladium-catalyzed, copper(I) carboxylate-mediated thioalkyne–boronic acid cross-coupling.[81] This coupling efficiently underwent under mild and nonbasic conditions with a wide range of thioalkynes and boronic acids as substrates, providing an alternative to the Sonogashira protocol.



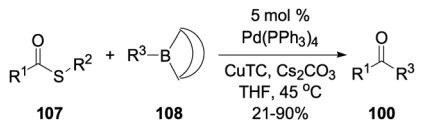
103 **104**, 47-89% (39)

Using heteroaromatic thioethers as the substrates, the *pseudo* Liebeskind–Srogl reactions efficiently underwent to produce functionalized heteroarenes (eqn (39)).[82] π-Deficient heteroaromatic thioethers (**105**) underwent efficient palladium-catalyzed cross-coupling with boronic acids in the presence of CuTC (eqn (40)).[83] The best results were obtained using the Pd_2dba_3/tris(2-furyl)phosphine (TFP) catalytic system. Other palladium catalysts also worked, but were less effective. The unreactive or less reactive MeS–ether substrates were successfully "activated" by replacement of the MeS group with the SCH_2CONH_2 or the SCH_2CONMe_2 pendant ligand, and $Zn(OAc)_2$ was an essential additive in some cases.

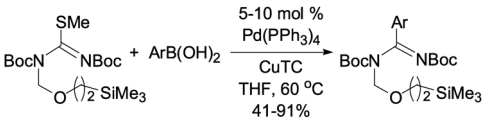


105 (X = O, S) 53-87% **106** (40)

With B-alkyl-9-BBN (**108**) as the nucleophilic reagent, the palladium-catalyzed, Cu(I)-mediated cross-coupling of thioesters (**107**) was performed in the presence of a base such as Cs_2CO_3 (eqn (41)),[84] revealing an additive effect (base effect) different from that in the conventional Liebeskind–Srogl cross-coupling reactions of thioorganics with other boronic acids. Using this synthetic protocol, aryl–alkyl and alkyl–alkyl ketones bearing a variety of functional groups were synthesized in moderate and excellent yields. The Liebeskind–Srogl method was successfully applied for the synthesis of protected benzamidines (**110**).[85] The SEM-protected thiopseudourea **109** functioned as the amidine-forming cross-coupling partner under Liebeskind–Srogl reaction conditions, and the fully protected benzamidines **110** were obtained in good to excellent yields (eqn (42)). Another effective catalytic system was Pd_2dba_3/TFP/dioxane for this purpose.

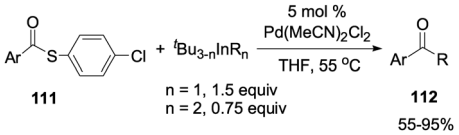


107 **108** **100** (41)

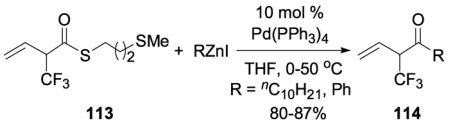


109 **110** (42)

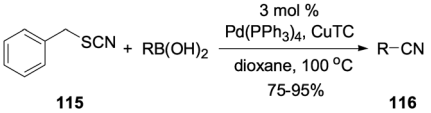
Liebeskind–Srogl cross-coupling has exhibited its versatility in carbon–carbon bond formation by means of other organometallic reagents as substrates.[72–74] Organoindium compounds were reported to couple with thioesters. In the presence of $Pd(MeCN)_2Cl_2$ as catalyst, the reaction of thioesters (**111**) with aryl, primary and secondary alkyl organoindium reagents underwent to give aryl–alkyl ketones **112** in 55–95% yields (eqn (43)).[86] This method has two advantages over the cross-coupling of thioesters with organo-boron and -tin reagents: (a) no added copper(I) reagent was required to mediate the reaction, and (b) for the case of alkyl transfer, no added base was required to activate the organoindium reagents for the cross-coupling as is usually required for the coupling of alkylboron reagents with thioesters.[84] In a similar fashion by using $Pd(PPh_3)_4$ as catalyst, alkyl- and arylzinc reagents were used for this purpose (eqn (44)).[87] Under Liebeskind–Srogl reaction conditions, nitriles were efficiently synthesized from the cyanide-free reactions of alkyl-, benzyl- or arylthiocyanates with aryl and alkenyl boronic acids, which can be considered as a complementary to the classic cyanation of aryl halides using a cyanide source and a transition metal catalyst (eqn (45)).[88]



111 **112** 55-95% (43)



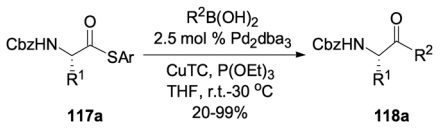
113 **114** (44)



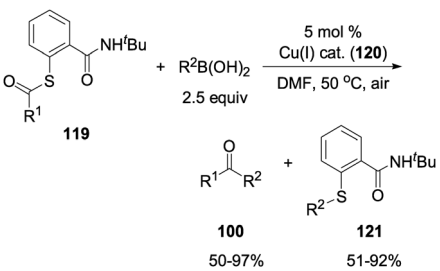
115 **116** (45)

α-Amino acid thioesters **117a** derived from *N*-protected peptides were coupled with aryl, π-electron-rich heteroaryl, or alkenyl boronic acids in the presence of stoichiometric CuTC and catalytic Pd_2dba_3/triethylphosphite to afford the corresponding *N*-protected peptidyl ketones **118a** in up to 99% yields with excellent enantiopurity (up to 99% ee) (eqn (46)).[89] Triethylphosphite played a key role as a supporting ligand to inhibit undesired palladium-catalyzed decarbonylative β-elimination of

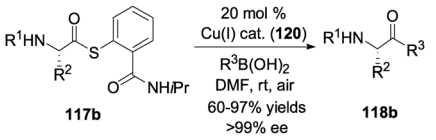
the amino acid thioesters. The desired reaction proceeded at room temperature under nonbasic conditions and demonstrated a high tolerance to different functionalities. This procedure provides a potential route to the C-terminal or side-chain modification of proteins. The anaerobic cross-couplings of thioorganics with boronic acids usually require the presence of catalytic quantity of a palladium source and stoichiometric quantity of a Cu(I) carboxylate. However, in 2007, Liebeskind *et al.* reported a unique example, *i.e.*, a mechanistically unprecedented system for the construction of carbon–carbon bonds: the copper(I)-catalyzed cross-coupling of a thioorganic with a boronic acid under aerobic conditions (eqn (47)).[90] In the Liebeskind–Srogl reaction sequence, the Cu(I) ion pairs with the thiolate in a thermodynamically strong Cu–SR bond, while a full equivalent of the borophilic carboxylate counterion drives the $B(OH)_2$ moiety to its thermodynamic sink, *i.e.*, $R'C(CO)OB(OH)_2$. This implies that the reaction can be rendered catalytic in Cu(I) if a Cu(I) oxygenate could be regenerated *in situ* from Cu–SR. By using thioesters **119** bearing a *S*-pendant such as –(2-$C_6H_4CONH^tBu$) as the nucleophilic reagents and 5 mol% Cu(I)-3-methylsalicylate (**120**) as catalyst under aerobic conditions in the presence of a second sacrificial equivalent of the boronic acid (total 2.5 equiv.), the cross-coupling was successfully realized to give ketones **100** and thioethers **121**. Such a protocol may find applications in the selective functionalization of complex molecules. With a similar strategy, highly enantiopure peptidyl ketones **118b** were synthesized from copper(I)-catalyzed coupling of peptidic *S*-acylthiosalicylamide (**117b**) with boronic acids in air at room temperature under pH-neutral conditions (eqn (48)).[91] Neither metal-binding nor oxidation-sensitive peptide residues interfered with the reaction. Liebeskind–Srogl coupling was also reported as a tool to construct carbon–carbon bonds in the diaryl ether subunits of some medicinally important natural products such as verbenachalcone.[92] By applying a new concept to design a small molecule chemical analogue at the metallothionein system in which an N–O reactant serves the same conceptual purpose of the S–S reactant of the biological system, copper(I) was also rendered catalytically viable in the presence of thiolate (eqn (49)).[93] The control experiments demonstrated that both the Cu and the internal *O*-methyl oxime moiety are essential for the catalytic turnover. The S–N trap **123** was also obtained during the product



