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Lewis-acid assisted cross metathesis of acrylonitrile with functionalized olefins catalyzed by phosphine-free ruthenium carbene complex

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The exchange of the PPh_3 ligand in the complex [1,3-bis(2,6-dimethylphenyl)4,5-dihydroimidazol-2-ylidene](PPh_3)-$(Cl)_2$Ru=CHPh (**7**) for a pyridine ligand at ambient temperature leads to the formation of the stable phosphine-free carbene ruthenium complex [1,3-bis(2,6-dimethylphenyl)4,5-dihydroimidazol-2-ylidene]$(C_5H_5N)_2(Cl)_2$ Ru=CHPh (**8**). The resulted ruthenium complex exhibits highly catalytic activity for the cross metathesis of acrylonitrile with various functionalized olefins under mild conditions, and its activity can be further improved by the addition of a Lewis acid such as $Ti(O^iPr)_4$. In the mixture products, the *Z*-isomer predominates.

Introduction

Recently, olefin metathesis has attracted much attention as a powerful tool for C–C bond formation.[1] The commercial availability of well-defined transition metal catalysts (Fig. 1), such as the molybdenum alkoxyimidoalkylidene **1**,[2] ruthenium benzylidene catalysts **2** and **3**,[3] and ether-tethered ruthenium alkylidene derivative catalyst **4**,[4] has made olefin metathesis practical for application to synthetic organic chemistry.

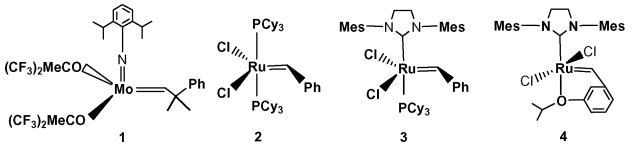

Fig. 1 Olefin metathesis catalysts, Mes = 2,4,6-trimethylphenyl.

On the other hand, cross-metathesis (CM), a method for the intermolecular formation of carbon–carbon double bonds, has been underutilized in comparison with other metathesis reactions. This is primarily due to the lack of reaction selectivity and olefin stereoselectivity.[5] The discovery of the highly active and stable ruthenium-based "second generation" Grubbs' catalyst **3**, $(H_2IMes)(PCy_3)(Cl)_2$Ru=CHPh (where H_2Imes = 1,3-dimesityl-4,5-dihydroimidazol-2-ylidene), has dramatically advanced the utility of CM.[6] However, the original synthetic route of complex **3** was not practical for large scale operation, because it heavily relied on column chromatography purification steps and the use of expensive PCy_3.[7]

Although several examples of selective Mo- and Ru-catalyzed acrylonitrile CM have appeared in the literature,[8] these complexes are very air- and moisture-sensitive and show a restricted tolerance of several heteroatom functionalities. The presence of acids, reactive carbonyl groups and alcohols significantly leads to the catalyst inactive.[9] Most of phosphine-ligated ruthenium catalysts have given poor results for this transformation.[10] More recently, (H_2IMes)(3-bromopyridine)$_2(Cl)_2$Ru=CHPh was found to be more effective than **3**.[11] This result stimulated us to develop a economical and convenient method for preparing the similar phosphine-free carbene complex on a large scale. In this paper, we report an inexpensive and highly efficient ruthenium complex **8** to perform acrylonitrile CM with various functionalized olefins.

Results and discussion

Synthesis of complex 8

In contrast to complex **3** and **4**, the synthesis of the ruthenium complex **8** was relatively simple and easily for scale operation, because it was not heavily reliant on column chromatography purification steps and the use of expensive PCy_3. The ruthenium complex **7** was prepared by treatment of complex **6** and **5** with potassium *tert*-butoxide in toluene. Complex **7** can be purified by several washes with hexane and isolated as brown microcrystalline solids in good yields of 77% (Fig. 1). A bispyridine ruthenium complexes **8** can be prepared by adding an excess pyridine to **7** (Fig. 2). These reactions are complete within minutes, in the absence of any solvent. The product **8** is isolated in 91% yield by precipitation with hexane and without further purification. The resulted complex **8** exhibits good air- and moisture stability.

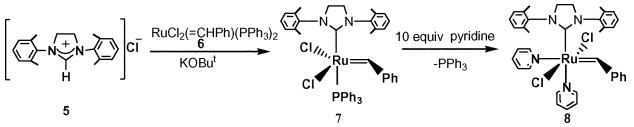

Fig. 2 Synthesis of bispyridine complex **8**.

