Chiral Sulfilimines

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Rhodium-Catalyzed Stereoselective Amination of Thioethers with *N*-Mesyloxycarbamates: DMAP and Bis(DMAP)CH_2Cl_2 as Key Additives**

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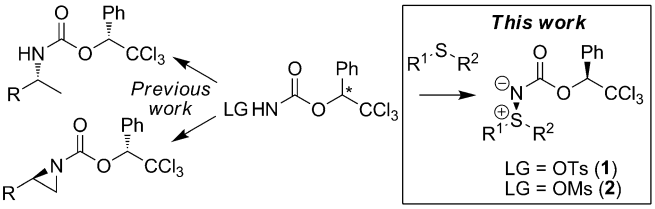
Abstract: *A stereoselective Rh-catalyzed intermolecular amination of thioethers using a readily available chiral N-mesyloxycarbamate to produce sulfilimines in excellent yields and diastereomeric ratio is described. A catalytic mixture of 4-dimethylaminopyridine (DMAP) and bis-(DMAP)CH_2Cl_2 proved pivotal in achieving high selectivity. The X-ray crystal structure of the (DMAP)$_2$·[Rh$_2${(S)-nttl}$_4$] complex was obtained and mechanistic studies suggested a Rh^{II}-Rh^{III} complex as the catalytically active species.*

Chiral sulfilimines[1] are characterized as bearing a dative N–S bond with strong polarization towards the nitrogen atom.[2] Relative to chiral sulfoxides, the chemistry of chiral sulfilimines[3] remains largely underdeveloped because of the limited synthetic methods currently available. The recent discovery of sulfilimine cross-links in collagen IV networks has illustrated the importance of this class of compounds, thus highlighting the need for the development of methods to generate this moiety.[4] The amination of thioethers with electrophilic aza reagents is the oldest known and most applied method for preparing chiral sulfilimines.[1a,5] A number of transition-metal complexes have been reported to catalyze the amination of thioethers, presumably via the formation of metal–nitrene species.[5e,6] Although metal-catalyzed diastereoselective reactions with chiral substrates[7] or chiral reagents[8] have been delineated, they often have limited substrate scope. The catalytic enantioselective amination of thioethers with iminoiodinanes has been developed using chiral Cu,[9] Mn,[10] Ru,[11] and Fe complexes.[12] Although high yields and selectivities are typically observed in the synthesis of aromatic sulfilimines, only modest yields and selectivities are reported with hindered and aliphatic substrates. Consequently, there remains a need for a general and highly stereoselective method to prepare chiral sulfilimines.

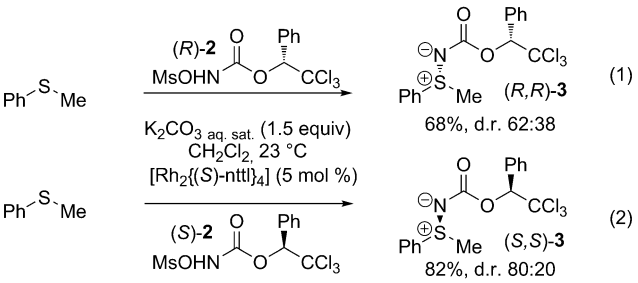
Our research group has been interested in the use of *N*-sulfonyloxycarbamates as metal–nitrene precursors.[13] Stable and available chiral *N*-tosyl- and *N*-mesyloxycarbamates **1** and **2** readily undergo asymmetric C–H amination and aziridination reactions in the presence of chiral Rh^{II} dimers or Cu^{I} catalysts (Scheme 1).[14]



Scheme 1. Stereoselective aminations with chiral *N*-tosyl- and *N*-mesyloxycarbamate. LG = leaving group, Ts = toluene-4-sulfonyl, Ms = mesyl.

Herein, we report the use of chiral *N*-mesyloxycarbamate **2** to perform the stereoselective intermolecular amination of thioethers in the presence of a chiral dirhodium(II) carboxylate catalyst. A catalytic mixture of achiral 4-dimethylaminopyridine (DMAP) and bis(DMAP)CH_2Cl_2 was found to be crucial for the stereoinduction of the process.

The amination of thioanisole was first investigated using the *tert*-leucine-derived Rh catalyst [Rh$_2${(*S*)-nttl}$_4$][15,16] in the presence of both enantiomers of **2** [Eqs. (1) and (2)]. Although the rate of reaction for (*R*)-**2** and (*S*)-**2** were similar, improved selectivity was noted with the latter.



