

First Transition-Metal Complex Catalyzed Addition of Organic Disulfides to Alkenes Enables the Rapid Synthesis of *vicinal*-Dithioethers

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The sulfur–sulfur bond in organic disulfides may be cleaved by nucleophilic, electrophilic, and radical processes.¹ Several transition-metal complexes have also been shown to be effective reagents for cleavage of the sulfur–sulfur bond in organic disulfides by oxidative addition, leading to the formation of various new sulfur-containing transition-metal complexes.² In catalytic reactions, however, sulfur-containing compounds have long been known to act as catalyst poisons because of their strong coordinating properties.³ Therefore, transition-metal complex catalyzed transformation of organic disulfides remains open to study.⁴ Recent progress in this field includes the addition and carbonylative addition reactions of diaryl disulfides to alkynes,⁵ multiple insertion of isocyanides into a sulfur–sulfur bond in diaryl disulfides,⁶ and carbonylation of organic disulfides to thioesters.⁷ However, the catalyst systems that have been reported so far are strictly limited to palladium and cobalt catalysts. In addition, there has not been a previous report of an efficient addition reaction of organic disulfides to alkenes.⁸

On the other hand, the preparation of a variety of mono- and polynuclear (thiolato)ruthenium complexes has recently been the subject of increased interest as a result of their structural diversity, physical properties, and potential to provide unique reaction sites.⁹ We have also reported the synthesis of novel thiolate-bridged Ti–Ru complexes, Cp₂Ti(μ-SR)₂RuClCp*¹⁰ [Cp: cyclopentadienyl, Cp*: pentamethylcyclopentadienyl]. Therefore, the ruthenium complex seems to be one of the most promising catalysts for the transformation of sulfur-containing compounds.¹¹ During our investigation of the reactivity of Cp₂Ti(μ-SR)₂RuClCp* complexes

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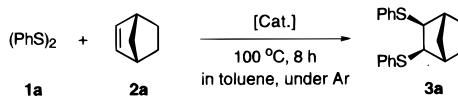
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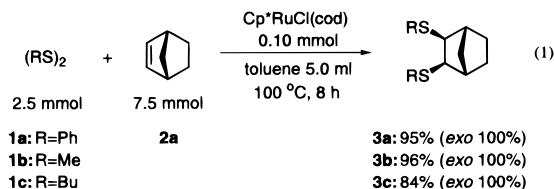
Table 1. Effect of the Catalyst on the Synthesis of **3a** by Addition of **1a** to **2a**^a

		
catalyst	conv. of 1a (%) ^b	yield of 3a (%) ^c
Cp ₂ Ti(μ-SPh) ₂ RuClCp*	60	60
Cp*RuCl(cod)	95	95
Cp*RuCl(cod) ^d	91	88
CpRuCl(PPh ₃) ₂	90	75
Ru(cod)(cot)	2	trace
Ru ₃ (CO) ₁₂ ^e	4	trace
RuCl ₂ (PPh ₃) ₃	7	5
RuH ₂ (PPh ₃) ₄	0	0
Pd(PPh ₃) ₄	0	0
Pd(OAc) ₂	0	0
RhCl(PPh ₃) ₃	2	trace
Pt(PPh ₃) ₄	0	0

^a **1a** (2.5 mmol), **2a** (7.5 mmol), catalyst (0.10 mmol), and toluene (5.0 mL) at 100 °C for 8 h under an argon atmosphere. ^b Determined by GLC. ^c Determined by GLC based on the amount of **1a** charged. ^d Cp*RuCl(cod) (0.050 mmol). ^e Ru₃(CO)₁₂ (0.033 mmol).

as well as ruthenium catalysis,¹² we found the first example of the transition-metal complex catalyzed addition of organic disulfides to alkenes. We report here the development of this new ruthenium-catalyzed reaction which enables a simple and selective synthesis of *vicinal*-dithioethers.

Treatment of diaryl and dialkyl disulfides (**1a–c**) with 2-norbornene (**2a**) in the presence of 4 mol % Cp*RuCl(cod) [cod: 1,5-cyclooctadiene] in toluene at 100 °C for 8 h under an argon atmosphere gave the corresponding *vicinal*-dithioethers (**3a–c**) in high isolated yields with high stereoselectivity (*exo* 100%) (eq 1).¹³ Note that dialkyl disulfides (**1b, c**), which are considered



poor substrates for the palladium-catalyzed addition of disulfides to alkynes,^{5a} also gave the corresponding adducts (**3b, c**) in high yields.