Cross-metathesis reaction

We initially investigated the use of the complexes **8**, **2**, **3**, **4** and **7** for the self-CM reaction of acrylonitrile (Table 1). With the exception of the complex **8**, other complexes showed no or low activity for this reaction. With catalyst **8**, we observed a maximum 39% conversion of acrylonitrile to 1,4-dicyano-2-butene product with 2 mol% catalyst loading. Though the yield is not high, it has already been the best result at present. Furthermore, the reaction was performed in different solvents (replacing dichloromethane with toluene) at higher temperature with a higher catalyst loading of (10 mol% *vs.* 2 mol%), but the yield did not improve. We suspect that the moderately strong coordination of cyano group with the ruthenium center resulted in deactivating the catalyst during self-CM reaction of acrylonitrile. In order to testify this idea, we also explored the use of the carbene ruthenium complex **8** for the metathesis of 1-hexene in various polar solvents with coordination ability. The results are summarized in Table 2. Obviously, the stronger the

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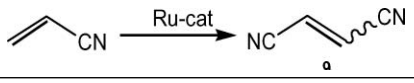
Table 1 Ru-catalyzed CM of acrylonitrile



a

Catalyst	Solvent	Temperature/°C	Time/h	Yield of **9**[a] (%)
2 (2 mol%)	CH_2Cl_2	45	12	0
2 (10 mol%)	CH_2Cl_2	45	24	0
3 (2 mol%)	CH_2Cl_2	45	12	2
3 (10 mol%)	CH_2Cl_2	45	24	12
4 (2 mol%)	CH_2Cl_2	45	24	21
7 (10 mol%)	CH_2Cl_2	45	24	15
8 (2 mol%)	CH_2Cl_2	45	24	39
8 (10 mol%)	Toluene	110	12	38

[a] Isolated yield.

Table 2 Influence of solvent on 1-hexene metathesis reaction[a]

Entry	Solvent	TOF	Conversion (%) of 1-hexene[b]
1	Neat	142.8	85.7
2	1-Butanol	73.5	44.1
3	THF	113.8	68.3
4	Acetone	57	34.2
5	Acetic acid	31.3	18.8
6	Ethyl acetate	47.3	28.4
7	Acetonitrile	1.3	7.8

[a] Reaction conditions: 8 (0.05 mmol), 1-hexene (50 mmol), solvent (50 mmol), 60 °C, 2 h. [b] Yields are based on GC.

coordination ability of the solvent is, the lower the yield is. For example, substitution of acetic acid for THF as solvent, results in the conversion of 1-hexene from 68.3% decreasing into 18.8%.

In situ NMR spectra further showed existence of a cyano-substituted alkylidene during metathesis of acrylonitrile using the carbene ruthenium complexes **8**. The cyanocarbene moiety is distinguished by a ^{1}H NMR resonance at δ 18.31 for the carbene proton, a ^{13}C NMR resonance at δ 237 for the carbene resonance, a ^{13}C NMR resonance at δ 115 for the cyano group. The species has a slower initiation rate than **2**, which suggests that a cyanocarbene intermediate, if trapped by phosphine, only reenters the catalytic cycle with difficulty.[8c]

In order to prevent the coordination of the cyano group towards the ruthenium carbene intermediate, some Lewis acids as co-catalyst were introduced to the reaction system. We intended to form a complex of Lewis acids with the cyanogroup and thus the metathesis reaction of acrylonitrile should be improved. The metathesis of acrylonitrile in the presence of Lewis acids was performed and the results are shown in Table 3. Lewis acids have a dramatic influence on the yield of the cross-metathesis reaction. Strong Lewis acids such as $AlCl_3$ and $AlEt_2Cl$ would decompose the catalyst in a short time, whereas the addition of Al(O*i*-Pr)$_3$ did not affect the CM of acrylonitrile (Table 3, entry 3). The systematic studies indicated that Ti(O*i*-Pr)$_4$ was the best promoter for this reaction. When the reaction was carried out in the presence of 1 equiv. of Ti(O*i*-Pr)$_4$, the expected product **9** was obtained in 60% yield (Table 3, entry 5). Decreasing the amount of Ti(O*i*-Pr)$_4$ only had little effect on this reaction. However, prolonged the reaction time and elevated the reaction temperature were beneficial for improving the yield.

