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cis-Dichloro Sulfoxide Ligated Ruthenium Metathesis Precatalysts

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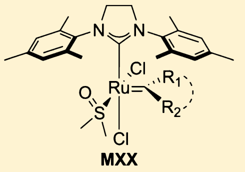
Supporting Information

ABSTRACT: Novel sulfoxide-ligated ruthenium complexes were prepared by reacting second-generation metathesis precatalysts with *p*-toluenesulfonyl chloride in the presence of a small excess of sulfoxide. (SIMes)Ru(*S*-DMSO)(Ind)Cl_2 (**M54**) and (SIMes)Ru(*S*-DMSO)(CHPh)Cl_2 (**M54a**) were characterized crystallographically and, in agreement with NMR spectroscopy, were found to adopt an unusual *cis*-dichloro configuration. Despite having traditionally latent geometry, the new complexes were found to be highly reactive precatalysts for routine metathesis transformations. Additionally, the robustness, scalability, and industrial utility of **M54** as a ruthenium synthon are demonstrated.



MXX	R_1	R_2
M54	3-phenylindenylidene	
M54a	Ph	H
M54b	$CH{=}C(CH_3)_2$	H

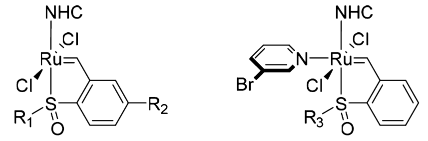
Ruthenium-based olefin metathesis transformations are abundant in the scientific literature, and the precatalysts responsible are routinely lauded for their broad functional group tolerance and relative insensitivity to typical organometallic catalyst poisons.[1−3] Sustained synthetic efforts have focused on modifying the ligand sphere to effect improved activity, stability, and selectivity.[4,5] Additional objectives relevant to industrial precatalyst development include high yield, both chemical and space−time, facile synthesis and purification, inexpensive inputs, and uniqueness of composition.

While sulfoxide complexes of ruthenium have significant precedence,[6−8] examples of sulfoxide-ligated ruthenium metathesis precatalysts are limited (Chart 1). Discrete neutral and cationic ruthenium−allenylidene complexes with coordinated dimethyl sulfoxide[9] and the combination of $RuCl_2(DMSO)_4$ and ethyl diazoacetate[10,11] have been shown to be effective ROMP precatalysts. Sulfoxide-chelated precatalysts have also been prepared and were found to be stable, tunable, and applicable to ring-opening, ring-closing, and cross-metatheses.[12−14]

Chart 1. Sulfoxide-Containing Ruthenium Metathesis Precatalysts

$RuCl_2(=C=C=CAr_2)(PCy_3)_n(DMSO)_2$ n = 1, Ar = Ph
n = 2, Ar = Ph, 4-XPh,
(X = F, Cl, or OMe)

$[RuCl(=C=C=CPh_2)(PCy_3)_m(DMSO)_2]OTf$ m = 1 or 2



NHC	R_1	R_2
SIMes	^{i}Pr or Ph	H
SIMes	^{i}Pr	NO_2
IMes	^{i}Pr, Cy, ^{t}Bu, Bn, Me, Ph, or *p*-NO_2Ph	H

NHC	R_3
SIMes	*p*-NO_2Ph
IMes	^{t}Bu, Ph, or *p*-NO_2Ph

Sulfoxides are an underrepresented functional group in olefin metathesis with a mixed history. While cross-metathesis[15] and ring-closing metatheses[12,15−17] of dialkyl sulfoxides have proven quite successful, studies with aryl alkyl sulfoxides either were unsuccessful[18] or required forcing reaction conditions;[19,20] poor reactivity has been ascribed to catalyst poisoning[18] or carbene oxidation.[21] Additionally, excess dimethyl sulfoxide has been demonstrated to facilitate catalyst decomposition[22] and was successfully used as a reagent for residual ruthenium removal.[23]

Herein, we report the preparation, catalytic evaluation, and synthetic utility of *cis*-dichloride sulfoxide ligated ruthenium metathesis precatalysts.

In the course of studies focused on the preparation of pyridine-free variants of (SIMes)Ru(py)(Ind)Cl_2 (**M31**),[24] methods of phosphine protonation, complexation, alkylation, and oxidation were investigated.[25] Interestingly, *p*-toluenesulfonyl chloride was identified as a mild phosphine oxidant[26] allowing for the facile conversion of (SIMes)Ru(PPh_3)(Ind)-Cl_2 (**M20**)[24] to the acetonitrile-ligated (SIMes)Ru(CH_3CN)-(Ind)Cl_2 (**M34**).[25] Characterization of **M34** was challenging due to the dynamic nature of the labile complex. Though not useful for the purpose of direct characterization, an assay of traditional NMR solvents revealed that dissolution in DMSO-d_6 quantitively afforded free acetonitrile and a new ruthenium species.