The effect of the catalyst was examined in the reaction of **1a** with **2a**. The results are summarized in Table 1. Among the catalysts examined, Cp*RuCl(cod) and CpRuCl(PPh₃)₂, showed high catalytic activity. Other zero and divalent ruthenium complexes, such as Ru(cod)(cot) [cot: 1,3,5-cyclooctatriene], Ru₃(CO)₁₂, RuCl₂(PPh₃)₃, and RuH₂(PPh₃)₄, were almost completely ineffective. The catalytic activity of a Ti–Ru complex, Cp₂Ti(μ-SPh)₂RuClCp*, was lower than that of Cp*RuCl(cod) itself. The present reaction is characteristic of ruthenium catalysts,

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(13) Excess alkene substrates used in the present reaction can be recovered from the product mixture. For example, 3.3 mmol of 2-norbornene (44%) was recovered after the addition reaction of (PhS)₂ (**1a**) to 2-norbornene (**2a**). In addition, the reaction of (PhS)₂ (**1a**) with an equimolar amount of 2-norbornene (**2a**) reduced both the conversion of (**1a**) and the yield of adduct (**3a**) to 82% and 78%, respectively.

Table 2. Cp*RuCl(cod)-Catalyzed Addition of **1a** to Terminal Alkenes^a

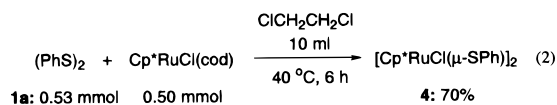
Run	Disulfide	Alkene	Product	Isolated Yield (%)
1 ^b	(PhS) ₂ 1a	CH ₂ =CH ₂ 2b	PhS-CH ₂ -CH ₂ -SPh 3d	72
2 ^c		 2c	PhS-CH ₂ -CH(SiMe ₃)-SPh 3e	75
3		 2d	PhS-CH ₂ -CH(CO ₂ Me)-SPh 3f	66
4		 2e	PhS-CH ₂ -CH(OH)-SPh 3g	60
5		 2f	PhS-CH ₂ -CH(Ph)-SPh 3h	55
6 ^d		 2g	PhS-CH ₂ -CH(C ₆ H _{13-n})-SPh 3i	62

^a **1a** (2.5 mmol), **2** (25 mmol), Cp*RuCl(cod) (0.10 mmol), and toluene (5.0 mL) at 100 °C for 8 h under an argon atmosphere. ^b CH₂=CH₂ (15 atm) for 20 h. ^c For 48 h. ^d At 180 °C for 20 h.

and no reaction occurred with Pd(PPh₃)₄,^{4f,5} Pd(OAc)₂,^{4b,d} RhCl(PPh₃)₃,^{4b} and Pt(PPh₃)₄,^{4b,e} complexes, which are highly active catalysts for the transformation and carbonylation of sulfur-containing compounds.

The addition of diphenyl disulfide (**1a**) to ethylene (**2b**) and several terminal alkenes (**2c–g**) also proceeded smoothly with a Cp*RuCl(cod) catalyst, and the results are listed in Table 2. In all cases, **1a** was completely consumed, and the corresponding adducts were obtained in high yields. No byproduct could be detected by GLC. Some functional groups, such as trimethylsilyl (**2c**), methoxycarbonyl (**2d**), and hydroxy groups (**2e**), did not affect the reaction. On the other hand, the reaction of **1a** with simple terminal alkenes such as 1-octene (**2g**) required severe reaction conditions. Under the usual reaction conditions (100 °C for 8 h), **3i** was obtained in only 15% yield. On the other hand, **3i** was obtained in 62% yield by the reaction at 180 °C for 20 h. Unfortunately, except for 2-norbornene, attempts to obtain *vicinal*-dithioethers with less strained internal alkenes, e.g., cyclohexene, *cis*-4-octene, and dimethyl maleate, were not successful.

