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Acrylonitrile Cross-Metathesis: Coaxing Olefin Metathesis Reactivity from a Reluctant Substrate

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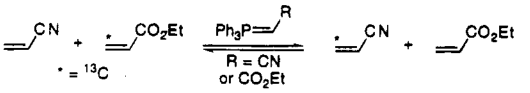
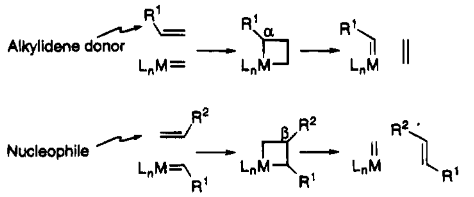
Functionalized olefin metathesis has been a goal in transition metal catalysis for some time now. This goal has driven the search for milder, more selective catalysts and the move toward the more electronegative transition metals lying further to the right in the periodic table. Acylonitrile is a functional olefin which has eluded all previous attempts at productive olefin metathesis. Herein we report the first examples of this useful reaction.

In 1985, Mol and co-workers systematically studied the metathesis reactions of unsaturated nitriles in the presence of WCl_6-SnMe_4 or Re_2O_7-Al_2O_3-$SnMe_4$ catalyst and found that acrylonitrile would not undergo either self-metathesis or cross-metathesis reactions.[1] Likewise, we have found that no identifiable new products are obtained when acrylonitrile is treated with either of the two well-defined catalysts $Mo(CHCMe_2Ph)(NAr)[OCMe(CF_3)_2]_2$[2] (Ar = 2,6-*i*-$Pr_2C_6H_3$) or $Ru(CHCHCPh_2)(PCy_3)_2Cl_2$.[3] Indeed, the sole reported example of an olefin metathesis reaction involving acylonitrile seems to be the phosphorane-catalyzed methylene exchange reaction depicted in eq 1.[4]



(1)

The now well-established Chauvin mechanism[5] for olefin metathesis requires that two roles be played by terminal olefins in a productive metathetical coupling reaction. Olefins must donate alkylidene ligands, placing the olefin substituent α to the transition metal center (eq 2). They must also react as nucleophiles with electrophilic (at the metal) alkylidene intermediates, placing the olefin substituent *β* on the metallacycle precursor to the coupled product (eq 3). These two roles place different steric and electronic demands on the olefin substituent, and one olefin need not (and in some cases cannot) fulfill both functions. In fact, we recently showed that selective cross-metathesis can result when different olefins from a reacting pair fulfill the two functions.[6] We reasoned that acrylonitrile's failure to undergo productive self-metathesis may be due to its low nucleophilicity and that selective cross-metathesis might result if a suitable catalyst were treated with a mixture of acrylonitrile and a more nucleophilic olefin. This indeed turned out to be the case, as illustrated in Table 1.



(2)

(3)

Cross-metathesis reactions were run by treating a mixture of acrylonitrile and a second olefin with Schrock's molybdenum catalyst $Mo(CHCMe_2Ph)(NAr)[OCMe(CF_3)_2]_2$ (5 mol %).[2,7] Initial attempts to optimize reaction conditions showed that the reaction is slowed down considerably by coordinating solvents but does not proceed well in pentane or toluene. Dichloromethane seems to represent the best compromise of coordinating and solvating ability, leading to complete conversion of starting material within 2−3 h with yields as reported in Table 1. Reactions run in Et_2O were somewhat slower but in some cases proceeded in higher overall yield.

Reaction efficiency is substrate dependent; however, it is less so than for previously reported cross-metathesis reactions of styrenes. Selectivity and yield are lower for alkyl-substituted olefins bearing electron-withdrawing substituents. This is consistent with the idea that the alkyl-substituted olefin is reacting as a nucleophile with an electrophilic molybdenum center. Acrylonitrile cannot be efficiently cross-metathesized with styrenes, suggesting that both types of olefins are good alkylidene donors and poor nucleophiles.

A simple paradigm emerging from our cross-metathesis studies is depicted in Scheme 1. High cross-metathesis selectivity arises when one olefin in a reacting pair possesses a π-substituent and the other olefin possesses a small, electron-rich, nonconjugated substituent. Based on this paradigm, we explored the olefin metathesis reactivity of a number of π-substituted terminal olefins including enones, enoic esters, vinylboranes, enynes, and dienes. In none of these cases were the desired cross-metathesis reactions found.[8] The unique place of styrene and acrylonitrile among all π-substituted olefins studied so far is striking and suggests, perhaps not surprisingly,[9] that factors other than those delineated in Scheme 1 are also important to achieving high cross-metathesis selectivity.

