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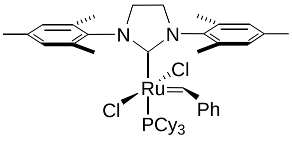
[13] Compound **7** was characterized by ^{1}H NMR spectroscopy, with HMQC and COSY analyses, and high-resolution mass spectrometry. ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 7.06-8.30$ (ArH), 5.87 (d, $J = 1.8$ Hz, 1H; H4), 5.57 (d, $J = 2.1$ Hz, 1H; H4′), 5.34 (d, $J = 7.1$ Hz, 1H; NH), 4.77 (d, $J_{CH} = 159.4$ Hz, 1H; H1′), 4.57 (d, $J = 9.6$ Hz, $J_{CH} = 154.3$ Hz, 1H; H1), 4.34 (d, $J = 7.9$ Hz, $J_{CH} = 162.9$ Hz, 1H; H1″); HR-MS $[M+Na]^+$ calcd for $C_{84}H_{77}N_3O_{24}S_1Cl_4Na$: 1706.3264; found: 1706.3344. Compound **8** was characterized by ^{1}H NMR spectroscopy, with HMQC analysis, and high-resolution mass spectrometry. ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 6.75-8.23$ (ArH), 6.40 (d, $J = 7.0$ Hz, 1H; NH), 6.07 and 5.61 (d, $J = 3.1$, 3.5 Hz, 1H each; H4″ and H4‴), 5.39 and 5.25 (d, $J = 3.1$, 4.0 Hz, 1H each; two α-H1), 5.23, 4.81, 4.47, and 4.34 (d, $J = 8.3$, 7.9, 7.9, 7.5 Hz, four β-H1), 0.88 (d, $J = 7.0$ Hz, 3H; H6^{fuc}). MS (MALDI-TOF) calcd for $C_{165}H_{161}Cl_4N_3O_{40}$: 2963; found: 2963. Removal of the protecting groups on compound **8** by steps including Zn–AcOH, Ac_2O–pyridine, NaOMe–MeOH, and H_2–Pd/C gave the *N*-acetylated Globo H hexasaccharide **9**, confirmed by NMR. ^{1}H NMR (600 MHz, CD_3OD): $\delta = 7.04$, 6.83 (d, $J = 9.2$ Hz, 2H each; ArH), 5.22, 4.93 (d, $J = 4.0$, 4.0 Hz, 1H each; two α-H1), 4.55, 4.52, 4.45 (d, $J = 8.3$, 7.5, 7.5 Hz, 1H each; three β-H1), 2.00 (s, $COCH_3$), 1.08 (d, $J = 6.6$ Hz, 3H; H6^{fuc}). HR-MS $[M+Na]^+$ calcd for $C_{45}H_{71}NO_{31}Na$ 1144.3902, found 1144.3928.

Synthesis of *α,β*-Unsaturated Amides by Olefin Cross-Metathesis[**]

Tae-Lim Choi, Arnab K. Chatterjee, and
Robert H. Grubbs[*]

Dedicated to Professor Gilbert Stork
on the occasion of his 80th birthday

Over the past few years, olefin metathesis has become a useful reaction in organic,[1] polymer[2] and bioorganic chemistry.[3] Among olefin metathesis reactions, ring-closing metathesis (RCM) and ring-opening metathesis polymerization (ROMP) have received the most attention. However, cross-metathesis (CM) is also of increasing utility in C=C bond formation under mild conditions.[4, 5] The synthesis of trisubstituted[6] and functionalized alkenes[7] by cross-metathesis has become possible due to the development of the more active and more stable catalyst **1**, containing the 1,3-dimesityl-4,5-dihydroimidazol-2-ylidene ligand.[8] Catalyst **1** not only has activity comparable to early transition metal catalysts, but also retains the functional group tolerance comparable to catalyst **2**.[9] Herein, we report a versatile cross-coupling reaction of various *α,β*-unsaturated amides with terminal olefins and styrene, and that the CM efficiency is affected by the substituents on the amide nitrogen.