Furthermore, we were delighted to find that the complex **8** could be used in CM of acrylonitrile with different functionalized olefins, such as α,β-unsaturated esters, acids and aldehydes. The results are summarized in Table 4. The cross metathesis can be performed in good yields and the *Z*-isomer predominates in the mixture products. Among these substances, but-3-en-1-ol is more reactive for CM with acrylonitrile in the presence of Ti(O*i*-Pr)$_4$, and a yield of 92% was achieved (Table 4, entry 4). On the contrary, conjugate allyl alcohol (Table 4, entry 2) or allylic substituted alcohol (Table 4, entry 6) were proved to be less efficient. This is due primarily to the electronic and steric characteristic of the allyl alcohol. Further investigation showed that the olefins with various functional groups, such as hydroxide, carbonyl, ester and carboxyl resulted in different results. Generally, the CM of acrylonitrile with functional olefins including aldehyde or alcohol group is faster than that including ester or carboxylic acid group. We suspect that the ruthenium complex **8** can be decomposed in the presence of proton hydrogen of carboxylic acid.

Conclusions

In conclusion, we have demonstrated that the phosphine-free carbene ruthenium complex **8** can efficiently catalyze the cross metathesis of acrylonitrile with various functionalized olefins. The cross metathesis can be performed in good yields and the *Z*-isomer predominates in the mixture products. The coordination solvents have great negative effect on the reaction. The existence of a Lewis acid such as Ti(O*i*-Pr)$_4$ can effectively improve the reaction rate as well as the yield. The CM of acrylonitrile with functional olefins including aldehyde or alcohol group is faster than that including ester or carboxylic acid group.

Experimental

All manipulations were carried out under an inert atmosphere of nitrogen on a vacuum line using standard Schlenk techniques. All chlorinated solvents were dried from CaH_2 and all non-halogenated solvents were distilled from sodium or potassium benzophenone ketyl. NMR spectra were recorded on a VARIAN INOVA 400 MHz NMR spectrometer using $CDCl_3$ as the solvent. Mass spectral determinations were made on a Q-TOF mass spectrometry (Micromass, England). Analytical thin-layer chromatography (TLC) was performed using silica gel 60 F254 precoated plates (0.25 mm thickness).

[1,3-Bis(2,6-dimethylphenyl)-4,5-dihydroimidazol-2-ylidene](PPh$_3$)(Cl)$_2$Ru=CHPh (7)

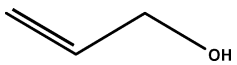
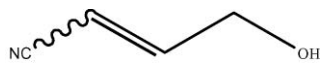
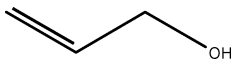
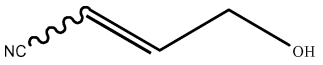
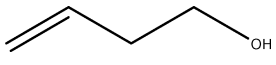
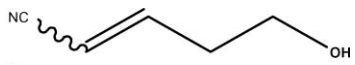
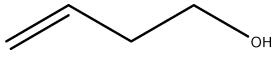
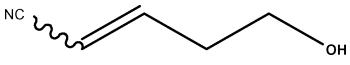
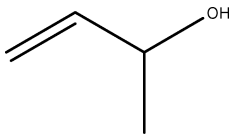
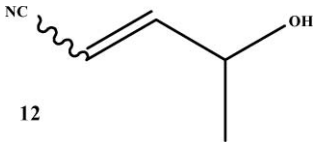
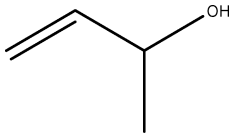
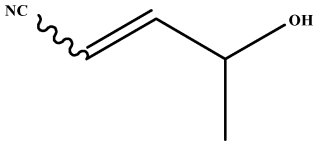
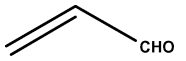
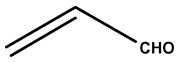
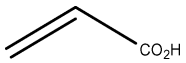
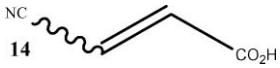
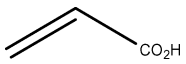
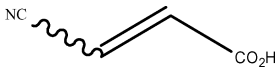
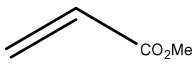
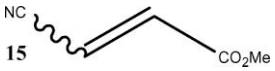
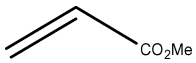
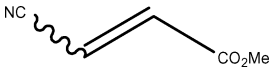
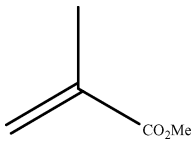
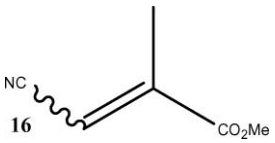
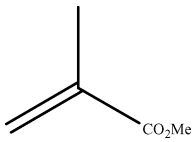
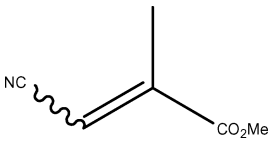
A solution of KO^{t}Bu (117 mg, 1.04 mmol) in dry THF (20 ml) was slowly added to a solution of 1,3-bis-(2,6-dimethylphenyl)-4,5-dihydroimidazolinium chloride[12] (437 mg, 1.02 mmol) in THF (20 ml) at ambient temperature under N_2. The suspension was stirred at room temperature for 2 h to give a yellow solution.

