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Room-temperature carbon–sulfur bond formation from Ni(II) σ-aryl complex via cleavage of the S–S bond of disulfide moieties

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ABSTRACT: The formation of ArSY (Y: C(=S)NMe$_2$, Ph, P(=O)(OEt)$_2$) by reductive elimination from σ-aryl complexes (M(PPh$_3$)$_2$PhBr, M = Ni, Pd), associated with disulfides (YS–SY, Y: C(=S)NMe$_2$ (1), Ph (2), P(=O)(OEt)$_2$ (3)), at ambient temperature, has been investigated. Various mechanistic features of disulfide bond (S–S) cleavage have been elucidated using disulfide 1 by ^{31}P NMR spectroscopy and matrix-assisted laser desorption/ionization–time of flight mass spectrometric investigations. Based upon the results of nucleophilic cleavage of the S–S bond by PPh$_3$, studies of the reductive elimination process show that when M(PPh$_3$)$_2$PhBr is mixed with disulfide 1, competitive reactions occur between the PPh$_3$ ligand, disulfide 1 and a trace amount of water, leading to low C–S coupling yields; an oxidation reaction of PPh$_3$ with disulfide and water occur prior to C–S cross-coupling, and phosphonium ion intermediates are likely involved. However, when the disulfide 1 is pretreated with PPh$_3$, the Ni(II) σ-aryl complex affords the C–S coupling product nearly quantitatively at room temperature. The pretreatment method is also effective for the coupling reaction of disulfide 2 and Ni(II) σ-aryl complex. The difference between Ni(II) and Pd (II) σ-aryl complexes on C–S bond formation by reductive elimination can be explained by the affinity of metal for the thiolate ligands derived from the cleaved disulfide. Copyright © 2013 John Wiley & Sons, Ltd.

Keywords: C–S cross-coupling; nickel complex; disulfide; room temperature reaction

Introduction

Aromatic carbon–sulfur bond formation is an important synthetic organic transformation.[1,2] In the past few decades carbon–sulfur coupling reactions based on nickel,[3–7] palladium[8–19] or copper[20–27] catalysis have become popular methods for the synthesis of functional aryl sulfides, which are of particular interest in organic electronics, such as high refractive index polymers,[28,29] and in bioactive compounds.[30,31] Other transition metal-catalyzed systems (namely iron-[32] or cobalt-based[33,34] systems) have also been reported to catalyze C–S bond formation.

Although disulfides are more desirable to use as thiolation reagents compared to thiols because of their stability and because they are less pungent than the corresponding thiols, classic Ni- and Pd-catalyzed coupling systems[4,35] with disulfides have required high reaction temperatures and long reaction times. More recently Ananikov *et al.* reported the reaction of dichalcogenides with Ni(0) or Pd(0), and their application in the catalytic addition reaction of dichalcogenides to alkynes at high temperatures.[36–38] To the best of our knowledge, disulfide-derived carbon–sulfur coupling at room temperature has rarely been studied.[39] Furthermore, little is known about C–S cross-coupling with a variety of disulfides except for diphenyl disulfide.

To achieve the goal of attaining a cross-coupling reaction that affords C–S bond formation at room temperature as shown in Scheme 1, the catalytic cycle would include the following stages: (i) oxidative addition of an organic halide (R–X); (ii) reaction of the disulfide with the M(II) complex; and (iii) C-heteroatom reductive elimination. This report concentrates on the process of disulfide reaction with the M(II) complex and the proceeding reductive elimination with Ni(II) or Pd(II) σ-aryl complexes to access carbon–sulfur bond formation under room temperature conditions.

Results and Discussion

Mechanistic Aspects of S–S Bond Cleavage

First, we conducted studies on the S–S bond cleavage process. The nucleophilic cleavage of the S–S bond by PPh$_3$ and its usability in synthesis of unsymmetrical disulfide have been documented, where the nucleophilic attack by Ph$_3$P on ArSSAr is thought to form the benzene thiolate anion (ArS$^-$) and thiophenoxyphosphonium ion Ph$_3$P$^+$–SAr.[40,41] Meanwhile, the disulfide moiety has also been found to react with transition metal ions in several different pathways. For example, disulfides can (i) form simple adducts or coordination complexes[42–44] and (ii) undergo oxidation S–S bond cleavage reactions from the transition metal.[36–38,44–49] Such oxidative S–S bond cleavage can sometimes involve homolysis of the S–S bond and it is well known that the homolysis step is assisted by high