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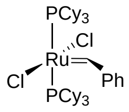

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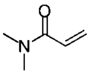
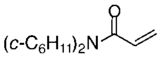
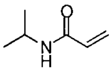
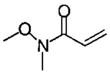
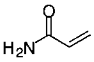
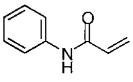
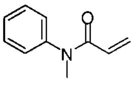
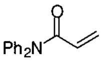
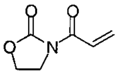
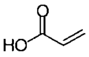
Several unsaturated amide substrates were screened for CM with terminal olefins (Table 1). Initially, dimethylacryl-

Table 1. Cross-metathesis reactions with terminal olefins[a] and styrene.[b]

Entry	Acrylamide	Terminal olefin[c]	Isolated yield of CM [%][d] Terminal olefin (*E*/*Z*)	Styrene
1a		**I**	**3**: 39 (25:1)	**4**: 25
1b[e]		**I**	**3**: 83 (25:1)	
2		**I**	**5**: 77	**6**: 57
3		**II**	**7**: 80	**8**: 62
4		**II**	**9**: 89 (60:1)	**10**: 66
5		**III**	**11**: 89	**12**: 69
6		**II**	**13**: 90	**14**: 69
7		**II**	**15**: 97 (28:1)	**16**: 83
8		**II**	**17**: 100 (40:1)	**18**: 87
9		**I**	**19**: 87 (60:1)	**20**: 40[f]
10		**II**	**21**: 100	**22**: 63

[a] Reaction with 5 mol% catalyst **1** and 1.25 equiv terminal olefin (0.2 M in CH_2Cl_2) at 40 °C for 15 hours. [b] Reaction with 5 mol% catalyst **1** and 1.9 equiv styrene (0.2 M in CH_2Cl_2) at 40 °C for 15 hours. [c] See Scheme 1 for the chemical formulas. [d] Isolated ratio or no *cis* product observed by ^{1}H NMR spectroscopy. The compound numbers are used in the Supporting Information. [e] Reaction with 10 mol% catalyst **1** and 1.5 equiv terminal olefin. [f] Yield determined by ^{1}H NMR spectroscopy.

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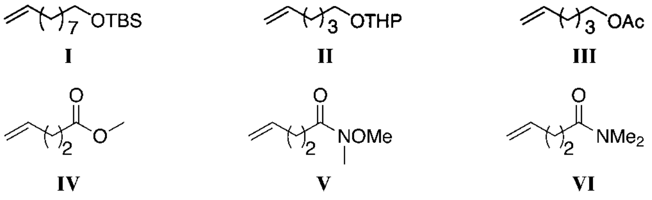
Supporting information for this article is available on the WWW under http://www.angewandte.com or from the author.

amide (entry 1a) was tried and a disappointingly low yield of 39 % of CM product was obtained. However, upon using higher catalyst loading and a higher excess of terminal olefin, the yield was improved to 83 % (entry 1b). Other substrates showed good to excellent yields ranging from 77 to 100 % with excellent diastereoselectivity (>25:1 *trans*:*cis*). Particularly valuable is the compatibility with Weinreb amides[10] (entry 4) and oxazolidinone imides (entry 9).[11] These functional groups are widely used in organic synthesis (for example oxazolidinone imides in asymmetric reactions[12] such as Michael additions,[13] aldol,[14] and Diels–Alder reactions[15]) and CM provides synthons for further manipulations. In an unexpected related result, CM of acrylic acid gave a quantitative yield of the cross product (entry 10). Thus, this route provides an efficient method for the synthesis of a variety of acrylic acids that avoids harsh reaction conditions such as oxidation of alcohols to acids. In addition, it has been demonstrated that, in the presence of catalyst **1**, not only simple terminal olefins but also styrenes react with functionalized olefins in high yields.[16] The yields with styrene are lower and show a similar trend (ranging from 25 to 87 %) to CM with terminal olefins (Table 1).