Table 3 Metatheses of acrylonitrile in the presence of Lewis acids[a]

Entry	Lewis acid	Temperature/°C	Time/h	Yield of **9**[b](%)
1	$AlEt_2Cl$ (1 equiv.)	45	1	0
2	$AlCl_3$ (1 equiv.)	45	1	0
3	Al(Oi-Pr)$_3$ (1 equiv.)	45	12	41
5	Ti(Oi-Pr)$_4$ (1 equiv.)	25	2	60
6	Ti(Oi-Pr)$_4$ (50 mol%)	45	2	61
7	Ti(Oi-Pr)$_4$ (20 mol%)	45	12	68

[a] Reaction conditions: **8** (0.04 mmol), acrylonitrile (2 mmol), CH_2Cl_2 (20 ml), 60 °C, 2 h. [b] Isolated yield.

Table 4 The CM of acrylonitrile with functionalized olefins[a]

Entry	Cross partner	Lewis acid	Product	Yield (%)[b]	Z : E ratio[c]
1		None	 **10**	56	3 : 1
2		$Ti(Oi\text{-}Pr)_4$		80	3 : 1
3		None	 **11**	61	4 : 1
4		$Ti(Oi\text{-}Pr)_4$		92	4 : 1
5		None	 **12**	52	2 : 1
6		$Ti(Oi\text{-}Pr)_4$		73	2 : 1
7		None	 **13**	61	4 : 1
8		$Ti(Oi\text{-}Pr)_4$		84	4 : 1
9		None	 **14**	35	3 : 1
10		$Ti(Oi\text{-}Pr)_4$		70	3 : 1
11		None	 **15**	44	4 : 1
12		$Ti(Oi\text{-}Pr)_4$		75	4 : 1
13		None	 **16**	36	1 : 1
14		$Ti(Oi\text{-}Pr)_4$		61	1 : 1

[a] Reaction conditions: **8** (0.04 mmol), 1 equiv. cross partner, acrylonitrile (2.10 mmol), $Ti(O\textit{i}\text{-}Pr)_4$ (20 mol%), CH_2Cl_2 (20 ml), 45 °C, 12 h. [b] Isolated yield. [c] The (Z/E)-ratio was determined by ^{1}H NMR.

The solution was then added (by way of a stainless steel cannula fitted with a filter) to $(PPh_3)_2Cl_2Ru{=}CHPh$ **6**[13] (0.200 g, 0.243 mmol) suspended in toluene (40 ml). The reaction mixture was stirred for 30 min at 70 °C, resulting in a clear dark brown solution. The solvent was completely removed under vacuum. The residue was dissolved into 10 mL of hexane and filtered, and the resulting solution was cooled to −50 °C. After 1 h, the solution was filtered to obtain the product as brown microcrystals, which were washed with cold hexane and dried under vacuum to give complex **7** as a light brown powder. Yield: 211 mg, 77%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 19.25 (s, 1 H, Ru–CH), 7.69–6.56 (multiple peaks, 24H, PPh_3, para CH, meta

CH, and 2,6-dimethylphenyl aromatic CH), 7.67 (d, 2H, ortho CH, $J = 7.2$ Hz), 4.12 (t, 2H, CH_2CH_2, $J = 7.2$ Hz), 3.95 (t, 2H, CH_2CH_2, $J = 7.2$ Hz), 2.64 (s, 12H, ortho CH_3). ^{13}C NMR (100 MHz $CDCl_3$): $\delta = 292.3$ (d, Ru=CHPh), 219.7, 152.6, 139.7, 138.3, 137.4, 134.2, 132.2, 130.5, 129.4, 129.2, 128.7, 128.6, 128.4, 127.8, 127.6, 125.5, 51.9, 50.2, 21.6, 18.9. ^{31}P NMR (161.9 MHz, $CDCl_3$): $\delta = 37.29$ (s). Q-TOFMS: calculated: 767.1896 $[M–Cl]^+$; found: 767.1916 $[M–Cl]^+$.