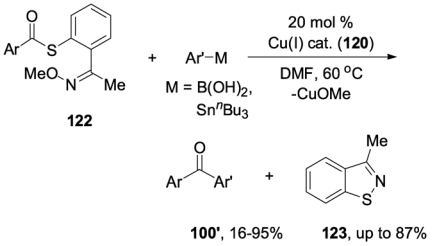
117a 118a (46)



100 121 (47)
50-97% 51-92%



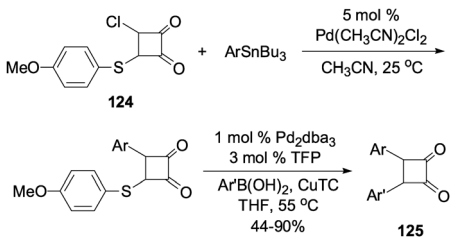
117b 118b (48)



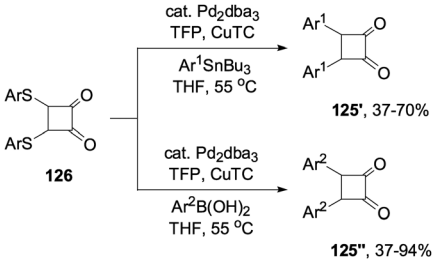
(49)

isolation. In this case, large excess of the nucleophilic reagent (Ar′M) and Cu(I) reagent, and a palladium precatalyst was not necessary. This process may be identified as the 3rd generation of Liebeskind–Srogl cross-coupling.

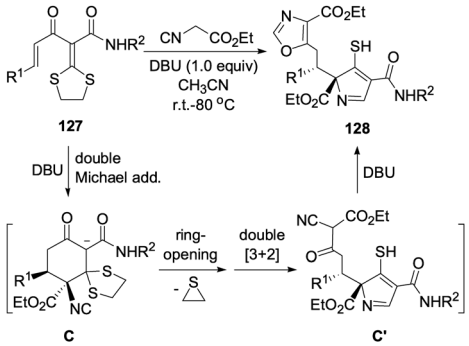
With a multiple functionalized substrate, *i.e.*, 3-chloro-4-arylthio-cyclobutene-1,2-dione (**124**), sequential Stille–Libeskind–Srogl reactions with boronic acids were carried out. It was found that **124** participated in Stille coupling exclusively at the C–Cl site with organostannanes in the absence of Cu(I), and then functionalization occurred at the C–S site with boronic acids by switching to the Liebeskind–Srogl reaction conditions (in the presence of CuTC) to afford the bifunctionalized cyclobutenediones (**125**) (Scheme 6).[94] Symmetrical disubstituted cyclobutenediones (**125′** and **125′′**) were also obtained from the cross-coupling reactions of bisarylthiocyclobutenediones (**126**) with both organostannanes and (hetero)arylboronic acids in the presence of a catalytic amount of palladium and a stoichiometric amount of CuTC in 37–94% yields (Scheme 7).[95]



Scheme 6 Stille–Libeskind–Srog cross-couplings.



Scheme 7 Catalytic double C–S cleavage.

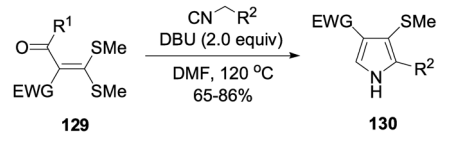


(50)

4. Catalytic C–S cleavage in dithioacetals

Dithioacetal functionalities are very useful protecting, stabilizing and promoting groups in organic synthesis, due to their easy deprotection to the corresponding aldehydes and ketones under acidic conditions.[96–114] Because a strong bond can be easily formed between a catalytic metal and the sulfur atom, it is usually difficult to render the metal-involved reactions of dithioacetals catalytic. In addition, dithioacetals are sensitive to acids, the organic transformations of dithioacetals *via* C–S bond cleavage are usually carried out by means of strong base catalysts as well as Brønsted acids. In this section, only a few examples on base-promoted transformations of ketene dithioacetal derivatives are presented.

Divinyl ketones are generally associated with Nazarov and related reactions.[115] In the presence of DBU as catalyst, α-alkenoyl ketene dithioacetals **127**, *i.e.*, the divinyl ketones with terminal *gem*-dialkylthio substituents, reacted with ethyl isocyanoacetate afforded C_2-tethered pyrrole/oxazole pairs **128** in 50–89% yields under mild conditions (eqn (50)).[116] The process involves [5 + 1] annulation of **127** and ethyl isocyanoacetate, ring-opening of the intermediate and then two consecutive [3 + 2] isocyanide cycloadditions. The chemoselective fragmentation of the cyclohexanone intermediate is crucial for the formation of the target product **128**. In a similar fashion, base-catalyzed 1,3-dipolar cycloaddition of acyclic ketene dithioacetals **129** with carbanions derived from activated methylene isocyanides efficiently afforded substituted 1H-pyrroles **130** (eqn (51)).[117] Precise control over the introduction of a number of substituents and functionalities such as tosyl, carbalkoxy, aryl, cyano, nitro, acetyl, benzoyl, and cyclic amino, *etc.* at the three positions of the pyrrole ring has been achieved. The newly formed pyrroles **130** could be dethiomethylated with RANEY® Ni in refluxing ethanol, furnishing the corresponding 3-substituted pyrroles **131** in good yields. With α-oxoketene dithioacetals **132** as substrates in the presence or the absence of an amine, ^{t}BuOK-catalyzed highly efficient one-pot synthesis of 3-amino/alkylthiocyclobut-2-en-1-ones (**135** and **136**) was performed (eqn (52)).[118] The reaction sequence was initiated by the deprotonation of **132** with the ^{t}BuOK base, and the subsequent ring-closing, elimination and substitution afforded the desired products, *i.e.*, *S*- and *N*-substituted cyclic enones **135** and **136**.



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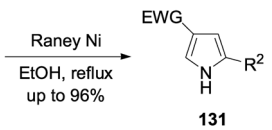

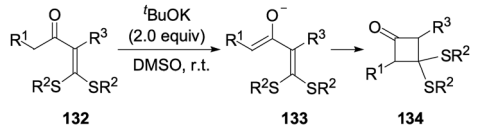

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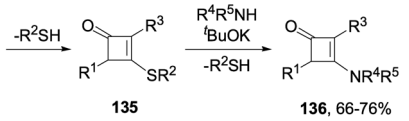
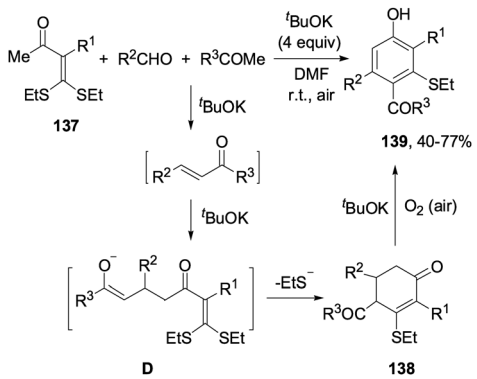
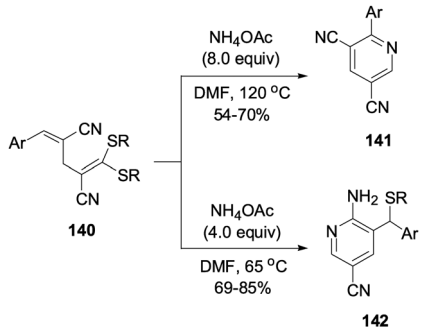