Two notable differences between acrylonitrile cross-metathesis and previously reported styrene cross-metathesis reactions are the higher catalyst/substrate ratio required and the cis selectivity observed in acrylonitrile reactions. The higher catalyst/substrate ratio required for efficient acrylonitrile cross-metathesis reactions most likely results from an (as yet undetermined) acrylonitrile-mediated catalyst decomposition pathway which shortens catalyst life.[10] The high cis selectivity

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(7) A representative procedure: to a mixture of 100 mg (0.713 mmol) of 1-decene and 76 mg (1.426 mmol) of acrylonitrile in 2 mL of methylene chloride was added 27 mg (0.036 mmol, 5 mol %) of $Mo(CCHCMe_2Ph)(NAr)[OCMe(CF_3)_2]_2$. The resulting mixture was stirred at room temperature for 3 h and then passed through a pad of silica gel and rinsed with CH_2Cl_2/EtOAc (1:1 v/v). The solvent was removed under reduced pressure, and the crude residue was chromatographed on silica gel (10:1 hexane/EtOAc eluent) to give 85 mg (72%) of non-2-enenitrile as a 9:1 mixture of olefin isomers, with the cis isomer predominating.

(8) The reasons for failure are varied and not always completely understood. Some dienes are poor substrates because they are too readily self-metathesized to trienes. For enynes, alkyne insertion and oligomerization appear to be the main competing side reactions. Olefins bearing polar functionality (other than acrylonitrile) destroy catalytic activity in a not yet clearly defined manner which undoubtedly involves some type of heteroatom coordination, possibly followed by a Wittig-type reaction removing the alkylidene ligand.

(9) (a) One of several subtle features of the imidoalkylidene catalyst systems not depicted in this simplified scheme is the possibility of syn and anti rotamers. Such rotamers have been structurally characterized[9b] and have been shown to have relative reactivities which can vary over several orders of magnitude, with the anti rotamer being more reactive.[9c,d] (b) Schrock, R. R.; Crowe, W. E.; Bazan, G. C.; DiMare, M.; O'Regan, M. B.; Schofield, M. H. *Organometallics* **1991**, *10*, 1832−43. (c) Oskam, J. H.; Schrock, R. R. *J. Am. Chem. Soc.* **1993**, *115*, 11831−45. (d) Oskam, J. H.; Schrock, R. R. *J. Am. Chem. Soc.* **1992**, *114*, 7588−90.

(10) Consistent with this idea is the fact that when excess substrate is present, actual turnover numbers are relatively insensitive to catalyst/substrate ratio.

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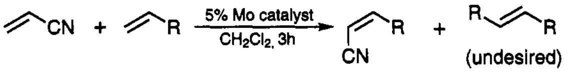
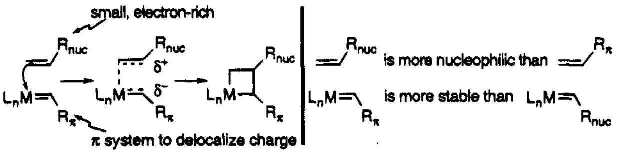
Table 1. Cross-Metathesis Reactions[a]



entry	R	NCCH=CHR (%)	cis: trans[b]	RCH=CHR (%)
1	$(CH_2)_5CH_3$	56 (75)	9:1	4[b]
2	$(CH_2)_7CH_3$	72 (92)	8.5:1	4[b]
3	$(CH_2)_3Br$	45	7.3:1	11[b]
4	$(CH_2)_2Br$	17.5	9:1	20[b]
5	$(CH_2)_4OBn$	77	9:1	0[c]
6	$(CH_2)_3OBn$	60	7.6:1	<1[c]
7	$(CH_2)_2OBn$	40	4:1	0[c]
8	$(CH_2)_4OTBS$	90	6.7:1	7[c]
9	$(CH_2)_3OTBS$	68	5.6:1	0[c]
10	$(CH_2)_2OTBS$	73	5.3:1	10[c]
11	CH_2TMS	76	3:1	0[b]
12	*o*-$MeOC_5H_4CH_2$	72	9:1	9[b]
13	$(CH_2)_6CH=CH_2$	53[d]	8:1	19[b]
14	$(CH_2)_2C(O)OBn$	44	5.6:1	6[b]
15	$(CH_2)_3CH(OMe)_2$	79	7:1	11[b]
16	$CH_2CMe_2CH_2CH(OMe)_2$	64[e]	3:1	0[b]

[a] Reported yields are for isolated products unless otherwise indicated. No products from acrylonitrile self-metathesis were detected in any reaction mixture. Yields in parentheses are for reactions run in Et_2O for 10 h. [b] Determined by ^1H NMR. [c] Determined by GC. [d] A total of 15 mol % catalyst was used over 30 h; the dinitrile product was isolated. [e] Reaction was run for 12 h.