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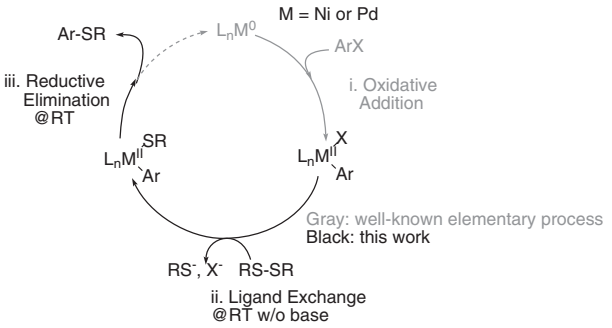
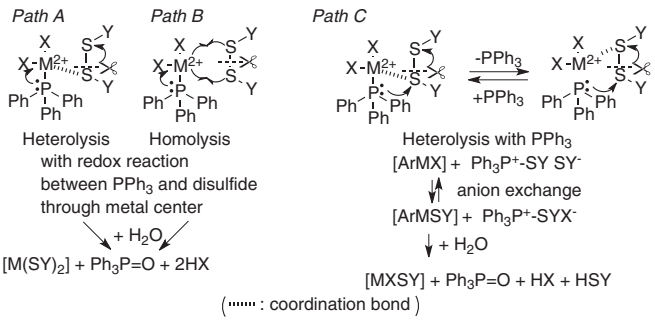


Scheme 1. Typical catalytic cycle of aryl halide and disulfide cross-coupling reaction.

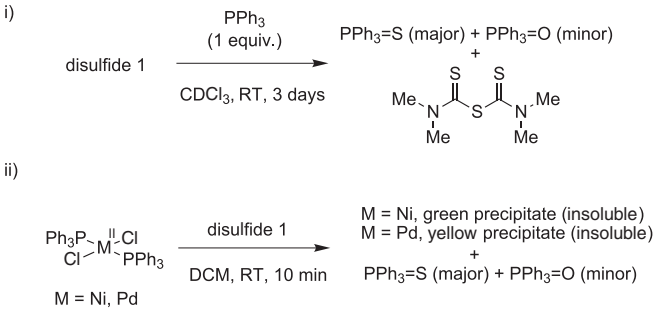
temperatures (>100 °C).[46] In our case, there are three possible pathways that for the cleavage of disulfide by the group 10 metal complexes: redox-driven homolysis (path A), heterolysis (path B) and phosphine-ligand-assisted heterolysis (path C) as shown in Scheme 2. These paths A, B and C can be called oxidative cleavage, radical-assisted cleavage, and nucleophile-assisted cleavage, respectively. The first two pathways may afford M(0) as an intermediate;[36–38,50–52] meanwhile pathway C does not affect the oxidation state of the M(II) metal center. In order to clarify the role of PPh_3 and the metal during S−S bond cleavage in disulfides, two reactions as shown in Scheme 3 were tested.

The reaction of disulfide **1** and PPh_3 yielded S=PPh_3, O=PPh_3 and tetramethylthiuram (Fig. 1a for ^{31}P NMR and Fig. 1b for ^1H NMR). The nucleophilic attack by PPh_3 on disulfide **1** most likely forms the thiolated phosphonium ion (PPh_3^+−S(CS)NMe_2) and the thiolate anion ($^-$S(CS)NMe_2) as intermediates.[40] Nucleophilic attack of the thiolate anion to the phosphonium ion would result in the formation of tetramethylthiuram and S=PPh_3. The thiolated phosphonium ion can also react with the trace amount of water in the deuterated chloroform to from O=PPh_3 as shown in Scheme 4.[40,53]

The reaction of disulfide **1** with $Ni(PPh_3)_2Cl_2$ (Scheme 3(ii)) afforded a green insoluble precipitate, O=PPh_3 and S=PPh_3 (supporting information, Fig. S1). The insoluble precipitate was analyzed using matrix-assisted laser desorption/ionization–time of flight mass spectrometry (MALDI-TOF-MS) and a thiocarbamate-coordinated complex, Me_2NCS_2-$NiPPh_3Cl$, was detected (supporting information, Fig. S2). We also examined ^{31}P NMR and MALDI-TOF mass spectra for the Pd complex and the results were similar to the Ni analogue (supporting information, Figs S3 and S4) although an additional complex, Me_2NCS_2-Pd-$SPPh_3Cl$, was also detected. The formation of O=PPh_3 and S=PPh_3 presumably occurs via a similar mechanism as described



Scheme 2. Possible disulfide bond cleavage mechanisms.



