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Z-Selective Homodimerization of Terminal Olefins with a Ruthenium Metathesis Catalyst

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Supporting Information

ABSTRACT: The cross-metathesis of terminal olefins using a novel ruthenium catalyst results in excellent selectivity for the *Z*-olefin homodimer. The reaction was found to tolerate a large number of functional groups, solvents, and temperatures while maintaining excellent *Z*-selectivity, even at high reaction conversions.

Olefin metathesis using a variety of transition metals has gained widespread popularity as a robust method for the formation of carbon−carbon bonds.[1] Ruthenium-based catalysts, in particular, have been used in a wide variety of applications including biochemistry,[2] materials chemistry,[3] and synthetic organic chemistry.[4] However, despite its widespread appeal, olefin metathesis is an equilibrium reaction; therefore, metathesis applications which require the formation of kinetic products are generally difficult if not altogether prohibited.[1,5] Nevertheless, an increasingly sophisticated understanding of catalyst selectivity (with both ruthenium[6] and Group VI metals[7]) has permitted the development of new catalysts that are capable of selectively forming kinetic products. Despite this progress, the cross-metathesis of terminal olefins to selectively form the *Z*-olefin product remained an elusive goal until the recent work of Hoveyda, Schrock, and co-workers.[8] The Hoveyda−Schrock systems showed excellent selectivities and good turnover numbers (TONs). However, the researchers concluded that obtaining similar selectivities using ruthenium-based catalysts would be challenging. Herein, we show that the cross-metathesis homocoupling of terminal olefins to selectively form *Z*-olefins is not only possible with ruthenium but a viable alternative to the use of catalysts based on Group VI metals.

We recently reported on the synthesis of a C−H activated ruthenium metathesis catalyst wherein the *N*-heterocyclic carbene (NHC) is chelated to the metal center through a Ru−C bond (Figure 1).[9] Surprisingly, this catalyst represented the first example of a metathesis active complex which had undergone C−H activation.[1e,10] Furthermore, despite **1**'s relatively poor activity in ring-opening metathesis polymerization (ROMP) and ring-closing metathesis (RCM) reactions, it displayed remarkable *Z*-selectivity for the cross-metathesis product of allylbenzene (**2**) and *cis*-1,4-diacetoxy-2-butene (**3**) (Scheme 1). With this result in hand, we reasoned that **1** would excel in a catalytically less complex reaction, such as the homocoupling of terminal olefins (Scheme 2).

Due to the relatively large adamantane group on **1** and the associative initiation mechanism of complexes of this type, **1** requires fairly high temperatures in order to initiate (ca. 70 °C).[11] Unfortunately, cross-metathesis reactions performed at this temperature and low olefin concentration gave relatively low conversion and showed significant amounts of catalyst decomposition. We suspected that the poor performance of **1** under these conditions was a result of the ethylene generated as a byproduct of the reaction, and indeed, exposure of **1** to an atmosphere of ethylene at room temperature resulted in complete decomposition within minutes.

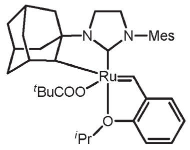
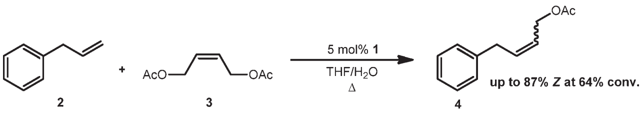


Figure 1. Previously reported C−H activated catalyst **1**.

While the decomposition of **1** in the presence of ethylene was disappointing, it is not uncommon among metathesis catalysts and can be mitigated by efficient removal of the gas from solution.[12] Therefore, a series of cross-metathesis reactions were run under static vacuum, and under these conditions, **1** performed admirably (Table 1). For instance, **1** was stable at 70 °C in both THF and MeCN as long as oxygen was rigorously excluded, and it gave high conversions and Z-selectivity for a variety of terminal olefin substrates. Some substrates showed a slight decrease in selectivity with increasing conversion, a result which is most likely caused by decomposition products of **1**.[13]

In contrast to the Group VI metal systems, olefin migration instead of metathesis was observed in some substrates (**10**, see Figure S1).[14] Attempts to prevent olefin migration via the use of additives such as benzoquinone or mild acid met only with catalyst decomposition.[13] This type of reactivity, although usually undesirable, can be valuable in certain situations.[15] Regardless, olefin migration can be eliminated via careful optimization of reaction conditions (*vide infra*). Finally, substrates with even a small amount of substitution (**11**) were

Scheme 1. Previously Reported Z-Selectivity of 1



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Scheme 2. Homocoupling of Terminal Olefins with 1

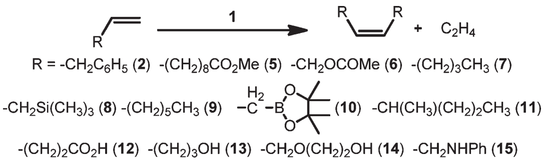

Table 1. Cross-Metathesis of Terminal Olefins with 1 at 70 °C under Static Vacuum[a]

substrate	solvent	time, h	conv,[c] %	Z,[c] %
allylbenzene (**2**)	THF	6 (10)	>95 (>95)	83 (67)
methyl undecenoate (**5**)[b]	THF	4 (6)	78 (93)	87 (85)
allyl acetate (**6**)	THF	3 (6)	53 (60)	89 (83)
1-hexene (**7**)[b]	THF	6 (7.5)	83 (87)	80 (80)
allyl trimethylsilane (**8**)	THF	6 (10)	63 (72)	>95 (>95)
1-octene (**9**)	THF	3 (6)	83 (97)	80 (68)
allyl pinacol borane (**10**)	THF	6	10	>95
3-methyl-1-hexene(**11**)	THF	12	0	0
allylbenzene (**2**)	MeCN	2.5 (21)	12 (15)	>95 (>95)
methyl undecenoate (**5**)	MeCN	2.5 (21)	7 (11)	>95 (70)

[a] 2 mol % catalyst in solvent (0.6 M in substrate) at 70 °C under static vacuum. [b] 4 mol % catalyst. [c] Measured by ^{1}H NMR spectroscopy.