Inspired by the apparent thermodynamic stability, the direct synthesis of corresponding sulfoxide complexes was explored.

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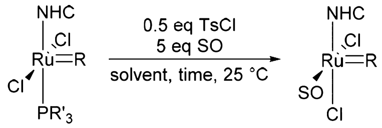
Table 1. Preparation of Sulfoxide-Ligated Ruthenium Complexes



entry	NHC	R	R′	SO[a]	solvent	time (h)	product	ν(S=O) (cm^{-1})	^{13}C C(S=O)C (ppm)[e]	^{1}H $H_3C(S{=}O)CH_3$ (ppm)[e]
1	SIMes	Ind[b]	Ph	DMSO	CH_2Cl_2	1	**M54** 346 mg, 86.3%	1104.9	48.4, 46.0	2.64, 2.08
2	SIMes	CHPh	Cy	DMSO	CH_2Cl_2	1	**M54a** 269 mg, 70.7%	1115.4	48.5, 44.5	2.41, 2. 18
3	SIMes	CHCH=$C(CH_3)_2$	Cy	DMSO	MTBE[c]	24	**M54b** 298 mg, 78.8%	1114.0	48.1, 44.8	2.68, 2.20
4	IMes	Ind	Ph	DMSO	CH_2Cl_2	1	**C745** 240 mg, 59.9%	1105.5	48.4, 46.4	2.68, 2.19
5	SIMes	Ind	Ph	TMSO[d]	CH_2Cl_2	3	**C773** 354 mg, 83.0%	1114.5	64.3, 59.5	2.85, 2.60

[a]SO = sulfoxide. [b]Ind = 3-phenylindenylidene. [c]MTBE = methyl *tert*-butyl ether. [d]TMSO = tetramethylene sulfoxide. [e]Acquired in CD_2Cl_2.

Gratifyingly, the combination of second-generation metathesis precatalysts with 0.5 equiv of *p*-toluenesulfonyl chloride in the presence of a slight excess of sulfoxide[27] afforded the desired complexes, which were isolated by precipitation in high purity and moderate to good yields (Table 1, entries 1, 2, 4, and 5). Alternatively, to improve the isolated yield, the reaction to prepare **M54b** (Table 1, entry 3) was conducted as a slurry in methyl *tert*-butyl ether and the desired complex was isolated by filtration upon complete conversion. Resembling the sulfoxide scope observed for small-molecule transformations (vide infra), reactions with methyl phenyl sulfoxide and diphenyl sulfoxide failed to afford isolable species. Complexes successfully isolated, which generally displayed poor solubility in nonpolar solvents, were characterized by ^{1}H and ^{13}C NMR spectroscopy, infrared spectroscopy, and high-resolution mass spectrometry.

NMR resonances were well-resolved and displayed significant asymmetry typically observed in *cis*-dichloro ruthenium metathesis catalysts.[28−32] Dissolution of **M54**, **M54b**, **C745**, and **C773** in halogenated solvents afforded ^{1}H NMR spectra consistent with a single complex, whereas two minor benzylidene resonances were observed in the spectrum of **M54a** (Figure S12). These minor resonances were suppressed if the spectrum was acquired in DMSO-d_6 (Figure S13).[33] All complexes exhibited restricted rotation about the Ru−S bond; α hydrogens of the sulfoxide moiety occupy two distinct magnetic environments (Table 1). Though ^{13}C chemical shifts were in good agreement with those of previously published S-bound ruthenium(II) sulfoxide complexes,[9,34] resonances for α protons were shifted upfield in comparison to examples from the literature.[7,9] Previously rationalized as the result of interaction with proximal aromatic rings,[35,36] the sulfoxide methyl group (C_{32}) and mesityl ring of the *N*-heterocyclic carbene (Figure S2) are indeed adjacent in the solid state.[37,38] Additionally, each complex featured a strong infrared absorbance between 1100 and 1115 cm^{-1} indicative of an S-bound sulfoxide.[39]

