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Ionic Liquid Anchored "Boomerang" Catalysts Bearing Saturated and Unsaturated NHCs: Recyclability in Biphasic Media for Cross-Metathesis

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A new complex of ruthenium bearing the unsaturated N-heterocyclic carbene IMes (IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene) and an ionic alkylidene moiety was synthesized and fully characterized. The X-ray structure of this catalyst and that of its SIMes (SIMes = 1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene) analogue were determined. The catalytic performances of these catalysts and their recyclability were investigated for olefin cross-metathesis in a [Bmim][PF$_6$]/organic solvent biphasic medium. The results show the importance of the proper choice of organic solvent. The solvent effect/catalytic behavior could be explained in terms of clathrate formation.

Introduction

Ionic liquids (IL) or molten salts have attracted much attention these last few years due to their diverse beneficial properties.[1] They have excellent thermal stability, negligible vapor pressure, and favorable solvating properties for organic and inorganic compounds and organometallic complexes, and they are immiscible with some organic solvents and are easily recyclable. Moreover, various chemical reactions can be performed in room-temperature ionic liquid (RTIL) including transition-metal-catalyzed reactions[2] and biocatalysis.[3] Thus, ionic liquids have been used as reaction media for enantioselective Diels–Alder reactions,[4] hydroformylations,[5] palladium-catalyzed cross-coupling reactions[6] and olefin metathesis.[7]

Since ruthenium-based olefin metathesis[8] is recognized as a powerful transformation for the generation of carbon–carbon double bonds, it has been widely employed in organic synthesis.[9] However, due to problems of product contamination with Ru waste, its use in industrial processes remains scarce.[10] In order to develop more environmentally friendly catalytic systems, the "boomerang" (release-and-return styrenyl ligand) catalyst **1** reported by Hoveyda[11] has been tagged in numerous ways, notably with ionic moieties such as quaternary ammonium for complex **2**,[12] pyridinium for catalysts **3**–**5**,[13] or imidazolium for complexes **6**[14] and **7**[15] (Figure 1). Among these complexes, those bearing an imidazolium pattern, catalysts **6** and **7**, reported respectively by Mauduit and Yao, were found to be the most

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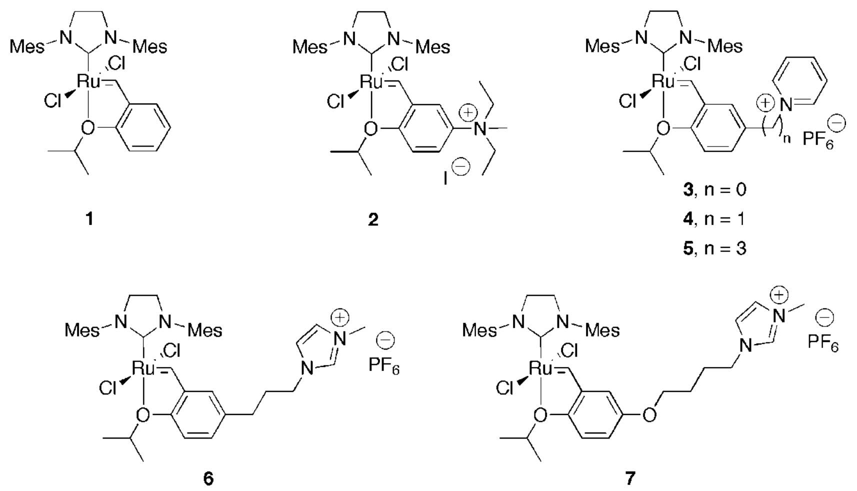


1

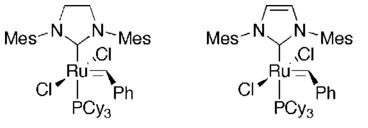
2

3, n = 0
4, n = 1
5, n = 3

6

7

Figure 1. Hoveyda precatalyst **1** and its ionic liquid supported analogues.