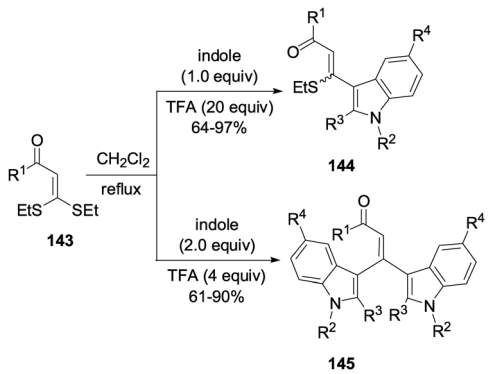
(53)

By means of a one-pot three-component reaction of α-oxoketene dithioacetal **137**, an aldehyde and a ketone in the presence of a ^{t}BuOK base (4 equiv.), polysubstituted phenols **139** were efficiently constructed *via* a [4 + 1 + 1] annulation and subsequential metal-free oxidative aromatization in air at room temperature (eqn (53)).[119] This process comprises an aldol condensation/intermolecular Micheal addition/intramolecular Michael addition/elimination of ethanethiol, and is highly chemo- and regioselective because the two ketones exhibit different reactivities. Upon varying reaction temperatures, [5C + 1N] annulation of dithioacetals formed pyridine derivatives. In the presence of NH_4OAc as an amination reagent, 1,1-bisalkylthio-1,4-pentanedienes **140** were conveniently transformed to pyridines **141** or **142** (Scheme 8).[120]

In 2009, Yu *et al.* reported the direct alkenylation of indoles with α-oxoketene dithioacetals **143** in the presence of trifluoroacetic acid (TFA) to form mono- and bisindole products **144** and **145** under controlled conditions (Scheme 9).[121] The monosubstituted products **144** were considered as the important precursors to indole alkaloid meridianin derivatives through condensation with guanidines, suggesting their potential application in the synthesis of pharmaceutically useful compounds. Hydrobromic acid, Lewis acids $CuBr_2$ and $TiCl_4$ were found to be unique catalysts in carbon–carbon bond formation with

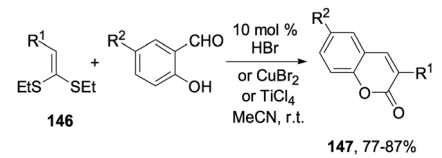


Scheme 8 Pyridine synthesis *via* C–S cleavage.



Scheme 9 TFA-mediated C–S cleavage of α-oxoketene dithioacetals with indoles.

ketene dithioacetals through C–S cleavage (eqn (54)),[122] offering an efficient route to coumarins **147**. When **146** reacted with benzoquinones under similar conditions, benzofurans were also prepared. By means of $BF_3{\cdot}OEt_2$ as the Lewis acid catalyst in CH_3NO_2, domino carbocationic rearrangement of substituted 2-indolylcyclopropyl ketene dithioacetals **148** afforded the corresponding β-ketocarbothioate **149** (eqn (55)).[123] Coumarins and their derivatives were obtained from Lewis acid $InCl_3$-catalyzed domino reactions of α-oxoketene dithioacetals (**150**) with 2-hydroxyarylaldehydes under solvent-free conditions (eqn (56)).[124] No co-catalyst and activator were required and MeSH was formed as the only side product.



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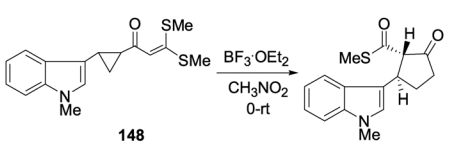

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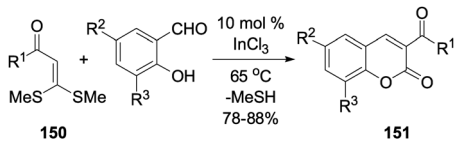
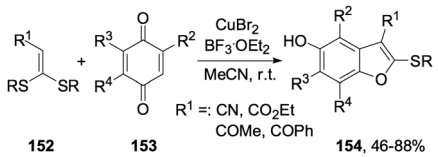


(56)

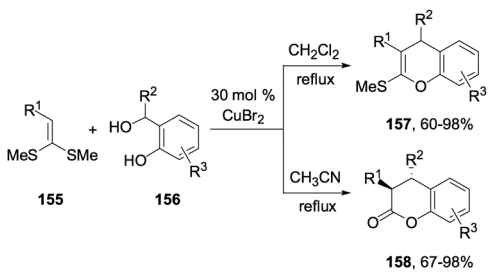
Although base- and acid-catalyzed transformations of dithioacetals have been well documented, transition metal-promoted reactions of their carbon–sulfur bonds have not been realized until recently. In 2009, Liu *et al.* reported $CuBr_2$-catalyzed synthesis of coumarins from the same reaction as shown in eqn (54).[125] In this case, 2 mol% $CuBr_2$ was used as catalyst with $BF_3{\cdot}OEt_2$ (10 mol%) as cocatalyst, the conjugate addition and sequential cyclization of α-electron-withdrawing group-substituted ketene dithioacetals **152** with quinones **153** in acetonitrile at room temperature produced benzofurans **154** (eqn (57)).[126] One-pot synthesis of polyfunctionalized 4*H*-chromenes **157** and dihydrocoumarins **158** was achieved by $CuBr_2$-catalyzed carbon–carbon coupling of benzyl acohols with ketene dithioacetals **155** (Scheme 10).[127] A remarkable solvent effect was observed on the chemoselective formation of *O*-heterocycles.



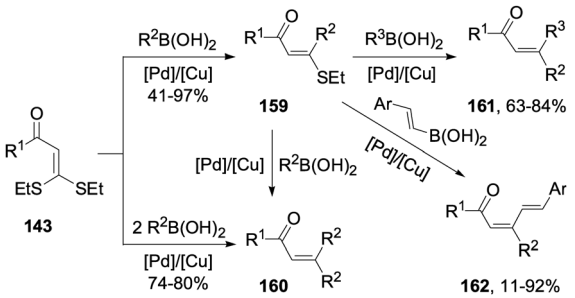
(57)

In 2011, Yu *et al.* reported rare examples of transition metal-catalyzed C–S cleavage in α-oxoketene dithioacetals **143** by means of 20 mol% $Pd(PPh_3)_4$ as catalyst, CuTC as mediator, and boronic acids as the nucleophiles (Scheme 11).[128] Mono-, di- and trisubstituted olefins **159–161** and functionalized conjugate dienes **162** were efficiently obtained under mild conditions, respectively.

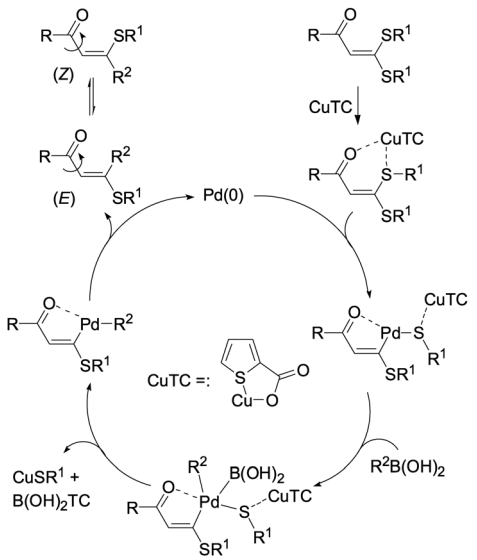
This synthetic methodology featured a wide substrate scope, high regio- and stereoselectivities *via* the α-oxo directing functionality, providing a versatile route to highly functionalized polysubstituted olefins and conjugate dienes. Such a α-oxo directing Liebeskind–Srogl cross-coupling mechanism is proposed as shown in Scheme 12.