Electron-donating substituents, such as alkyl groups, on the amide nitrogen resulted in lower yields, whereas electron-withdrawing substituents gave higher yields of cross products. These observations suggest that the amide carbonyl group is chelated to the metal center (**A** in Scheme 2), whereby the degree of chelation would depend on the electron density at the oxygen atom. As chelation decreases catalyst turnover the nitrogen substituents would affect the CM yields.[17] Chelation effects in olefin metathesis catalysts are not unprecedented. Schrock et al. isolated a metallacyclobutane moiety possessing a 4-membered chelate with Mo- and W-based catalysts.[18] Although Ru-based catalysts are much less oxophilic than those of the early metals, and the more electron-rich catalyst **1** should be even less prone to chelation than **2**,[19] chelation to form 5- and 6-membered rings with both catalyst **1** and **2** has been previously observed or proposed.[20] Moreover, amides having more electron-rich carbonyl groups have a higher propensity for chelation. In addition, dicyclohexylacrylamide (entry 2) gave a higher yield in CM than dimethylacrylamide (entry 1a), despite the similar electronic properties. Steric interactions between the cyclohexyl groups and the bulky imidazolylidene ligand of **1** should decrease carbonyl chelation and increase catalyst turnover.



Scheme 1. Formulas of the terminal olefins in Table 1 and Figure 1.

Kinetic studies were performed in order to obtain detailed information about the CM reactions with terminal olefins (see *Supporting Information*). As expected, the more electron-rich amides reacted more slowly than electron-poor amides. Most notably, when dimethylacrylamide was the CM partner, only 33 % of the terminal olefin had participated in CM or dimerization after 1 hour. In contrast, when diphenylacrylamide was used, 93 % of the terminal olefin participated in metathesis reactions in the same period of time. This strongly supports our speculation that a chelation effect of electron-rich amides slows down the metathesis activity by lowering catalytic turnover.

A further kinetic study of the homodimerization of four terminal olefins (Figure 1) provided support for the proposed catalyst inhibition by chelation.[21] Of the four olefins, the nonfunctionalized terminal olefin **I** dimerized fastest, followed by the other substrates (**IV**, **V**, then **VI**). The fact that the rate of dimerization decreases as the electron density on the carbonyl group increases (**IV** < **V** < **VI**) supports the six-membered chelate intermediate (**B** in Scheme 2).[22]

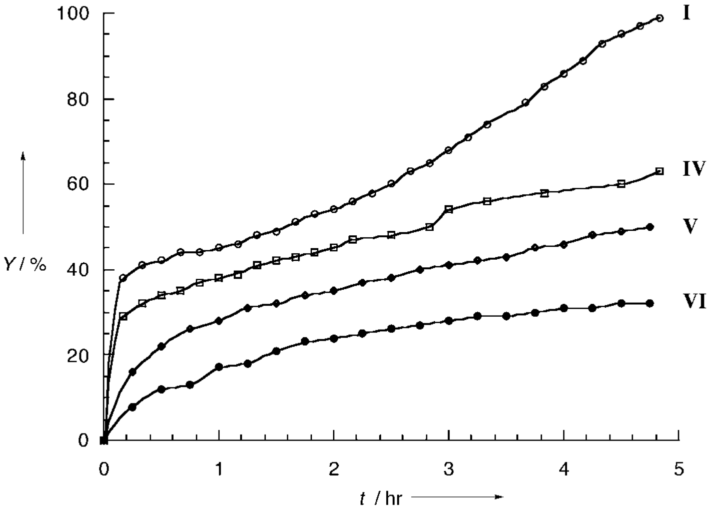
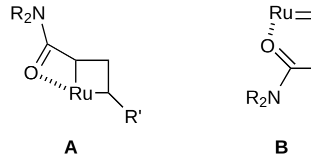


Figure 1. Kinetic studies of various terminal olefins (**I**, **IV**–**VI**) by ^{1}H NMR spectroscopy. See Scheme 1 for the chemical formulas.



Scheme 2. Proposed structures of chelation in the CM reaction.

In conclusion, α,β-unsaturated amides are excellent cross-metathesis partners with terminal olefins and styrene. This method allows for an efficient one-step formation of functionalized α,β-unsaturated amides under mild conditions. More electron-rich amides give lower yields due to lower metathesis activity resulting from carbonyl chelation to the Ru center.

Experimental Section

Full procedures and the characterization data are given in the *Supporting Information*.