8 **9**

Figure 2. Second-generation ruthenium-based catalysts.

competent for recycling. Whereas ring-closing metathesis (RCM) has been extensively studied with these catalytic systems, cross-metathesis (CM) remains almost unexplored and the only results reported so far show poor recyclability.[14c] CM, the intermolecular variant of olefin metathesis, has shown great potential in multistep procedures and in the synthesis of natural products.[8c]

Herein, we report the synthesis of the new imidazolium-containing ruthenium catalyst **11**. This complex has been fully characterized and its reaction profile compared to those of its analogue **6** and other "boomerang" type catalysts. The activity of **11** has been investigated for a benchmark olefin metathesis reaction in ionic liquid/organic solvent biphasic media.

Results and Discussion

The stability of the active species appears as a crucial issue in obtaining good recyclable systems. This explains why second -generation ruthenium-based catalysts, bearing an N-heterocyclic carbene (NHC), are widely used in such applications. In 1999, Grubbs and Nolan reported independently the substitution of one tricyclohexylphosphine by an NHC, leading to the formation of catalysts **8**[16] and **9** (Figure 2),[17] which exhibit better thermal stability and consequently better activity when harsher reaction conditions are required. Of note, the catalytic performance of complex **9**, bearing the unsaturated NHC IMes (1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene), was found in some applications to be inferior to that exhibited by **8**, containing SIMes (1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene).[18] However, the IMes ligand seems to display higher stability, which is an interesting feature for the development of recyclable systems. Moreover, to the best of our knowledge,[19] complexes bearing SIMes and IMes as ligands have not been compared so far for "boomerang" type catalysts or in recyclable systems.

Refluxing the previously described ligand **10**[14a] in DCM in the presence of an excess of the benzylidene catalyst **9** and copper(I) chloride gave, after crystallization at –20 °C in a toluene/DCM mixture, the expected complex **11** in good yield (Scheme 1).[20] The ^{1}H NMR spectrum of **11** shows a single low-field resonance around 7 ppm corresponding to the NHC protons. The ^{13}C NMR spectrum has characteristic resonances at 296.7 ppm for the Ru═C carbenic carbon and at 182.7 for the NHC carbenic carbon, while catalyst **6** with a saturated NHC exhibits this resonance at around 210 ppm. Slow diffusion of octane in a saturated solution of **11** in DCM afforded suitable single crystals for X-ray diffraction studies. Since no X-ray data on a "boomerang" type catalyst bearing an IMes NHC has been reported so far, we decided to compare it to the structure of **6**. Complex **6** was also synthesized using the ruthenium–indenylidene catalyst **12**[21,22] as precursor (Scheme 2). Of note is the equally excellent isolated yield (93%) when **12** was used, as compared to 90% when the benzylidene complex **8** was used.

A single-crystal X-ray diffraction study was performed to unambiguously determine the atom connectivity in both complexes. Ball and stick representations are shown in Figure 3, and selected bond lengths and angles are reported in Table 1. Both complexes show the expected distorted square-based

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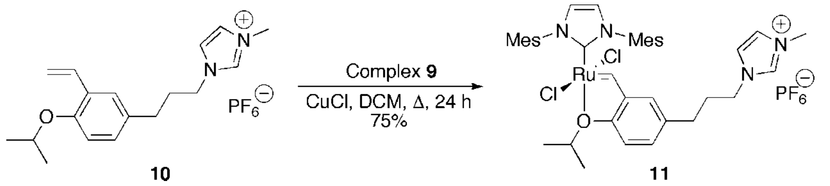
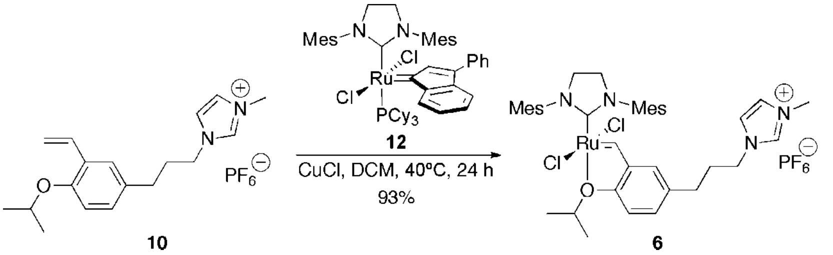
Scheme 1. Synthesis of Precatalyst 11