Scheme 3. (i) Metal-free S−S bond cleavage reaction with PPh_3; (ii) reaction of $M(II)(PPh_3)_2Cl_2$ metal complex with disulfide **1**.

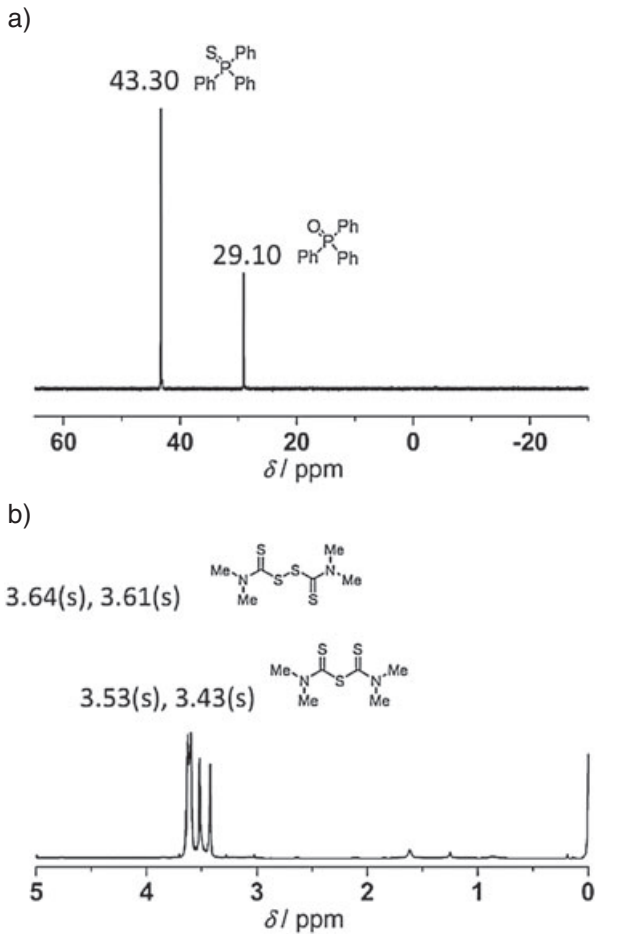
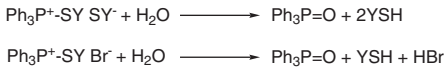


Figure 1. (a) Crude ^{31}P NMR spectrum of reaction of disulfide **1** with PPh_3[54]; (b) crude ^1H NMR spectrum of reaction of disulfide **1** with PPh_3.[55]



Scheme 4. Possible reaction for the formation of O=PPh_3.[40,53]

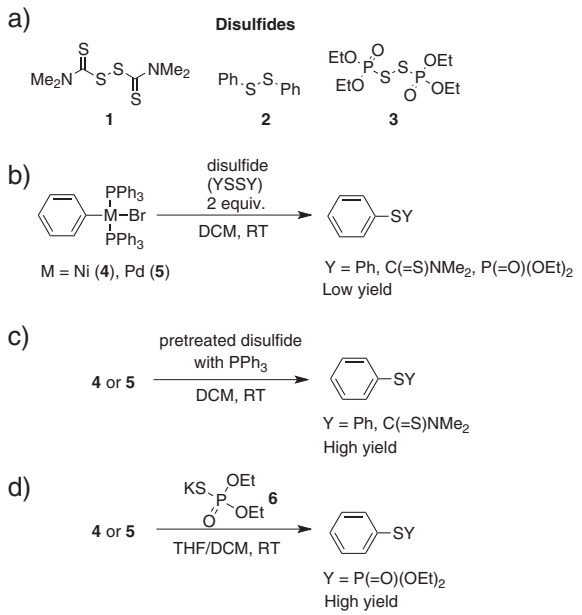
above for the reaction in Scheme 3(i). However, in this case the released thiolate anion can coordinate to the metal centers, providing the complexes observed in MALDI-TOF-MS.