The stoichiometric reaction of **1a** with Cp*RuCl(cod) gave a novel thiolate-bridged diruthenium complex, [Cp*RuCl(μ-SPh)]₂ (**4**), in 70% yield (eq 2, and Figure 1).^{14,15} To clarify the



intermediacy of complex **4** in the present reaction, complex **4** was reacted with an excess of **2a** at 100 °C for 6 h, which gave **3a** in an isolated yield of 12% (*exo* 100%) together with the deposition of ruthenium metal (eq 3). Complex **4** also showed high catalytic activity for the addition of **1a** to **2a** to give **3a** in

(14) Crystallographic data for **4**: C₃₂H₄₀Cl₂S₂Ru₂, fw=761.83, monoclinic, space group P2₁/n [No. 14], dark green prism, *a* = 11.873(4) Å, *b* = 9.556(4) Å, *c* = 14.089(3) Å, β = 92.13(2)°, *V* = 1597.3(8) Å³, *Z* = 2, *D*_{calc} = 1.584 g/cm³, μ(Mo Kα) = 12.64 cm⁻¹, Rigaku AFC7R diffractometer, 3667 reflections (unique), *R* = 0.043, *wR* = 0.046, GOF = 1.04.

(15) A similar oxidative addition of diferrocenyl dichalcogenides to [Cp*Ru(μ₃-Cl)]₄ has already been reported: Matsuzaka, H.; Qu, J.-P.; Ogino, T.; Nishio, M.; Nishibayashi, Y.; Ishii, Y.; Uemura, S.; Hidai, M. *J. Chem. Soc., Dalton* **1996**, 4307.

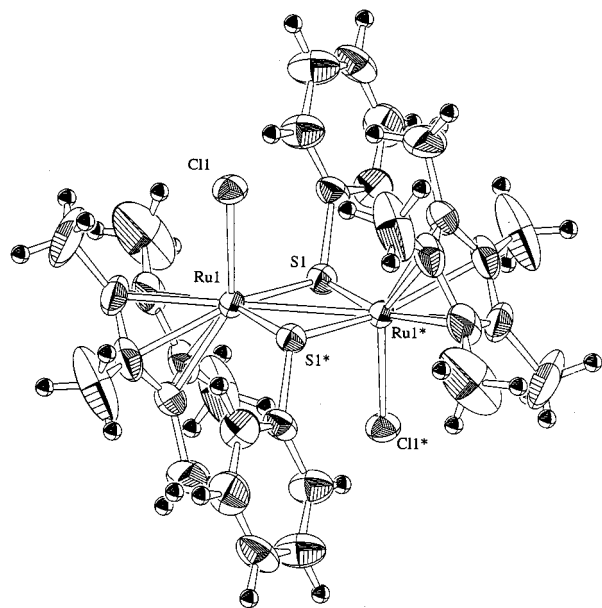
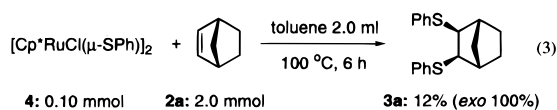


Figure 1. ORTEP diagram of [Cp*RuCl(μ-SPh)]₂ (**4**). Selected bond lengths [Å]: Ru1–Ru1* = 2.860(1), Ru1–S1 = 2.315(2), Ru1–S1* = 2.323(2), Ru1–Cl1 = 2.470(2). Selected bond angles (deg): Ru1–S1–Ru1* = 76.15(5), S1–Ru1–S1* = 103.85(5).



97% yield (*exo* 100%). Although complex **4** is considered to be catalytically active, further mechanistic study involving a kinetic study is required to determine whether the reaction proceeds on the multimetallic ruthenium center. In any case, the high stereoselectivity in the reaction of 2-norbornene is due to the invariable *exo*-coordination of 2-norbornene to an active ruthenium species¹⁶ because the π-electron density of the *exo* face of 2-norbornene is higher than that of the *endo* face.¹⁷ Stereoselective *cis*-thioruthenation and reductive elimination with a retention of stereochemistry gives *vicinal*-dithioether **3** exclusively in *exo* form.¹⁸

In conclusion, we have found the first practically useful catalytic system for the formation of *vicinal*-dithioethers from organic disulfides and alkenes. This reaction will open up new opportunities in transition-metal complex catalyzed sulfur chemistry, since organosulfur compounds are quite useful intermediates in organic synthesis.¹⁹ The development of an enantioselective version of this reaction as well as its mechanistic aspects is the subject of current investigation.

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Supporting Information Available: Complete experimental procedures, lists of spectral data and elemental analyses for all of the new compounds, and crystallographic data for **4** (30 pages, print/PDF). An X-ray crystallographic file, in CIF format, is available through the Web only. See any current masthead page for ordering information and Web access instructions.

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