Scheme 2. Synthesis of Precatalyst 6 using the Ruthenium−Indenylidene Complex 12 as Precursor

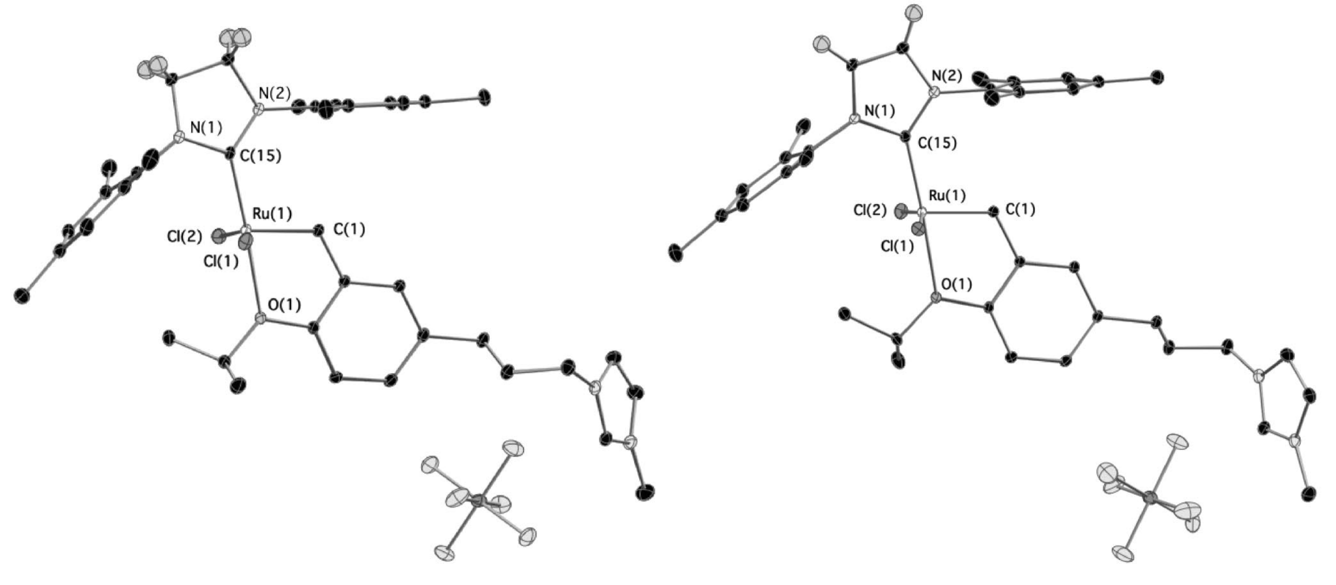


pyramidal geometry around the ruthenium metal center. Only minor metrical differences were observed between the two structures. The IMes (C)−Ru bond distance was found longer than that found in SIMes−Ru; however, for complex **11** the Ru−O bond is significantly shorter than for that found in **6**, suggesting stronger coordination due to the trans effect of the NHC. The smaller N(1)−C(15)−N(2) angle in IMes in comparison to that in SIMes is a peculiarity observed between unsaturated and saturated NHC ligands. The X-ray data have also been compared to those of previously reported “boomerang” type complexes that bear SIMes.[11a,23] All Ru=C and Ru−Cl bond distances are in the respective ranges of 1.820–1.833 and 2.318–2.359 Å. Of note, both complexes **6** and **11** show a Ru−O bond distance shorter than the average reported in the literature (2.250–2.300 Å). Despite an ostensible tilt of the NHC, the C(15)−Ru(1)−O(1) angle is almost as linear as those previously reported (176.2–179.8°).