The two test reactions strongly suggest the involvement of PPh_3 in the room temperature cleavage of the disulfide bond,

which shows that the most feasible pathway for S—S bond cleavage is Scheme 2 path C. Ananikov *et al*. also observed the formation of E=PPh_3, where E = S or Se when reacting dichalcogenides in the presence of Ni or Pd catalysts at high temperatures.[36,37] However, in their case, $M(SY)_2$ species was observed not MXSY that we observe, suggesting that at high temperatures path A or B is operating.[36] Although we cannot completely eliminate paths A and B in our case, we believe that it is unlikely that these paths are operating because high temperatures are typically required for such reactions.[56]

C—S Cross-Coupling

As noted above, ligated and/or unligated PPh_3 can behave as a trigger for the S—S bond cleavage in disulfides at room temperature. Next, we selected several disulfides (**1–3**) and performed reactivity screening with the Ni(II) or Pd(II) σ-aryl complexes (**4**, **5**) in dichloromethane at room temperature with and without pretreatment of the disulfide with PPh_3 as shown in Scheme 5 to study the reductive elimination step. Table 1 summarizes the yields of the C—S coupling product. In most cases, where the disulfide was not pretreated with PPh_3, their restructured phosphine compounds such as O=PPh_3 and S=PPh_3 were observed via ^{31}P NMR spectroscopy (see supporting information Figs S5–10 for details) showing that the ligated PPh_3 or the dissociated PPh_3 ligand was cleaving the S—S bonds. The reaction of disulfide **1** or **3** with Ni complex **4** afforded low yields of C—S coupling products, while the reaction with disulfide **2** only gave trace amounts of the desired C—S coupling product as detected by GC-MS. In comparison with Ni complex (**4**), Pd complex (**5**) was not effective for C—S cross-coupling. In order to prevent loss of the metal complex via reaction of the reagents with the PPh_3 ligand, comparison reactions with the Ni complex and disulfide **1** and **2** pretreated with PPh_3 were carried out, which afforded the desirable C—S coupling product almost quantitatively (Scheme 5c and Table 1). However, the Pd complex did not afford



Scheme 5. (a) Structure of disulfides tested; (b) reaction of the disulfides with the σ-aryl complexes; (c) reaction of PPh_3-pretreated disulfides with σ-aryl complexes; (d) reaction of potassium thiolate **6** with σ-aryl complexes.

Table 1. Comparison of the yield of the carbon–sulfur bond formation with various disulfides with and without PPh_3 pretreatment

Disulfide	Without PPh_3 pretreatment yield (%)[a]		With PPh_3 pretreatment yield (%)[b]	
	Ni	Pd	Ni	Pd
1	32	Trace[c]	90	0
2	Trace[c]	Trace[c]	92	0
3	9	0	93[d]	0

[a]The yield was estimated by ^1H NMR using tri(*o*-tolyl)phosphine as an internal standard.
[b]Isolated yield.
[c]Trace amount of C—S coupling product was detected by GC-MS.
[d]Potassium thiolate was used instead of pretreatment method.

the C—S coupling products even with the pretreated disulfide. This is not surprising because most of the reported Pd-catalyzed C—S coupling reactions require a bidentate phosphine ligand with a large bite angle.[9,10,12] Moreover, several square planar Pd(II) σ-aryl complexes which have PPh_3 and thiolate as ancillary ligands are fairly stable and they do not catalyze C—S bond formation.[18,57–61]

Unfortunately, it was very difficult to treat with disulfide **3** and PPh_3 owing to its high reactivity.[54] Thus potassium thiolate **6** was used instead of pretreated disulfide **3**. The reaction of Ni complex **4** and thiolate **6** gave C—S coupling product in good yield. Again, Pd complex **5** did not afford C—S coupling product.