Table 2. Cross-Metathesis of Terminal Olefins with 1 at 35 °C[a]

substrate	time, h	conv,[b] %	Z,[b] %	yield,[c] %
allylbenzene (**2**)	1	>95	92	81
methyl undecenoate (**5**)	5.5	>95	73	>95
allyl acetate (**6**)	4	>95	89	62
1-hexene (**7**)[d]	3	73	69	21
allyl trimethylsilane (**8**)	3	>95	>95	54
1-octene (**9**)	4	>95	83	79
allyl pinacol borane (**10**)	4	>95	>95	74
3-methyl-1-hexene (**11**)	24	0	–	–
pentenoic acid (**12**)	24	0	–	–
4-penten-1-ol (**13**)	1	>95	72	72
2-(allyloxy)ethanol (**14**)	1	87	66	73
N-allylaniline (**15**)	2	70	71	67

[a] 2 mol % catalyst in THF (3.33 M in substrate) at 35 °C. [b] Measured by ^{1}H NMR spectroscopy. [c] Isolated yield. [d] Run in sealed container.

Table 3. Solvent Screen for Cross-Metathesis of 5 with 1 at Room Temperature[a]

substrate	solvent	time, h	conv,[b] %	Z,[b] %
methyl undecenoate (**5**)	MeCN	3 (28)	19 (76)	94 (91)
	MeOH	3 (28)	49 (87)	88 (75)
	EtOH	3 (28)	50 (86)	89 (76)
	C_6H_6	3 (21)	13 (77)	>95 (84)
	Et_2O	3 (7)	50 (85)	93 (73)
	DMF	3 (21)	44 (77)	92 (87)
	CH_2Cl_2	3 (21)	35 (81)	93 (85)
	$(CF_3)_2CHOH$	3 (28)	0 (0)	–
	diglyme	3 (28)	31 (81)	95 (80)

[a] 2 mol % catalyst in solvent (2.25 M in substrate) at 25 °C. [b] Measured by ^{1}H NMR spectroscopy.

disappointingly resistant to homodimerization, even at temperatures exceeding 100 °C.

Although **1** is clearly functional at high temperature, the presence of deleterious side reactions encouraged us to search for conditions in which **1** would initiate at lower temperatures. Extensive optimization revealed that **1** could effect the homodimerization of terminal olefins at 35 °C with high olefin concentration (ca. 3 M). This result is not surprising, considering that the initiation of **1** should depend on olefin concentration. Nevertheless, we did not anticipate that the activity and selectivity of **1** would be superior at 35 °C. Furthermore, reactions performed at lower temperature and higher concentration had the additional advantage of not requiring any special technique to remove ethylene.[16]

For most substrates, reactions with **1** at 35 °C showed selectivity similar to that of reactions performed at 70 °C but with improved activity (Table 2). Isolated yields of the homodimerization products were also good. Gratifyingly, in the case of **10**, no detectable amount of olefin migration was observed, and excellent *Z*-selectivity was maintained up to very high conversion. Emboldened by this success, we attempted to dimerize several more advanced substrates (**11**–**14**). Unfortunately, in the case of hindered (**11**) or acidic substrates (**12**), no activity was observed. On the other hand, **1** was able to dimerize alcoholic substrates (**13**, **14**) with excellent conversion and good selectivity. This latter result is particularly important since it is the first example of *Z*-selective cross-metathesis with alcohol substrates.

Given that **1** not only is stable to water and other protic media but also shows increased activity, we deemed it appropriate to examine a wide variety of different solvents for the homodimerization of **5** at room temperature (Table 3).[9] Several polar and nonpolar solvents were tested, and the majority were conducive to the transformation. Coordinating solvents (e.g., MeCN) resulted in slower reactions but were able to achieve TONs roughly equivalent to those of reactions run in noncoordinating solvents. Protic solvents such as MeOH and EtOH yielded highly *Z*-olefin-enriched product, while hexafluoroisopropanol resulted in immediate catalyst decomposition.[17] The fact that high *Z*-selectivity is maintained in protic solvents further demonstrates the functional group compatibility of **1**. Nevertheless, mildly acidic substrates and solvents appear to result in catalyst decomposition.

In conclusion, we have demonstrated the first example of *Z*-selective homodimerization of terminal olefins using a ruthenium-based catalyst. Optimization of reaction conditions revealed that **1** was effective for a multitude of substrates at different temperatures and in a variety of solvents. The selectivity and activity (TONs from 20 to 50) of **1** were comparable to those obtained with previously reported molybdenum and tungsten catalysts. Notably, **1** was able to dimerize several challenging substrates, including alcohols, with excellent conversion and good selectivity for the *Z*-olefin. However, despite the recent success of ruthenium and Group VI systems, new catalysts, which undergo more turnovers and function under practical experimental conditions, are clearly needed to tackle more advanced olefin substrates and metathesis reactions.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Experimental details and NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) A small amount (ca. 15%) of migration was also observed for **8**, although in this case it did not appear to inhibit the cross-metathesis reaction.

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(16) A vent to an inert atmosphere was sufficient. See the Supporting Information.

(17) **1** was only sparingly soluble in MeOH.