Table 1. Selected Bond Lengths and Angles for Complexes 6 and 11

	6	11
	Bond Lengths (Å)	
Ru(1)−C(1)	1.832(2)	1.835(2)
Ru(1)−C(15)	1.978(3)	1.992(2)
Ru(1)−O(1)	2.2451(9)	2.2191(15)
Ru(1)−Cl(1)	2.3327(7)	2.3431(6)
Ru(1)−Cl(2)	2.3338(7)	2.3504(6)
	Bond Angles (deg)	
C(1)−Ru(1)−C(15)	102.33(11)	102.77(8)
C(1)−Ru(1)−O(1)	79.80(9)	80.47(7)
C(15)−Ru(1)−O(1)	177.26(8)	176.74(7)
Cl(1)−Ru(1)−Cl(2)	159.76(3)	161.486(19)
C(1)−Ru(1)−Cl(1)	98.38(9)	98.48(7)
C(1)−Ru(1)−Cl(2)	98.62(9)	97.08(7)
C(15)−Ru(1)−Cl(1)	92.48(8)	92.37(6)
C(15)−Ru(1)−Cl(2)	94.57(8)	93.92(6)
N(1)−C(15)−N(2)	107.2(2)	103.06(17)

The catalytic profiles of complex **11** have been evaluated using the benchmark CM reaction involving methyl acrylate (**14**) and a more reactive olefin **13** (Scheme 3). Reactions were performed with an initial catalyst loading of 5 mol % in a 4/1 [Bmim][PF$_6$]/cosolvent biphasic reaction mixture. At the end of the reaction, the product was isolated by extraction with cosolvent and then purification by silica gel chromatography. The *E*/*Z* ratio of **15** was determined by ^{1}H NMR spectroscopy.



6 **11**

Figure 3. Ball-and-stick representations of complexes **6** and **11**. Most hydrogen atoms are omitted for clarity.

Scheme 3. Benchmark Cross-Metathesis Reaction for Precatalyst Reactivity Evaluation

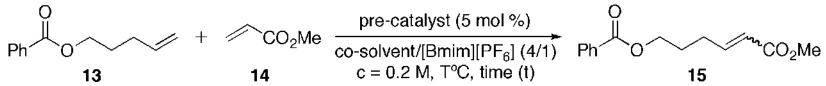


Table 2. Comparison of Precatalysts 6 and 11[a]

	precatalyst **6**		precatalyst **11**	
run	isolated yield (%)	*E*/*Z*[b]	isolated yield (%)	*E*/*Z*[b]
1	80	>99/1	79	>99/1
2	82	>99/1	86	>99/1
3	70	>99/1	65	>99/1
4	70	>99/1	42	>99/1
5	40	>99/1	19	>99/1

[a] Reaction conditions: toluene as cosolvent, 2 equiv of **14**, room temperature, $t = 3$ h. [b] Determined by ^{1}H NMR.

We first compared the catalytic efficiencies of **6** and **11** at room temperature, using toluene as cosolvent. These results are presented in Table 2. Whereas with the IMes-containing catalyst **11** the first two cycles allowed for the isolation of **15** in good yield, the next two cycles gave lower amounts of product (respectively 65 and 42% yields). Finally the fifth run afforded only a small amount of **15** after 3 h (19% yield). The activity of catalyst **11** was found to be close to that displayed by **6**, since 3 h of reaction at room temperature led to a similar isolated yield for the first run. However, the recycling of the catalytic system involving **6** bearing the saturated NHC was slightly better. Under these reaction conditions, no *Z* product was observed with either catalyst.