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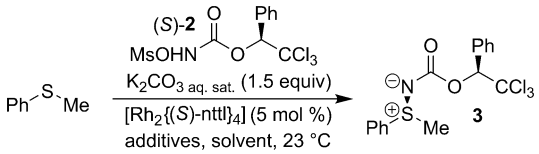
As it has previously been described that the addition of Lewis bases can improve the stereoselectivity of processes catalyzed by chiral Rh^{II} complexes (presumably through binding at the apical position),[17] several of these additives were evaluated in the reaction. Interestingly, they proved to have a significant effect on the stereoselectivity (Table 1).

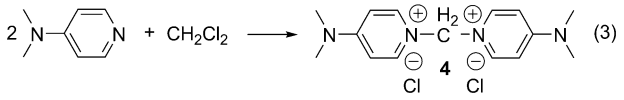
Table 1: Effect of additives in rhodium-catalyzed amination of thioanisole.



Entry[a]	Additives (mol%)	Solvent	Yield [%][b]	d.r.[c]
1	DMAP (5)	CH_2Cl_2	92	88:12
2	–	*i*PrOAc	85	75:25
3	DMAP (7)	*i*PrOAc	52	80:20
4	PPh_3 (5)	*i*PrOAc	41	76:24
5	bis(DMAP)CH_2Cl_2 (**4**) (5)	*i*PrOAc	77	94:6
6	nBu_4NCl (5)	*i*PrOAc	62	73:27
7	Me-viologen$(PF_6)_2$ (5)	*i*PrOAc	82	90:10
8	octyl-viologen$(PF_6)_2$ (5)	*i*PrOAc	70	88:12
9	**bis(DMAP)CH_2Cl_2 (4) (2.5) DMAP (7)**	***i*PrOAc**	**87**	**95:5**
10	bis(DMAP)CH_2Br_2 (2.5) DMAP (7)	*i*PrOAc	85	95:5
11	Me-viologen$(PF_6)_2$ (5) DMAP (7)	*i*PrOAc	85	94:6

[a] Thioether (0.15 mmol). [b] Yield of isolated product. [c] Crude *S,S/R,S* ratio determined by ^{1}H NMR spectroscopy.

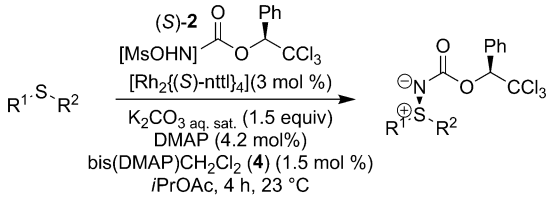
The use of 5 mol% DMAP in CH_2Cl_2 led to **3** being isolated in a yield of 92% with an improved d.r. value of 88:12 (entry 1). Notably, the effect was not as significant when the reaction was conducted in *i*PrOAc instead of CH_2Cl_2 [entries 2 and 3 versus Eq. (2) and entry 1]. Notably, lower yields are observed with a stronger coordinating ligand, namely PPh_3 (entry 4). DMAP and CH_2Cl_2 are known to react to produce the corresponding bis(DMAP)CH_2Cl_2 [**4**; Eq. (3)].[18]

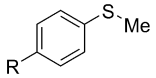
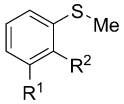
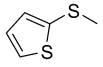
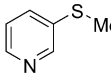
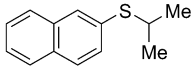
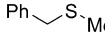
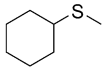


We hypothesized that **4** could be formed in situ (entry 1), and be responsible for the increase in the diastereomeric ratio. Indeed, when the amination of thioanisole was performed with **4** in *i*PrOAc, the d.r. value improved to 94:6 (Table 1, entry 5). Other ammonium salts were tested to understand the role of **4**. The use of nBu_4NCl had a detrimental effect, which suggests a negligible role of the Cl^- counterion. Other pyridinium salts were tested, but none proved as effective as **4** (entries 7 and 8). In contrast to viologen salts,[16] bis(DMAP)CH_2Cl_2 in solution partially reverts into DMAP and CH_2Cl_2, thus leading to a mixture of DMAP and **4**.[19] As improved results are obtained when these two species are present (entries 1 and 5 versus entries 3 and 7), it suggests that both a Lewis base additive and a pyridinium salt are necessary. Indeed, the best result was obtained when a mixture of DMAP and **4** was used, which produced **3** in 87% yield and a diastereomeric ratio of 95:5 (entry 9). Similar results were obtained using bis(DMAP)CH_2Br_2 or methylviologen$(PF_6)_2$ in the presence of DMAP (entries 10 and 11).