Single crystals suitable for X-ray diffraction studies were prepared by slow diffusion of diethyl ether into concentrated dichloromethane solutions of **M54** and **M54a** (Figure 1). In agreement with spectral data and theory,[40] both complexes adopt a *cis*-dichloro configuration with dimethyl sulfoxide bound through sulfur. Bond lengths for Ru−S (2.26−2.27 Å), S−O (1.48 Å), and S−C_{31}/C_{32} (1.78−1.79 Å) are in excellent agreement with those for published S-bound sulfoxide complexes of Ru(II).[39] Both complexes displayed geometries best described as distorted square pyramidal with τ parameters of 0.34 and 0.23, respectively.[41] Interestingly, the angles between the least-squares planes of the ylidene and mesityl rings were significantly different: 24.3° for **M54** in comparison to 33.8° for **M54a**. In combination with the respective centroid−centroid distances of 3.68 and 4.37 Å, these structural parameters suggest a close-contact interaction for **M54** and lack thereof for **M54a** (Figure S3).

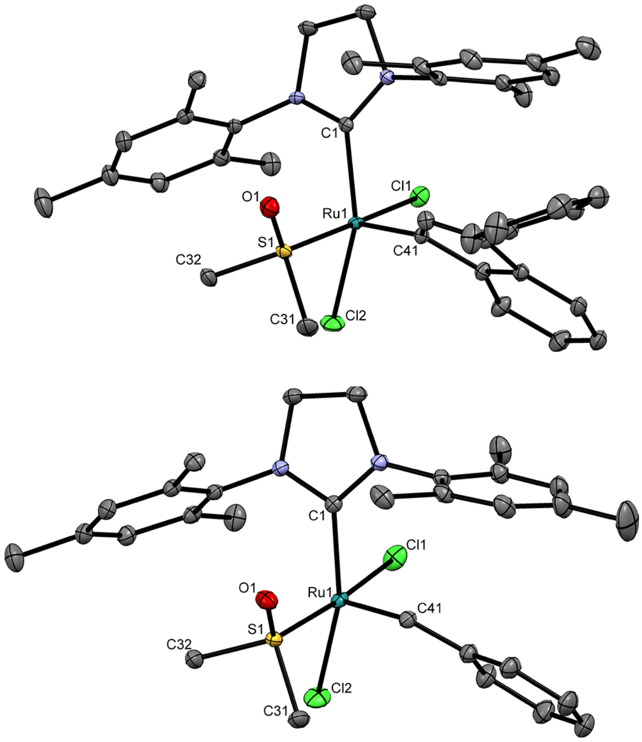


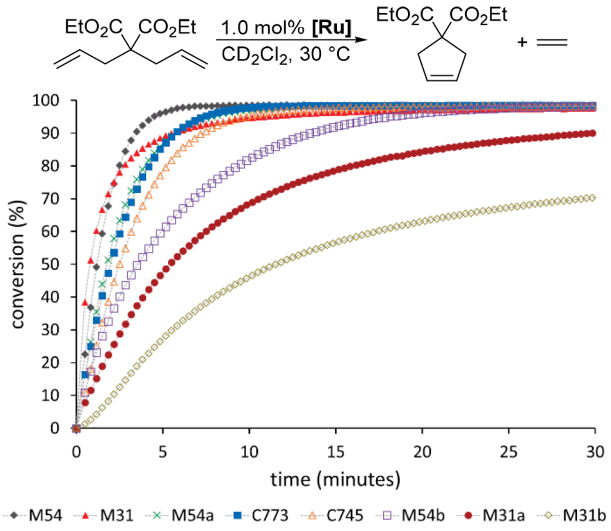
Figure 1. ORTEP diagrams of **M54** (top) and **M54a** (bottom). Displacement ellipsoids are drawn at 50% probability. Hydrogen atoms and solvent have been omitted for clarity.

Understanding that *cis*-dichloro complexes are generally latent species, requiring isomerization to afford active *trans*-

dichloro precatalysts,[42,43] we initially evaluated **M54**'s reactivity utilizing the relatively undemanding self-metathesis of *cis*-methyl oleate at ambient temperature to afford dimethyl 9-octadecenedioate and 9-octadecene (Table S1). Remarkably, maximum conversion was achieved in under 1 h for all catalyst loadings investigated and only 50 ppm of **M54** was required to achieve equilibrium. **M54** did not display any stereoselectivity; all reactions afforded the thermodynamic *cis*/*trans* ratio of each species.