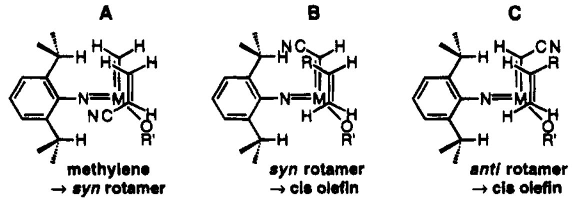
Scheme 1



observed in acrylonitrile cross-metathesis reactions is intriguing since related metathetical coupling reactions of terminal olefins invariably proceed with a high degree of trans selectivity.[11]

Although the mechanistic origin for the predominance of cis olefin product is far from clear, selectivity must be kinetically controlled (since the less stable product is being formed)[12] and is probably related to either the small size or the electron-withdrawing properties of the cyano substituent. We propose that incoming olefins add to the CNO face of imidoalkylidene intermediates[9c] and the syn, cyano-substituted alkylidene (*syn*-Mo=CHCN) is formed in the alkylidene donation stage of the catalytic process (Scheme 2A).[13] A cis olefin product could then result from reaction of $RCH=CH_2$ with *syn*-Mo=CHCN in a manner which minimizes steric interactions with the equatorial alkoxide[14] (Scheme 2B) or with *anti*-Mo=CHCN in a manner which minimizes steric interactions with the imido ligand[15] (Scheme 2C). Further experiments are required to distinguish between these possibilities.[16]

Scheme 2



methylene → ***syn* rotamer**

***syn* rotamer** → **cis olefin**

***anti* rotamer** → **cis olefin**

In summary, we have reported the first examples of productive acrylonitrile metathesis reactions. An interesting feature of these reactions is that a normally troublesome functional group not only is tolerated by the catalyst system but also influences the reaction in a useful manner (cis selectivity). Acrylonitrile is the largest volume organonitrile produced and therefore one of the least expensive reagents conceivable for the introduction of nitrile functionality into organic molecules. Since organonitriles are versatile synthetic intermediates (they are readily reduced to amines and aldehydes or hydrolyzed to acids), acrylonitrile cross-metathesis is a valuable reaction for functionalization of terminal olefins.

Acknowledgment. Support of this work by the Emory University Research Fund and the Petroleum Research Fund is gratefully acknowledged.

Supplementary Material Available: Experimental procedures and spectral data for all compounds (17 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(11) See, for example: (a) Fox, H. H.; Schrock, R. R.; Odell, R. *Organometallics* **1994**, *13*, 635–9. (b) Patton, J. T.; Boncella, J. M.; Wagener, K. B. *Macromolecules* **1992**, *25*, 3862–7. (c) Wagener, K. B.; Boncella, J. M.; Nel, J. G. *Macromolecules* **1991**, *24*, 2649–57. (d) Wagener, K. B.; Nel, J. G.; Konzelman, J.; Boncella, J. M. *Macromolecules* **1990**, *23*, 5155–7.

(12) This can be unambiguously demonstrated by isomerizing the cross-metathesis product in the presence of a neutral nucleophile (PMe_3 proved most convenient for our purposes) and a catalytic quantity of acid. Typical equilibrium ratios slightly favor the trans isomer.

(13) The syn rotamer selectivity observed in the reactions of alkylidenes with internal olefins has been attributed to avoidance of steric interactions between the incoming olefin and the equatorial alkoxide ligand. Similar steric effects should influence the reaction illustrated in Scheme 2A.

(14) The trans selectivity observed in related coupling reactions suggests that the imido ligand is usually sterically dominant in this product-forming step. However, the small cyano substituent could play a role in reversing the normally observed selectivity.

(15) Access to the more reactive anti rotamer of an imidoalkylidene complex requires alkylidene rotation to be rapid relative to productive metathesis. Normally, access to the anti rotamer is precluded by the presence of electron-deficient alkoxide ligands on the complex since such ligands do not weaken the metal–carbon π-bond enough to allow alkylidene rotation to occur readily.[9c,d] The presence of an electron-withdrawing nitrile substituent on the alkylidene carbon, however, should weaken metal–carbon π-bonding by competing for electron density from the alkylidene carbon and may thereby provide access to the anti rotamer.

(16) Various reactions of $Mo(CHCMe_2Ph)(NAr)[OCMe(CF_3)_2]_2$ with acrylonitrile produce the primary metathesis product $CH_2=CHCMe_2Ph$, but no identifiable alkylidene or metallacyclobutane products. The presumed coproduct, $Mo(CHCN)(NAr)[OCMe(CF_3)_2]_2$, appears to decompose under the reaction conditions employed for its formation.