A variety of thioethers were explored under the optimal reaction conditions (Table 2). Gram-scale amination with a catalyst loading of 1 mol% afforded 1.38 g of **3** with d.r. 94:6 (entry 2). Various diversely substituted aryl methyl thioethers produced sulfilimines in excellent yields and d.r. values (entries 3–9). Sulfilimine **12** was isolated in high yield and diastereomeric ratio, with no undesired reactions at the

Table 2: Rh-catalyzed amination of thioethers with (*S*)-**2**.

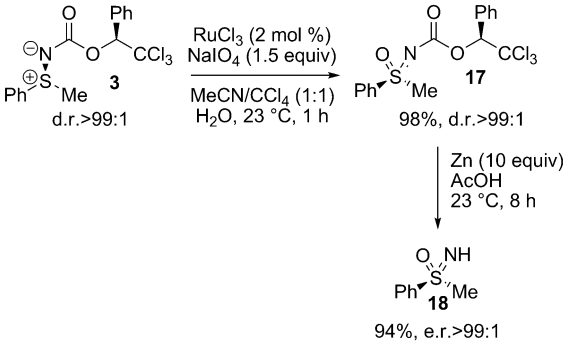


Entry[a]	Thioether	Crude d.r.[b]	Yield [%][c]	d.r.[d]
				
1	R = H	95:5	(**3**) 87	96:4
2	R = H	94:6	(**3**) 88 (gram-scale)[e]	94:6
3	R = Me	92:8	(**5**) 90	94:6
4	R = OMe	93:7	(**6**) 86	94:6
5	R = NO_2	91:9	(**7**) 84	94:6
6	R = Br	93:7	(**8**) 81	94:6
7[f]	R = F	93:7	(**9**) 89	93:7
				
8	R^1 = H, R^2 = Br	92:8	(**10**) 83	92:8
9	R^1 = Br, R^2 = H	95:5	(**11**) 89	95:5
10		95:5	(**12**) 90	99:1
11		94:6	(**13**) 77	94:6
12		82:18	(**14**) 76	83:18
13[f]		71:29	(**15**) 58[g]	93:7[g]
14[f]		89:11	(**16**) 78[g]	96:4[g]

[a] Thioether (1 mmol). [b] Crude *S,S/R,S* ratio determined by ^{1}H NMR spectroscopy. [c] Yield of isolated product. [d] Purified *S,S/R,S* ratio determined by ^{1}H NMR spectroscopy. [e] Thioether (4.2 mmol), [Rh_2{(*S*)-nttl}$_4$] (1 mol%), DMAP (1.4 mol%), and **4** (0.5 mol%). [f] [Rh_2{(*S*)-4-NO_2-nttl}$_4$] (3 mol%). [g] Recrystallization from $CHCl_3$/hexanes.

thiophene center (entry 10). Nitrogen heterocycles, such as pyridines, were also compatible with the reaction conditions (entry 11). Previously, sterically hindered and aliphatic thioethers have been problematic. Herein we demonstrate that **14**, which contains bulky isopropyl groups, was produced in 76% yield and a good d.r. value (entry 12). Other aliphatic sulfilimines could also be synthesized in excellent yields. Sulfilimine **15** was isolated in 88% yield, albeit with a modest diastereomeric ratio,[19] although recrystallization afforded **15** in 58% yield with d.r. 93:7 (entry 13). Sulfilimine **16** was obtained in 92% yield and d.r. 89:11,[19] and could also be isolated in 78% yield after recrystallization as a mixture with d.r. 96:4 (entry 14).

Ru-catalyzed oxidation of sulfilimine **3** afforded sulfoximine **17** in 98% yield with complete retention of the d.r. value (Scheme 2).[12,20] Cleavage of the carbamate was achieved using Zn in AcOH to produce free sulfoximine **18** in 94% yield as a single enantiomer.



Scheme 2. Synthesis of free sulfoximine **18**.