Scheme 10 Synthesis of *O*-heterocycles *via* C–S cleavage of ketene dithioacetals.



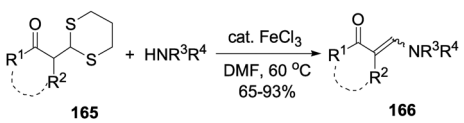
Scheme 11 Synthesis of multisubstituted olefins and conjugate dienes *via* C–S cleavage.



Scheme 12 A proposed mechanism for α-oxo directing Liebeskind–Srogl cross-coupling.

(58)

Using ketene dibenzylthioesters (**163**) as substrates, aerobic $Cu(OAc)_2$-catalyzed desulfitative carbon–carbon cross-coupling with boronic acids gave tetrasubstituted olefins **164** under relatively harsh conditions (eqn (58)).[129] $FeCl_3$ was also utilized to activate the C–S bonds in 1,3-dithanes **165** by O···Fe···S coordination interaction, rendering Fe(III) catalytic for the reactions of **165** with ammonia and secondary amines (eqn (59)).[130] With hydrazine hydrates instead of ammonia or amines, substituted pyrazoles were thus synthesized.[130,131]



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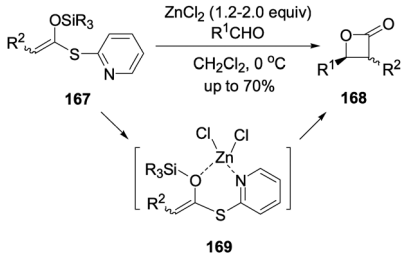
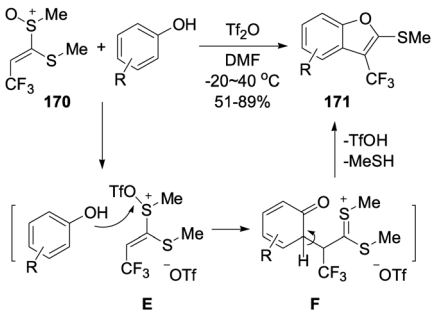


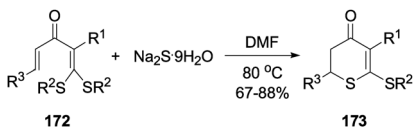
(60)

The analogues of ketene dithioacetals, *i.e.*, *O*,*S*-ketene acetals **167**, reacted with aldehydes at ambient temperature through a $ZnCl_2$-mediated tandem Mukaiyama aldol lactonization pathway to afford highly diastereoselective 1,2-disubstituted β-lactones **168** (eqn (60)).[132] Mechanistic and theoretical studies reveal that both efficiency of this process and high diastereoselectivity are highly dependent on the type of ketene acetals employed but independent of ketene acetal geometry. The precoordination between $ZnCl_2$ and thiopyridyl ketene acetal to form adducts **169** prior to aldehyde addition benefits the process.



(61)

Other methods have also been documented to promote the organic transformations of dithioacetals. For example, using 2-(2,2,2-trifluoroethylidene)-1,3-dithiane-1-oxide (**170**) as the trifluoromethylketene equivalent, triflic anhydride mediated the extended Pummerer annulation reactions with phenols, forming trifluoromethyl-benzo[*b*]furans **171** (eqn (61)).[112,133] Further reactions of the methylthio group in the products can bring diversity to highly substituted trifluoromethylbenzo[*b*]furans. α-Alkenoylketene dithioacetals **172** reacted with sulfur nucleophile $Na_2S{\cdot}9H_2O$ in DMF at 80 °C to produce highly substituted 2,3-dihydrothiopyran-4-ones (**173**) *via* a formal [5C + 1S] annulation (eqn (62)).[134] The simplicity of manipulation, ready availability of substrates and the broad range of the products make this [5 + 1] annulation strategy a promising route to *S*-heterocycles. Under radical cyclization conditions, the intramolecular cyclization of dithioacetals **161** led to 2,3-disubstituted benzo[*b*]thiophenes **162** in up to 68% yields (eqn (63)).[135]



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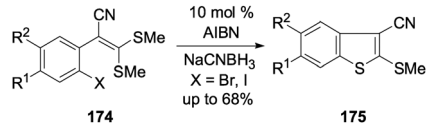
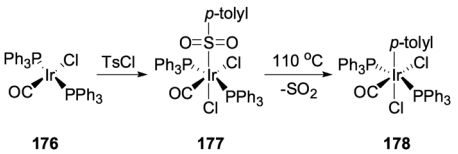


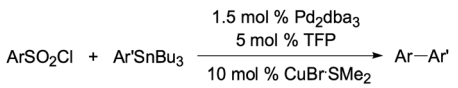
174 175 (63)

5. Catalytic C–S cleavage in sulfonyl chlorides

Organic sulfonyl chlorides are usually inexpensive and readily available. *p*-Toluenesulfonyl chloride (TsCl) is among one of the most commonly used reagents for functional group protection in organic synthesis. Desulfonylation of TsCl by a transition metal complex has been known for quite a long time. Treatment of complex $Ir(CO)(PPh_3)_3$ (**176**) with TsCl formed complex **177** which was decomposed to desulfitative complex **178** by loss of SO_2 upon heating (eqn (64)).[136] Although the C–S bond in a sulfonyl chloride can be considered as an activated bond, only limited work has been directed towards the catalytic desulfitative carbon–carbon cross-couplings of sulfonyl chlorides, *i.e.*, their relevant Stille, Suzuki, Sonogashira, Heck and Negishi reactions.[71–74] For the same purpose, arenesulfonates and arylsulfinates have only recently been utilized as the coupling electrophiles.



176 177 178 (64)



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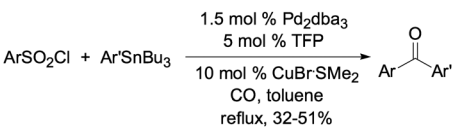
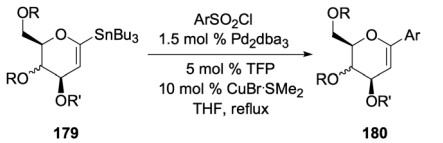
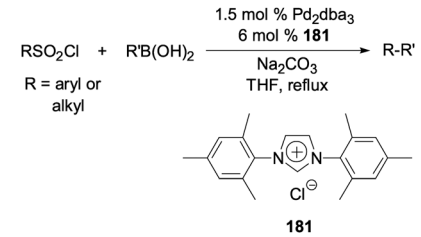


(66)

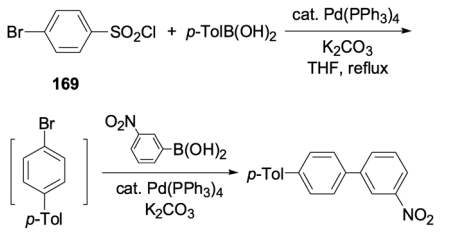
Palladium-catalyzed desulfitative Stille cross-couplings of sulfonyl chlorides were performed in the presence of a copper(I) reagent and tri-2-furylphosphine (TFP) as a ligand, forming biaryls as the products (eqn (65)).[137] Under a CO atmosphere, carbonylative Stille reactions of sulfonyl chlorides occurred (eqn (66)). As compared with the Stille reactions of organostannes with aryl halides or triflates,[138] the sulfonyl chloride substrates are more reactive than the corresponding chlorides and bromides, but less reactive than the corresponding iodides. By means of such a synthetic protocol, aryl and arylmethyl C-glycosides (**180**) were prepared (eqn (67)).[139] With sulfonyl chlorides as the electrophilic reagents, palladium-catalyzed Suzuki cross-couplings with boronic acids underwent in refluxing THF to give the products in up to 92% yields, also exhibiting the reactivity order ArI > $ArSO_2Cl$ > ArBr ≫ ArCl (eqn (68)).[140] The NHC ligand derived by α-elimination of HCl from **181** generated, with a palladium source, *i.e.*, Pd_2dba_3, the best catalyst.