[1,3-Bis(2,6-dimethylphenyl)-4,5-dihydroimidazol-2-ylidene](C$_5$H$_5$N)$_2$(Cl)$_2$Ru=CHPh (8)

Pyridine (2.0 ml, 25 mmol) was added to complex **7** (2.0 g, 2.5 mmol) in a 20 mL vial with a screw cap. The solution was stirred in air at room temperature for 10 min, during which time a color change from brown–red to bright green was observed. The reaction mixture was cannula transferred into 50 mL of cold (−5 °C) hexane, and a green solid precipitated. The precipitate was filtered, washed with 4 × 20 ml of hexene, and dried under vacuum to afford **8** as a green powder (1.6 g, 91% yield). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 19.10$ (s, 1H, CHPh), 8.63 (br, s, 4H, pyridine), 7.80 (br, s, 4H, pyridine), 7.64 (d, 2H, ortho CH, $J = 7.2$ Hz), 7.45 (t, 1H, para CH, $J = 7.8$ Hz), 7.26 (t, 2H, meta CH, $J = 7.8$ Hz), 7.17–6.93 (multiple peaks, 8H, pyridine, 2,6-dimethylphenyl aromatic CH), 4.14 (br, s, 4H, NCH_2CH_2N), 2.65 (br, s, 6H, ortho CH_3), 2.35 (br, s, 6H, ortho CH_3). ^{13}C NMR(100 MHz $CDCl_3$): $\delta = 307.3$ (m, Ru=*C*HPh), 220.4, 152.3, 150.0, 136.7, 136.0, 130.6, 130.3, 129.6, 129.0, 128.4, 128.1, 124.0, 123.8, 77.5, 77.2, 76.9, 48.3, 46.5, 22.8, 18.7. Q-TOFMS: calculated: 663.1828 $[M–Cl]^+$; found: 663.1830 $[M–Cl]^+$.

General procedure for CM of acrylonitrile and functionalized olefins

To a mixture of cross partner (1.05 mmol) and acrylonitrile (112 mg, 2.10 mmol) dissolved in dichloromethane (20 mL) was added Ti(O*i*-Pr)$_4$ (60 mg, 0.21 mmol) under nitrogen atmosphere by syringe. After stirring for 1 h at room temperature, ruthenium catalyst **8** (70 mg, 0.1 mmol) dissolved in dichloromethane was added by syringe. After 12 h of reflux, the reaction was complete as indicated by TLC. Saturated sodium bicarbonate was added to quench the reaction, the organic layer was separated and the aqueous layer was extracted with dichloromethane. The combined organic layers were dried over anhydrous magnesium sulfate for several hours, and then filtrated. The solution was concentrated *via* rotavapor. Flash column chromatography (hexane–EtOAc) of the crude oil gave the corresponding products. All compounds gave satisfactory spectroscopic and analytical data. Selected data for compounds are included. **9**: ^{1}H-NMR (400 MHz, $CDCl_3$): $\delta = 6.18$ (s, 1H *cis*), 6.27 (s,1H *trans*). **10**: ^{1}H-NMR (400 MHz, $CDCl_3$): $\delta = 6.81$ (dt, $J = 17$ Hz, $J = 3$ Hz, 1H *trans*), 6.48 (dt, $J = 16$ Hz, $J = 7$ Hz, 1H *cis*), 5.71 (m, 1H), 4.34 (dd, $J = 7$ Hz, $J = 2$ Hz, 2H *trans*), 4.23 (dd, $J = 7$ Hz, $J = 2$ Hz, 2H *cis*), 2.11 (s, 1H). **13**: ^{1}H-NMR (400 MHz, $CDCl_3$): $\delta = 9.70$ (d, $J = 7$ Hz, 1H), 6.90 (dt, $J = 17$ Hz, $J = 7$ Hz, 1H *trans*), 6.71 (dt, $J = 11$ Hz, $J = 7$ Hz, 1H *cis*), 6.40 (d, $J = 17$ Hz, 1H *trans*), 6.37 (d, $J = 11$ Hz, 1H *cis*). **14**: ^{1}H-NMR (400 MHz, $CDCl_3$): $\delta = 11.0$ (d, $J = 7$ Hz, 1H), 6.68 (dt, $J = 17$ Hz, $J = 7$ Hz, 1H *trans*), 6.45 (dt, $J = 11$ Hz, $J = 7$ Hz, 1H *cis*), 5.39 (d, $J = 17$ Hz, 1H *trans*), 5.31 (d, $J = 7$ Hz, 1H *cis*). **15**: ^{1}H-NMR (400 MHz, $CDCl_3$): $\delta = 6.75$ (dt, $J = 17$ Hz, $J = 7$ Hz, 1H *trans*), 6.64 (dt, $J = 11$ Hz, $J = 7$ Hz, 1H *cis*), 6.51 (dt, $J = 17$ Hz, $J = 2$ Hz, 1H *trans*), 6.43 (dt, $J = 11$ Hz, 2H *cis*), 3.84 (s, 3H).

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