The effect of DMAP and bis(DMAP)CH_2Cl_2 on the diastereomeric ratio of the amination of thioethers is very intriguing. Our optimization suggests that both species are required for optimal results. As a color change was observed when thioanisole and DMAP were added to $[Rh_2\{(S)\text{-nttl}\}_4]$,[19] UV/Vis spectra were recorded to study the coordination of the additives. A solution of $[Rh_2\{(S)\text{-nttl}\}_4]$ displayed a λ_{max} value at 630 nm (green solution; Figure 1). The addition of **2** (20 equiv) did not change the λ_{max} value, which suggests no coordination with the metal. Such a binding appears to be required to form the metal–nitrene species,[13d] but this event is still kinetically possible. The addition of thioanisole (20 equiv) to $[Rh_2\{(S)\text{-nttl}\}_4]$ shifted the λ_{max} value to 560 nm. The same λ_{max} value was measured when 1.4 equiv DMAP was added, whereas a solution of 2.8 equiv DMAP displayed a λ_{max} value at 530 nm. These data suggest that only one molecule of thioether can coordinate to the Rh center. In contrast, DMAP can form a 1:1 complex with the Rh catalyst or form a 2:1 DMAP/Rh complex (see below). Furthermore, when DMAP (1.4 equiv) was added to a solution of thioanisole (20 equiv) and $[Rh_2\{(S)\text{-nttl}\}_4]$, the λ_{max} value was also shifted to 530 nm, thus suggesting the formation of a thioether-Rh-DMAP complex.

Suitable crystals for X-ray analysis were obtained from a solution of $[Rh_2\{(S)\text{-nttl}\}_4]$ and DMAP (Figure 2). Two

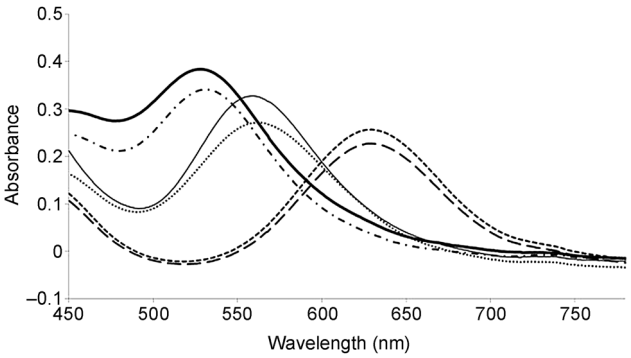


Figure 1. UV/Vis spectra of $[Rh_2\{(S)\text{-nttl}\}_4]$ in *i*PrOAc (–––); with **2** (20 equiv; -----), with thioanisole (20 equiv; ——), with DMAP (1.4 equiv; •••••); with thioanisole (20 equiv) and DMAP (1.4 equiv; –•–•); with DMAP (2.8 equiv; ▬▬).[21]

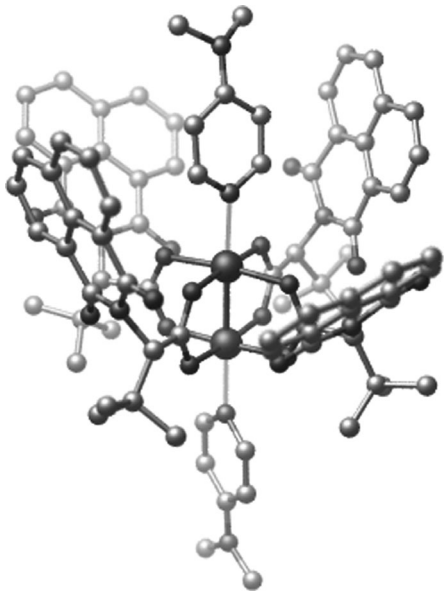


Figure 2. Crystal structure of the $(DMAP)_2{\cdot}[Rh_2\{(S)\text{-nttl}\}_4]$ complex. Thermal ellipsoids are shown at 50% probability. Hydrogen atoms and cocrystallized solvent are removed for clarity. One naphthalimide moiety was found disordered over two positions of which only the one with higher occupancy is shown.[21]

molecules of DMAP were bound to the complex (one to each Rh atom), and importantly, the all-up (or chiral crown) conformation typically observed for these types of complexes was preserved.[22] Although a similar coordination of DMAP to an analogous all-up chiral Rh dimer has been proposed,[17d,e] this represents the first crystallographic proof of its existence.