General procedure: To a flask charged with amide (1.0 equiv in CH_2Cl_2; 0.2 M) catalyst **1** (0.05 equiv in CH_2Cl_2) was added by cannulation followed by addition of either terminal olefin (1.25 equiv) or styrene (1.9 equiv) via syringe. The flask was fitted with a condenser and refluxed under argon for 15 h. The reaction was monitored by thin-layer chromatography. After the solvent was evaporated, the product was purified directly on a silica gel column.

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[21] In all cases, the metathesis reaction was slow enough for a new alkylidene to be observed by ^{1}H NMR spectroscopy ($\delta = 18.5$ in CD_2Cl_2) at the beginning of the reaction. A second alkylidene peak at $\delta = 18.6$, assigned to the chelated alkylidene, was detected in significant amounts during the dimerization of olefin **VI**. After 30 min, the two alkylidene peaks disappeared and only the methylideneruthenium complex ($\delta = 17.7$) was detected.

[22] In some cases, olefinic amides also gave good results in RCM reactions. Since the CM reaction is an intermolecular process unlike the RCM reaction, chelation effects are more pronounced. For examples, see: a) S. J. Miller, H. E. Blackwell, R. H. Grubbs, *J. Am. Chem. Soc.* **1996**, *118*, 9606; b) C. M. Huwe, O. C. Kiehl, S. Blechert, *Synlett* **1996**, *6*, 505; c) A. B. Dyatkin, *Tetrahedron Lett.* **1997**, *38*, 2065.

The First Ce^{IV} Metallasilsesquioxane Complex: $[Ce\{(c\text{-}C_6H_{11})_8Si_8O_{13}\}_2(py)_3]$**

Yurii K. Gun'ko,* Roisin Reilly, Frank T. Edelmann,* and Hans-Georg Schmidt

Metallasiloxanes containing Si-O-M functional groups (M = main group metal, transition metal, or f-block element) have been envisaged as molecular analogues of zeolites due to their astonishing geometrical relationship.[1] In recent years, the chemistry of metallasilsesquioxanes has been extensively covered.[2] Metallasilsesquioxanes of rare earth metals might be important as homogeneous analogues of silica-supported rare earth metal catalysts and rare earth silicates, which are potential materials for optoelectronics. Hence, this area of research is of considerable interest for several fields of chemistry, including catalysis and materials science. However, investigations on metallasilsesquioxanes of rare earth metals are often hampered by difficulties with crystallization and characterization of these compounds. Here we report the synthesis and structural investigation of the first Ce^{IV} metallasilsesquioxane, a possible homogeneous model of Ce^{IV} silicate oxidation catalysts, and a new synthetic route, which may provide access to other novel metallasilsesquioxane complexes.

Treatment of $[Ce\{N(SiMe_3)_2\}_3]$ with two equivalents of $(c\text{-}C_6H_{11})_8Si_8O_{11}(OH)_2$[3] in diethyl ether in the presence of an excess of pyridine exclusively afforded the diamagnetic complex $[Ce\{(c\text{-}C_6H_{11})_8Si_8O_{13}\}_2(py)_3]$ (**1**). Compound **1** could also be prepared by direct reaction of anhydrous $CeCl_3$ with two equivalents of $(c\text{-}C_6H_{11})_8Si_8O_{11}(OH)_2$ in THF/pyridine, albeit in somewhat lower yield (Scheme 1). Surprisingly, in both cases cerium was oxidized to the tetravalent oxidation state. The compound gave satisfactory C,H,N analyses and was fully characterized by IR and ^{1}H, ^{13}C, and ^{29}Si NMR spectra, as well as X-ray single-crystal diffraction.

The IR spectrum (KBr) of **1** exhibited characteristic pyridine bands at 1599 and 750 cm^{-1}. ^{1}H NMR spectroscopy in [D$_6$]benzene gave a complex spectrum for a diamagnetic compound with broad multiplets between $\delta = 0.91$ and 2.12 for the methine and methylene protons of the $c\text{-}C_6H_{11}$ substituents. The spectrum also showed three characteristic signals attributable to pyridine. In the ^{13}C NMR spectrum the

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