179 180 (67)

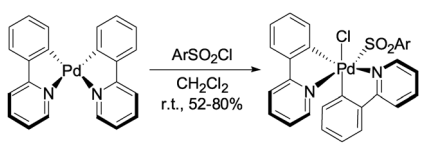


181 (68)



169 170 171, 52% (69)

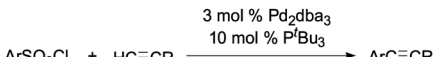
A one-pot, two-step Suzuki cross-coupling approach of sulfonyl chloride **182** gave double arylation product **184** *via* intermediate **183** (eqn (69)).[140] The controlled experiment by mixing equimolar amounts of TsCl and $PdCl_2(PhCN)_2$ in THF-d_8 at 45 °C followed by monitoring the ^{13}C NMR spectra revealed formation of a Pd–C bond, which suggests two possible mechanisms: (1) the metal inserts into the SO_2–Cl bond first with rapid subsequent elimination of SO_2, (2) the oxidative addition of the metal species first onto the C–S bond with subsequent elimination of SO_2. The former pathway has been mechanistically identified by Dong *et al.* (eqn (70)).[141] Rigid and electron- rich C,N ligands are known to stabilize Pd(IV) species and thus treatment of Pd(II) complex **185** with 4-methyl or 4-methoxybenzene sulfonyl chloride in dichloromethane at room temperature formed Pd(IV) sulfinate complexes **186** which could be isolated and structurally characterized by X-ray crystallographic graphic studies.



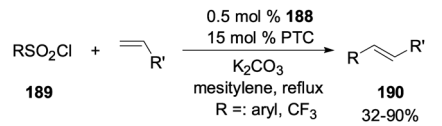
185 186 (70)

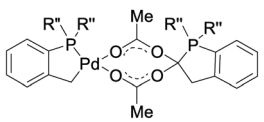
Vogel *et al.* reported palladium-catalyzed desulfitative Sonogashira reactions of arenesulfonyl chlorides with terminal alkynes, *i.e.*, aryl- and alkylacetylenes. A combination of Pd_2dba_3 and CuI provided the best catalyst for the reactions in refluxing THF in the presence of a K_2CO_3 base (eqn (71)).[142] It is noteworthy that the desulfitative cross-coupling of

arenesulfonyl chlorides with terminal alkynes did not occur in the absence of the copper cocatalyst. Desulfitative Mizoroki–Heck arylation and trifluoro-methylation of olefins with arene- and trifluoromethanesulfonyl chlorides were carried out under palladium catalysis, respectively. By using palladacycle **188** as catalyst in the presence of the phase transfer catalyst (PTC) $Me(Oct)_3NCl$, sulfonyl chlorides **189** underwent the Heck-type reactions with terminal alkenes (eqn (72)).[143] Nano Pd(0) in a nitrile-functionalized ionic liquid also behaved efficiently for the same type of reactions of sulfonyl chlorides.[144] It is to be noted that desulfitative homo-coupling was always accompanied in the cross-coupling reactions of sulfonyl chlorides with organozinc chlorides, which was confirmed by Tanaka *et al.* (eqn (73)).[145] In the presence of hexamethyldisilane under heating, arenesulfonyl chlorides were easily transformed into their corresponding biaryls through a homo-coupling pathway.



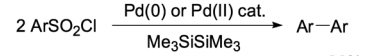
(71)



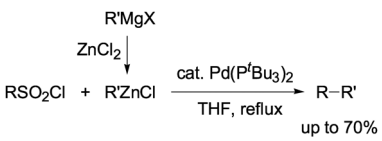


188 (R" = *o*-tolyl)

(72)

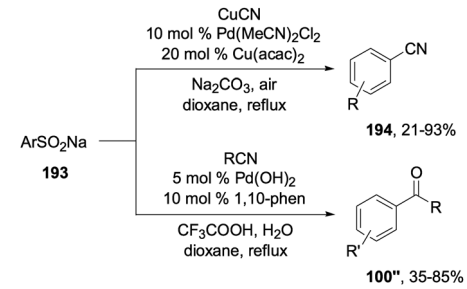


(73)



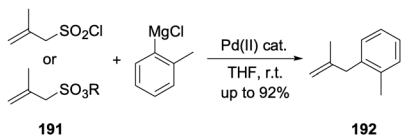
(74)

As electrophilic reagents, sulfonyl chlorides underwent palladium-catalyzed Negishi reactions with organozinc halides to construct new carbon–carbon bonds (eqn (74)).[146] Sulfonyl chlorides can also desulfonylatively react with other organometallic compounds. For example, desulfitative allylation of Grignard reagents and enolates using allylsulfonyl chlorides and esters **191** proceeded under very mild conditions (eqn (75)),[147–149] and iron(III) compounds such as $Fe(acac)_3$, $FeCl_3$ and FeF_3 were used as the efficient catalysts under ligand-free conditions.[150,151] $Ni(dppf)Cl_2$ was employed as the catalyst for solid-phase synthesis of biphenyls and terphenyls through the reductive cleavage/cross-coupling of the C–S bond of polymer-bound arenesulfonates with Grignard reagents.[152] Treatment of arenesulfonyl chlorides or sodium sulfinates (**193**) with copper(I) cyanide in the presence of a palladium catalyst afforded aryl nitriles **194**,[153] while using nitriles instead of CuCN led to aryl ketones **100″** from $Pd(OH)_2$-catalyzed

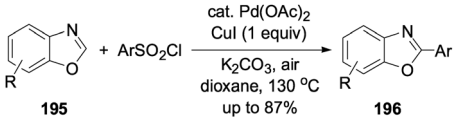


Scheme 13 Synthesis of nitriles and ketones from sodium arenesulfinates.

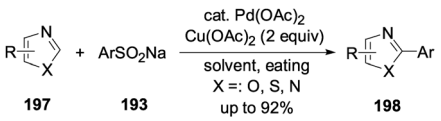
desulfitative addition of sodium sulfinates (Scheme 13).[154] Ligands and solvents played an important role in the reaction yields. This procedure provides a rapid and convenient route to aryl ketones on a small scale.