Conclusion and Scope

We have clarified the S—S bond cleavage process that occurs between disulfides and metal complexes at room temperature. The presence of PPh_3 is the key component in the heterolytic S—S bond cleavage. Since phosphonium salt formation reaction occurs prior to the C—S cross-coupling reaction, if the disulfide is not pretreated with PPh_3, the resulting product consists mainly of phosphine oxide which is derived from the phosphonium salt and water. On the other hand, once the disulfide is pretreated with PPh_3, the formed thiolate anion can react with the Ni(II) σ-aryl complex to afford the C—S coupling product in high yield. We believe this finding will assist with further improvements of room-temperature nickel or palladium-catalyzed C—S coupling reactions.

Experimental

^1H, ^{13}C, and ^{31}P NMR spectra were recorded on Bruker AV-300 and AV-400 spectrometers using $CDCl_3$ as a solvent and tetramethylsilane as an internal standard for ^1H NMR spectra (0.00 ppm), and $^{31}P\{^1H\}$ spectra were referenced to external H_3PO_4 (0.00 ppm). All reactions were carried out under a nitrogen atmosphere using standard Schlenk techniques. However, C—S coupling reactions could be carried out in an air atmosphere also. Bromobenzene, PPh_3, $NiBr_2$, $Pd(PPh_3)_4$, $Ni(PPh_3)_2Cl_2$, $Pd(PPh_3)_2Cl_2$, diethylphosphite, tetramethylthiuram disulfide, diphenyl disulfide, sulfur, K_2CO_3, all solvents (THF, dichloromethane, $CDCl_3$) were purchased from Aldrich and used without further purification. Disulfide **3** was prepared in two-step syntheses according

to the literature[62] and modification of disulfide formation reaction.[63] Ni complex (**4**)[64] and Pd complex (**5**)[65] were prepared according to a previously established procedure.

Reaction of Disulfide 1 and PPh_3

An NMR tube was charged with disulfide **1** (0.05 mmol) and PPh_3 (0.05 mmol) in $CDCl_3$ (1 ml). The resulting phosphorus compounds were tracked by ^{31}P NMR until the PPh_3 peak disappeared from the spectra (72 h).

Reaction of Disulfide 1 and $M(PPh_3)_2Cl_2$ (M = Ni, Pd)

A flask was charged with disulfide **2** (1.0 mmol) and metal complex (0.5 mmol) in DCM (5 ml). After stirring at room temperature for 10 min, the solution was filtered and both the drying residue and resulting solid were analyzed by NMR spectroscopy and mass spectrometry.

Reaction of Disulfide (1–3) and $M(PPh_3)_2PhBr$ (M = Ni (4), M = Pd (5))

A flask was charged with disulfide (0.04 mmol) and metal complex (0.01 mmol) in DCM (5 ml). After stirring at room temperature for 10 min, the solution was filtered and the drying residue was analyzed by NMR spectroscopy.

Reaction of Pretreated Disulfide (1 or 2) with PPh_3 and $M(PPh_3)_2PhBr$ (M = Ni (4), M = Pd (5)).

A flask was charged with disulfide (1.4 mmol) and PPh_3 (1.4 mmol) in DCM (10 ml). After stirring at room temperature for more than 6 h and less than 10 h, the solution was used as a stock solution of phosphonium thiolate (~0.07 M). The stock solution (2 ml) was added to a DCM solution of metal complex (0.07 mmol) and the mixed solution was stirred at room temperature for 10 min. The resulting solution was filtered and both the drying residue and resulting solid were analyzed by NMR spectroscopy and mass spectrometry. Isolated yield was calculated after purification by silica gel column chromatography (hexane/EtOAc = 3/1 as eluent for disulfide **1** with Ni complex, and hexane as eluent for disulfide **2** with Ni complex, respectively).

Reaction of Potassium Thiolate (6) and $M(PPh_3)_2PhBr$ (M = Ni (4), M = Pd (5))

A flask was charged with $HSP(=O)(OEt)_2$ (0.1 mmol) and K_2CO_3 (0.1 mmol) in THF (5 ml). After stirring at room temperature for 30 min, the solution was added to a DCM solution of metal complex (0.07 mmol) and the mixed solution was stirred at room temperature for 10 min. The resulting solution was filtered and both the drying residue and resulting solid were analyzed by NMR spectroscopy and mass spectrometry. Isolated yield was calculated after purification by silica gel column chromatography (hexane/EtOAc = 1/1 as eluent).

Supporting information

Supporting information may be found in the online version of this article.

Acknowledgments

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