Surprised by the rate and efficiency of this precatalyst, we benchmarked the series of sulfoxide precatalysts against the ring-closing metathesis of diethyl diallylmalonate (Scheme 1) and compared their reactivities to those of the fast-initiating pyridine-ligated complexes (SIMes)Ru(py)(Ind)Cl_2 (**M31**),[24] (SIMes)Ru$(py)_2$(CHPh)Cl_2 (**M31a**),[44] and (SIMes)Ru$(py)_2$(CHCH=C$(CH_3)_2$)Cl_2 (**M31b**)[45] (Figure S1). Reactions were conducted utilizing standard conditions: 1 mol % of catalyst, 30 °C, and a substrate concentration of 0.1 M in dichloromethane-d_2.[46]

Scheme 1. Comparative Study of Pyridine- and Sulfoxide-Ligated Precatalysts for the Ring-Closing Metathesis of Diethyl Diallyl Malonate Monitored by ^{1}H NMR Spectroscopy



M31a and **M31b** were the least reactive catalysts examined, failing to afford complete conversion within 30 min. **M31** was initially extremely reactive but slowed dramatically. The plots of ln([diethyl diallylmalonate]) versus time for these three precatalysts show deviations from linearity consistent with catalyst decomposition during the reaction (Figure S4).[46] Conversely, each sulfoxide complex investigated achieved complete conversion within the given time frame and displayed reaction profiles suggesting good catalyst stability. Interestingly, both sulfoxide and pyridine complexes shared the trend that indenylidene precatalysts reacted more quickly than their benzylidene congeners, which in turn reacted more quickly than variants bearing 1,1-dimethylvinylalkylidenes (i.e. **M31** > **M31a** > **M31b** and **M54** > **M54a** > **M54b**).[24,47] A reduction in reaction rate was observed when **M54** was modified by replacing the sulfoxide with the slightly sterically smaller tetrahydrothiophene oxide[48] (**C773**) or by introducing unsaturation in the *N*-heterocyclic carbene backbone (**C745**).[49,50]

Inspired by the synthetic versatility of the pyridine complex **M31a**,[44] we demonstrated similar synthetic utility by conversion of **M54** into two commercially relevant precatalysts, (SIMes)Ru(P(OPh)Ph_2))(Ind)Cl_2 (**M23**)[51] and second-generation Hoveyda−Grubbs, **HGII** (**M72**). Ligand exchange was facile; exposure of **M54** to a slight excess of phenyldiphenylphosphinite in dichloromethane at ambient temperature afforded quantitative conversion to the desired complex within 1 h. Precipitation and washing with isopropyl alcohol afforded analytically pure *trans*-**M23** in 82% yield. The *cis* isomer of **M23** was not observed during the course of the reaction. Similarly straightforward was the reaction between **M54** and 2-isopropoxy-*β*-methylstyrene. Though poor solubility necessitated heating the reaction mixture to 60 °C, complete conversion was observed in under 2 h and **HGII** (**M72**) was isolated in an unoptimized yield of 79%.

In an effort to improve the commercialization potential of these novel sulfoxide precatalysts, early-stage feasibility and optimization studies focused on the synthesis of **M54** in alternative solvents to reduce the health and environmental risks associated with dichloromethane. Gratifyingly, the reaction could be conducted in toluene or ethyl acetate without sacrificing yield or product purity (Table S2, entries 2 and 3). Additionally, utilizing the same reaction and workup conditions, impure lots of **M20** were successfully converted to pure **M54**, albeit in reduced yields (Table S2, entries 4 and 5).

The synthesis of **M54** and subsequent conversion to **HGII** (**M72**) were subjected to additional process development and conducted on a multi-kilogram scale. The synthesis of **M54** was performed on high-purity (>95%) **M20**, affording 9.2 and 10.2 kg of **M54**: 83 and 77% yields, respectively. When **M20** of moderate purity (~85%) was utilized, the purity of the isolated **M54** was excellent though the yield suffered (25 kg, 60% yield). Conversion of **M54** to **HGII** (**M72**) proceeded smoothly, affording batches of 698 g, 1.3 kg, and ultimately 18.5 kg; yields ranged from 86 to 96%.

Sulfoxide-ligated ruthenium metathesis precatalysts are an interesting addition to the wealth of precatalysts currently available. Despite their *cis*-dichloro configuration, sulfoxide-ligated metathesis precatalysts proved highly reactive toward olefins and demonstrated utility as ruthenium synthons on academic and industrial scale. Future studies will focus on elucidating the mechanism by which these precatalysts rapidly initiate, their utility in ring-opening metathesis polymerizations, and the synthesis of new monodentate and chelating sulfoxide ligand architectures.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.8b00895.

Synthetic procedures, characterization data, kinetic data, and crystallographic details (PDF)

Accession Codes

CCDC 1877638−1877639 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare the following competing financial interest(s): Umicore PMC has filed patents on the sulfoxide-ligated metathesis precatalysts used in this work, from which royalty payments may be derived.

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