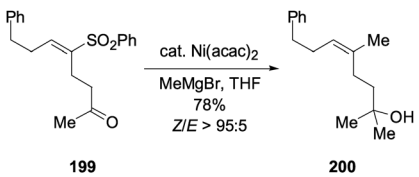
(75)



(76)



(77)



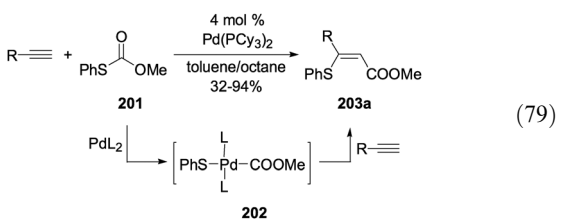
(78)

Recently, arenesulfonyl chlorides and sodium arenesulfinates have been reported for heteroarene C–H functionalization. Benzo[*d*]oxazoles (**195**) were desulfitatively arylated by arenesulfonyl chlorides in the presence of an equivalent amount of CuI under palladium catalysis (eqn (76)).[155] Using sodium arenesulfinates (**193**) as the coupling partners, azole, thiazole and imidazole derivatives **197** were also arylated under the oxidative conditions (eqn (77)),[156,157] demonstrating an alternative protocol for the preparation of functionalized heteroarenes. $Ni(acac)_2$-mediated desulfitative cross-coupling of vinylsulfones with Grignard reagent MeMgBr in THF afforded the methylated alkenes (eqn (78)).[158]

6. Diverse catalytic C–S cleavage

Organosulfur compounds, which are usually considered as the poisons to transition metal catalysts,[159] have been proved to be versatile reagents for a variety of transition metal-catalyzed transformations.[71–74] Palladium catalysts exhibited diverse

catalytic capability for C–S bond cleavage. In 2001, Tanaka *et al.* reported palladium-catalyzed thioesterification of terminal alkynes with *O*-methyl *S*-phenyl thiocarbonate (**201**), forming product **203a** (eqn (79)).[160] This procedure was readily applicable to various alkynes. During the reaction, the oxidative addition indeed proceeded at room temperature upon mixing $Pd(PCy_3)_2$ with **201** in hexane to afford intermediate *trans*-$Pd(SPh)(COOMe)(PCy_3)_2$ (**202**) which was structurally confirmed by X-ray crystallographic analysis. However, similar reactions of thioesters **204** mediated by $Pt(PPh_3)_4$ gave the decarbonylative addition products **203b** (eqn (80)).[161] The stoichiometric reactions of **204** and $Pt(PPh_3)_4$ were performed in C_6D_6 at 25 °C and monitored by $^{31}P\{^1H\}$ NMR determinations, revealing formation of a mixture of *trans*-$Pt(SR^3)[C(O)R^2](PPh_3)_2$ and *anti*-$(PPh_3)[R^2C(O)]Pt(\mu\text{-}SR^3)_2Pt[(CO)R^2](PPh_3)$. With internal alkynes as substrates, the reaction had to be carried out in xylene at an elevated temperature, *e.g.*, 140 °C (Scheme 14).[162] 5-Methylpyridine-2-thiolate-bridged dinuclear Pt(III), Pt(II), or Pd(II) complexes (1 mol%) were successfully applied as catalysts for the desulfitative reduction of pyridine-2-thiol by H_2 (60 atm) in DMF at 150 °C.[163]



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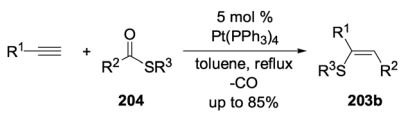
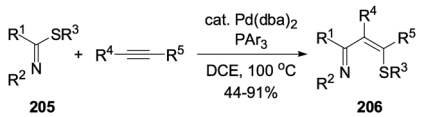
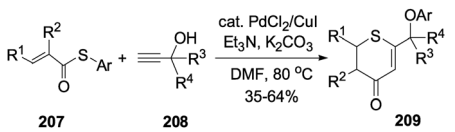


(80)

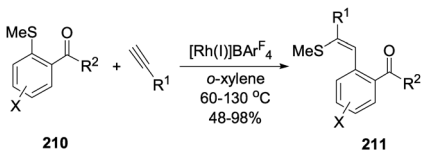
Palladium-catalyzed regioselective iminothiolation of alkynes was realized to form 4-SR substituted 1-azadienes (**206**) (eqn (81)).[164] The introduction of a CF_3 group into the iminocarbon moiety of iminosulfide substrates (**205**) is key to achieving the reaction. The oxidative addition of **205** to the Pd(0) species triggered the reaction to form a C–S cleavage complex by Pd metal. Subsequent regio- and stereoselective insertion of alkyne into the Pd–S bond of the intermediate complex generated an alkenylated Pd(II) species from which reductive elimination with regeneration of Pd(0) species completed the catalytic cycle. In the presence of a base, Pd/Cu-catalyzed reactions of α,β-unsaturated thioesters **207** and propargyl alcohols **208** efficiently produced 2,3-dihydrothiopyran-4-one derivatives (**209**) (eqn (82)).[165] Both carbon–sulfur bonds in **207** were cleaved as a result of the one-pot procedure. The reactions presumably proceeded through a sequence of Sonogashira-type reaction, Michael-addition of thiol (generated *in situ*) to the yne moiety, intramolecular aromatic nucleophilic substitution, and cyclization.



(81)



(82)



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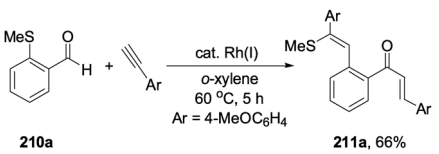
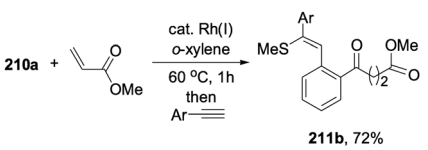
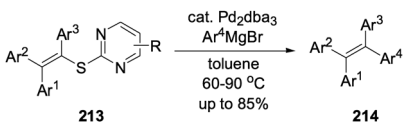


(84)



(85)

Rhodium-catalyzed alkyne carbothiolation was performed by means of aryl methyl sulfides **210** as substrates.[166] The overall process resulted in reincorporation of the original arene functional group, and a methyl sulfide, into the product **211** as an alkenyl sulfide (eqn (83)). The carbothiolation process can be combined with an initial Rh(I)-catalyzed alkene or alkyne hydroacylation reaction in a three-component cascade sequence (eqn (84) and (85)).



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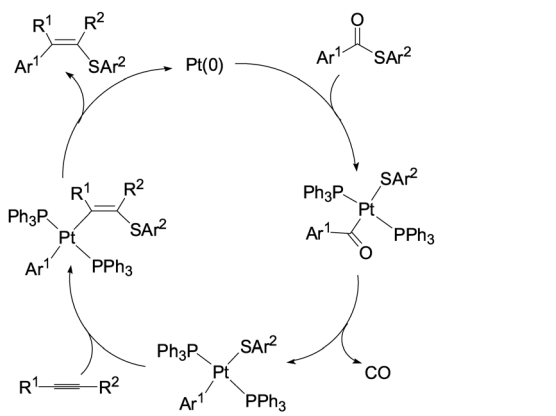
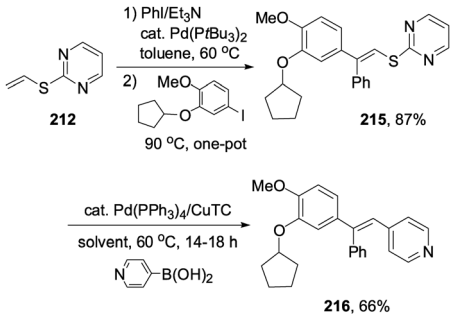


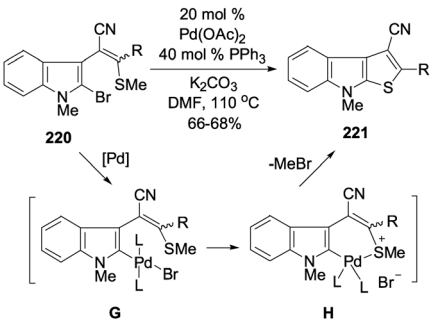
Scheme 14 Pt(0)-catalyzed decarbonylative addition of thioesters to internal alkynes.