Pyridinium salts are known for their oxidative properties (notably viologen salts).[23] As such, we hypothesized that they could play a role as single-electron oxidants. The redox potentials of $[Rh_2\{(S)\text{-nttl}\}_4]$ were measured by cyclic voltammetry (CV; Figure 3).[19] The dimer displayed a quasireversible oxidation at 1070 mV for the redox couple Rh^{II}-Rh^{II}/Rh^{II}-Rh^{III}. The addition of either thioanisole or **2** had no effect on the redox potential. Conversely, the addition of 1.4 equiv

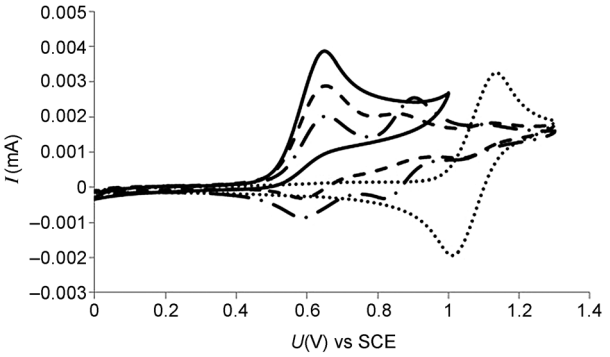


Figure 3. Cyclic voltammetric curves for the oxidation of $[Rh_2\{(S)\text{-nttl}\}_4]$ (••••); with DMAP (1.4 equiv; –•–•), with DMAP (2.0 equiv; ––––), and with DMAP (1.4 equiv) and thioanisole (5 equiv; ——).[21]

DMAP relative to the Rh complex led to CV spectra denoting two novel species with lower redox potential ($E_{1/2} = 870$ and 590 mV). When 2 equiv DMAP was added to $[Rh_2\{(S)\text{-nttl}\}_4]$, only one species was observed and the oxidation became irreversible ($E_{1/2} = 570$ mV).[24] The same irreversible species was also observed from a mixture of 5 equiv thioanisole, 1.4 equiv DMAP, and $[Rh_2\{(S)\text{-nttl}\}_4]$.

A number of mechanistic conclusions can be drawn from these data. The reaction proceeded in good yields (but moderate d.r. values) without any additive, which suggests that the typical Rh^{II}-Rh^{II} complex is catalytically active (with possibly the thioether as a binding ligand). With DMAP as a ligand, the d.r. value was increased, but the yield was seriously compromised. The coordination of the stronger Lewis base must decrease the Lewis acidity of the Rh center. The binding of **2** (thus, the formation of the metal–nitrene species) must be less favored. Under the optimal reaction conditions, a thioether-DMAP-Rh^{II} complex is presumably formed that displays a low and irreversible redox potential. This species is oxidized by **4**, which leads to a more Lewis acidic Rh^{II}-Rh^{III} complex[25] as the catalytically active species that acts with better stereocontrol. The addition of pyridinium salts (methylviologen$(PF_6)_2$) to $[Rh_2\{(S)\text{-nttl}\}_4]$ (without DMAP) also improved the d.r. values, which suggests that the thioether-Rh complex could also be oxidized.

In conclusion, high yields and d.r. values were observed for the amination of thioethers with (*S*)-**2** and $[Rh_2\{(S)\text{-nttl}\}_4]$, DMAP, and bis(DMAP)$CH_2Cl_2$ (**4**). These additives proved to have a significant effect on the selectivities. An X-ray crystal structure of the $(DMAP)_2{\cdot}[Rh_2\{(S)\text{-nttl}\}_4]$ complex was obtained, and studies of the redox potential suggested a Rh^{II}-Rh^{III} complex as the catalytically active species.

Experimental Section

General procedure: $[Rh_2\{(S)\text{-nttl}\}_4]$ (3 mol%), $K_2CO_{3\,aq\,sat.}$ (1.5 mmol), DMAP (5.1 mg), and **4** (4.9 mg) were added successively to a solution of thioether (1.05 mmol) in *i*PrOAc (10 mL) at RT. (*S*)-**2** (1.00 mmol) was added with vigorous stirring and the mixture stirred vigorously for 4 h at RT. The reaction mixture was filtered over a pad of celite, washed with EtOAc, and the filtrate was concentrated under vacuum. The crude product was purified by flash chromatography on silica gel using EtOAc in hexanes as the eluent.

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