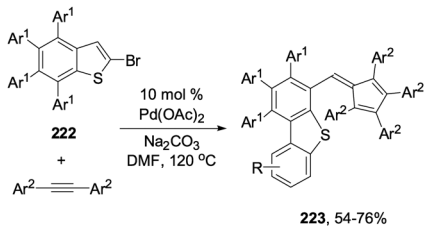
(87)

Vinyl 2-pyrimidyl sulfide (**212**) has been applied as a platform for tetrasubstituted olefin (**214**) synthesis in which the last step is a palladium-catalyzed C–C coupling *via* C–S cleavage of the intermediate sulfide **213** (eqn (86)).[167] This protocol can be considered as a programmable and diversity-oriented synthetic scheme for tetrasubstituted olefins through a site-selective and sequential assembly of π-components onto a C═C core of **212**. As for the C–S bond cleavage of **213**, palladium-catalyzed cross-coupling reactions with Grignard reagents (Ar^4MgBr) were particularly effective. In a similar fashion by using boronic acids instead of Grignard reagents as the nucleophiles in the presence of CuTC, trisubstituted olefin such as **216** was prepared (eqn (87)).[168] Catalytic hydrogenation of the C═C bond in **216** with H_2 in EtOH by means of the Pd/C catalyst gave CDP840, a potential therapeutic agent for asthma. Under palladium catalysis, chemo-selective cross-coupling reactions underwent in the BODIPY dynes **217**.[169] In the Stille reaction of **217a** (X = Br), the monosubstituted product **218** by C–S cleavage was formed in 26% yield as well as the major disubstituted product (65%), while the Liebeskind–Srogl cross-coupling reaction of **217b** (X = NO_2) with 4-methoxycarbonylphenylboronic acid quantitatively afforded the disubstituted product **219** (Scheme 15).

The intramolecular C–S cleavage/C–S formation strategy was documented to synthesize *S*-heterocyclic compounds.[170,171] (*o*-Bromoaryl/heteroaryl)-acrylonitrile (**220**) underwent palladium-catalyzed intramolecular arylation/heteroarylation to form polycyclic heterocycles **221** (eqn (88)).[170] Under similar conditions, the reactions of bromobenzothiophenes **222** with alkynes produced sulfur-based heterocycles and fulvenes **223** (eqn (89)).[171]



(88)



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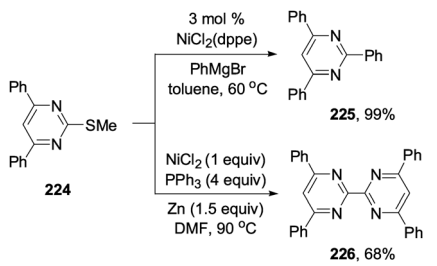
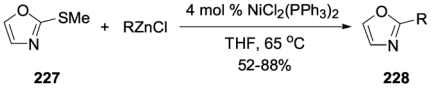


(90)

Nickel has been proved to be a useful catalyst to activate C–S bonds. Under the controlled conditions by using the $NiCl_2$(dppp) catalyst or a combination of stoichiometric $NiCl_2$/PPh_3/Zn in a 1.0 : 4.0 : 1.5 molar ratio, functionalized pyrimidyl methyl sulfide **224** underwent cross- or self-coupling to give the desulfitative products **225** and **226** (eqn (90)),[172] respectively. Thus, potentially useful fluorescent materials were obtained. Similar results were obtained in the synthesis of 1,10-bis(methyl)fluoranthene[173] and alkenes.[158] 2-Substituted oxazoles (**228**) were prepared *via* nickel-catalyzed cross-coupling reactions of 2-methylthiooxa-zole (**227**) with various organozinc reagents (eqn (91)).[174] This synthetic protocol was also extended for the chemoselective, one-pot synthesis of unsymmetrical 2,5-disubstituted oxazoles (**230**) (eqn (92)). Under reductive ligand-free conditions, the catalytic C–S cleavage of $C(sp^3)$- and $C(sp^2)$–SMe bonds was achieved by means of $Ni(COD)_2$ as catalyst and ethyldimethylsilane as the reductant (eqn (93)).[175] The procedure is potentially applicable with a wide substrate scope and high chemoselectivity. In the presence of a nickel hydride catalyst, *i.e.*, $[(dippe)Ni(\mu\text{-}H)]_2$, highly efficient deoxydesulfurization of dibenzothiophene sulfones (**233**) occurred to give sulfur-free biphenyls (**234**) as well as MgS and MgO (eqn (94)).[176]



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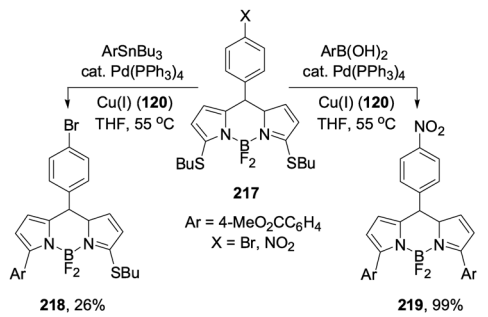
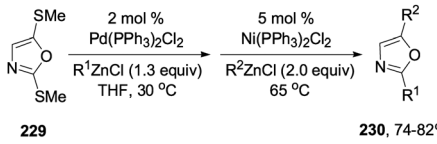


Scheme 15 Functionalization of dyes *via* C–S cleavage.



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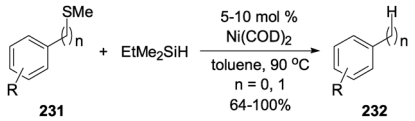

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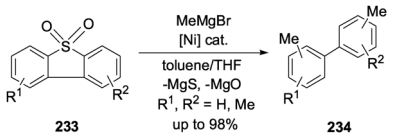
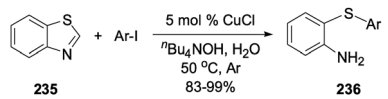
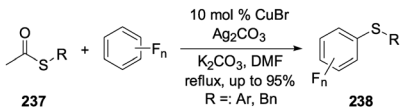


(94)

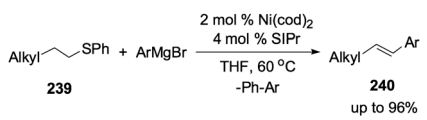
Ligand-free copper-catalyzed C–S cross-coupling of benzothiazole with aryl iodides was carried out in aqueous phase. The reactions were promoted by CuCl with tetrabutylammonium hydroxide as base (eqn (95)).[177] 2-Aminophenyl sulfide derivatives (**236**) were produced in 83–89% yields. In the presence of the sole copper(I) catalyst, *i.e.*, 10 mol% CuBr, thioesters **237** underwent cross-coupling with perfluoroarenes to afford polyfluoroaryl thioesters **238** (eqn (96)).[178] However, under the same conditions by using $Pd(OAc)_2$ as catalyst, the reaction of 4-methylphenyl thioacetate with pentafluorobenzene only formed the desired product in 17% yield.



(95)

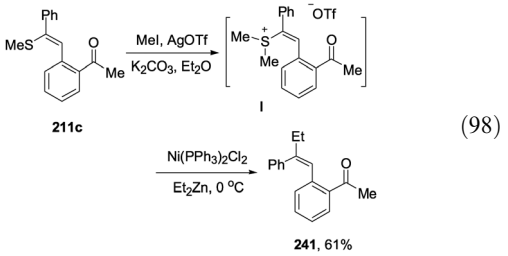


(96)



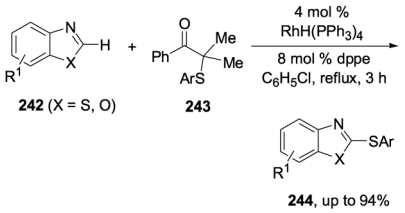
(97)

In the presence of an NHC ligand, *i.e.*, SIPr (ligand precursor: 1,3-bis(2,6-diisopropylphenyl)imidazolinium chloride, SIPr·HCl), nickel-catalyzed alkenylative cross-coupling of alkylsulfides **239** with arylmagnesium bromides produced alkenyl–aryl coupling products **240** (eqn (97)).[179] The key to this successful transformation is the use of the bulky NHC ligand SIPr, which suppresses the conventional biaryl coupling reaction. The C–S bond of an alkenyl sulfide can also be cleaved by Ag(I)-mediated alkylation and Ni(II)-catalyzed cross-coupling with Et_2Zn (eqn (98)).[166]



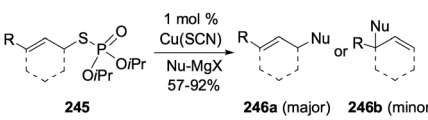
(98)

Under Rh(I) catalysis, direct functionalization of heteroarenes **242** such as benzothiazoles, benzoxazoles and benzothiophene was achieved by 2-(phenylthio)isobutyrophenone (**243**) *via* sp^3 C–S bond cleavage, generating 2-phenylthioheteroarenes **244** *via* sp^2 C–S bond formation (eqn (99)).[180] Monocyclic heteroarenes, *i.e.*, 1-methyl-1,2,3,4-tetrazole and 2-cyanothiophene, were converted into the corresponding 5-phenylthio derivatives. Compounds **243** thus behaved as efficient arylthio transfer reagents. The use of an appropriate phenylthio transfer reagent is crucial for the efficient transformation of the heteroaromatic C–H bonds into C–S bonds.

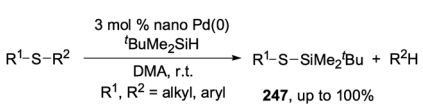


(99)

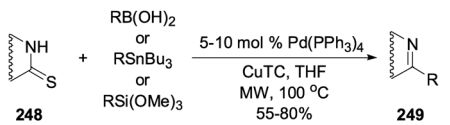
Copper(I)-catalyzed, α-selective, allylic alkylation reactions between phosphorothioate esters (**245**) and organomagnesium reagents have been documented by Wu *et al.*[181] With organomagnesium compounds as the hard nucleophiles, the challenging alkylation, vinylation and arylation selectively occurred at the α-position of **245** (eqn (100)). Such a Cu(I)-catalyzed allylic alkylation has never been reported before. This method features utilization of a wide range of Grignard reagents and electrophiles. Starting with allylic chlorides by using sodium diethylphosphorothioate as a stoichiometric additive, high α-selectivity was achieved. Palladium nanoparticles generated *in situ* from the *N*,*N*-dimethylacetamide (DMA) solutions of PdX_2 (X = Cl, OAc, CF_3COO) or Pd_2dba_3 by reduction with alkyl silanes selectively catalyzed the cross-coupling of thioethers with silane ^{t}BuMe$_2$SiH, forming the corresponding thiosilanes **247** (eqn (101)).[182]



(100)



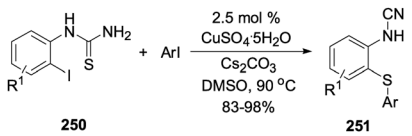
(101)



(102)

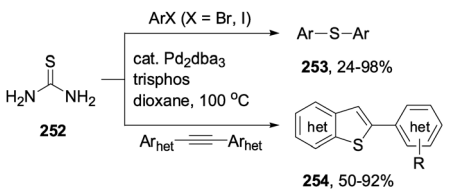
The C=S bonds in organosulfur compounds can also be catalytically cleaved by transition metals. The Liebeskind–Srogl coupling of cyclic thioamides and thioureas (**248**) with alkenylboronic acids, vinyl- and (hetero)arylstannanes, or arylsiloxanes gave the corresponding desulfitative products **249** under relatively mild and neutral conditions (eqn (102)).[183] The synthetic methodology can be applied to a wide range of heterocyclic structures with embedded thioamide fragments and microwave irradiation facilitated the cross-coupling reaction. $CuSO_4$ salt was used to catalyze the domino intra- and intermolecular C–S cross-coupling reactions of 2-(arylthio)arylcyanamides (**250**) with aryl iodides under ligand-free conditions, affording 2-(arylthio)arylcyanamides (**251**) through the *in situ* generated catalytically active Cu(I) species (eqn (103)).[184] 2-Aminothiazole was proposed to be the reaction intermediate which would undergo intermolecular C–S cross-coupling reaction with the *in situ* generated arylcopper(I) species to form the desired product.

Recently, the palladium-catalyzed domino C–S bond formation/cross-coupling/cyclization procedure was reported by Paradies *et al.*[185] Thiourea (**252**) was used as a cheap and easy-to-handle dihydrosulfide surrogate in the reaction. Structurally important biarylthioethers (**253**) and benzothiophenes and thieno[3,2-*b*]thiophenes (**254**) were obtained (Scheme 16), respectively. The formation of **253** follows the domino thiolation/cross-coupling pathway, while generation of **254** proceeds *via* domino thiolation/cyclization. The symmetrical biarylthioethers were obtained in high to excellent yields, and the *S*-heterocycles were prepared in high yields. This procedure provides a straight-forward access to pharmaceutically important molecules.



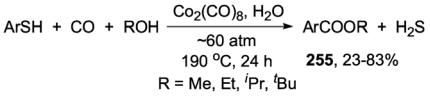
(103)

A reductive atmosphere promotes transition metal-catalyzed cleavage and formation of C–S bonds. Alper *et al.* reported the first examples of the carbonylation of mercaptans.[186] Under relatively harsh conditions, cobalt carbonyl catalyzed the desulfurization and carbonylation of mercaptans to carboxylic esters

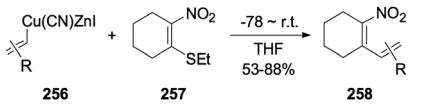


Scheme 16 Domino C–S bond cleavage and transformations.

255 and H_2S by means of carbon monoxide in aqueous alcohol (eqn (104)). In the presence of terminal alkynes, palladium,[187] platinum,[188,189] and rhodium[190] catalyzed the thioformylation,[187,190] hydrothiocarboxylation,[188] thiocarbonylation[189] of aromatic thiols and carbon monoxide. Thiocarbonylation of propargylic alcohols and mesylates,[191,192] allyl alcohols,[193] enynes,[194] dienes,[195,196] allenes,[197,198] iodoarenes[199] with thiols and carbon monoxides has been documented.



(104)



(105)

It should be noted that non-catalytic transformations of organosulfur compounds also play an important role in synthetic chemistry. Versatile reagents and diverse conditions have been applied to establish efficient processes involving C–S cleavage in organic and bioorganic synthesis. The C–S bonds in organosulfur compounds can also be cleaved by stoichiometric amounts of organometallic reagents. Copper(I) reagents, *e.g.*, zinc cuprates (**256**), derived from readily available vinyl halides, were reacted with 2-thioethyl nitrocyclohexene (**257**) *via* conjugate addition/elimination provided the desired nitrodienes (**258**) which could be utilized for the synthesis of nitroso acetals (eqn (105)).[200] Other methods such as steady state and laser flash photolysis (LFP),[201,202] addition of alkylsulfanyl radicals,[203] use of stoichiometric amounts of strong bases,[204] conversion to sulfur ylides[205] and bioinspired protocols[206,207] have also been employed to cleave C–S bonds for various purposes.

7. Conclusions

Mechanistic investigation of the reactions between transition metal complexes and organosulfur compounds such as thiophenes, benzothiophenes and dibenzothiophenes can provide fundamental understanding of C–S activation/cleavage in HDS processes. By selecting an appropriate cocatalyst or suitable organosulfur compounds as coupling partners to avoid poisoning of a C–S bond to the transition metal catalyst, efficient C–C cross-coupling can be realized *via* catalytic C–S bond activation/cleavage, providing versatile routes to functional organic compounds.

Acknowledgements

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