To explain the moderate recyclability in CM as compared to that observed in RCM, the large excess of unactivated olefin **14** required to avoid the self-metathesis of **13** was thought to be responsible.[14c] Reaction of **14** with the active species could lead to the formation of "stable" neutral catalytic intermediates, which are removed from the reaction mixture during the extraction step. We tried unsuccessfully to solve this problem using 1,7-octadiene as additive at the end of the reaction, in order to reanchor the catalytic species to the ionic ligand.[14c] To verify this hypothesis, the influence of olefin ratio was studied (Table 3). Using only 1 equiv of methylacrylate **14**, product **15** was isolated in good yield in the first run, without observation of the self-metathesis product of **13**. Nevertheless, under these conditions the second run led to a dramatic decrease of the product formed. We believe that the excess of **14** allows for reaction completion, and consequently the ionic ligand returns more straightforwardly onto the active species. The olefin ratio was also increased to 5 equiv of **14** with a benefit in recycling. Thus, three excellent consecutive cycles could be performed before observing the decay of the catalytic system.

Methods have been developed to improve the poor catalyst activity related to the high viscosity of some ionic liquids such as [Bmim][PF$_6$]. As an example, Yao[15] added dichloromethane to the ionic liquid to perform metathesis reaction and then removed it in vacuo before carrying out the extraction with diethyl ether. This catalytic system provided excellent activity, nevertheless the use of a biphasic system also proved efficient and appears easier to handle.[14b] Recently, Dixneuf[24] showed that the product could also be extracted using heptane. As presented in Table 4, other solvents composing the biphasic mixture were examined. Unexpectedly, the use of benzene allowed for reducing significantly the reaction time. However, this solvent is not appropriate because of its slight miscibility with [Bmim][PF$_6$], leading to the extraction of significant amounts of both ionic liquid and catalyst. When methyl *tert*-butyl ether (MTBE) was used as cosolvent, only 56% of cross-metathesis product was isolated after 6 h and surprisingly traces of the Z product **15** were observed by ^{1}H NMR. As a result, the recycling was found inefficient. We first believed that this weak activity was due to the usual poor solubility of organometallic complexes in ethereal solvents. Metathesis transformations are usually carried out in dichloromethane or toluene. Therefore, the cross-metathesis reaction was performed with catalyst **11** in MTBE without ionic liquid; after 1 day at room temperature no product could be detected in the crude mixture (Scheme 4). Nonetheless, the same reaction performed in toluene gave only 11% of **15**, whereas the control experiment reaction in DCM was complete after 2 h. We believe the use of aromatic solvents as cosolvents leads to the formation of a new liquid phase, namely a clathrate,[25] by π-stacking interactions between the imidazolium moiety and the aromatic solvent. The physical properties of such clathrates have not been reported, but it appears that they possess a weaker viscosity and allow for a better solvation of organometallic complexes. Benzene is known to form better clathrate phases with [Bmim][PF$_6$];[25] thus, this might explain the higher activity of the catalyst when benzene was used as cosolvent.

Finally, the effect of the temperature was studied. As ruthenium catalysts bearing an IMes ligand are supposedly more stable, we thought that performing reactions at 50 °C for shorter reaction times could improve the recyclabitily (Table 5). At 50 °C, using toluene as cosolvent, the reaction was found to be faster and only 30 min was necessary to reach complete conversion. The first three cycles were carried out in almost quantitative yields, and the fourth cycle led to a good yield. However, the following cycles proved less efficient: only 32% yield for the fifth cycle and no product in the sixth cycle. Moreover, a temperature increase does not appear judicious, since the reaction selectivity decreased as significant amounts of the *Z* product were detected (up to 10%).

Conclusion

In summary, we have reported the synthesis of a novel ionic liquid supported olefin metathesis catalyst bearing the unsaturated NHC ligand IMes. This "boomerang" type precatalyst and its saturated NHC-containing analogue have been characterized by single-crystal X-ray diffraction studies. The structure comparison of complexes **6** and **11** suggests a stronger coordination of the oxygen to the metallic center for the unsaturated NHC complex **11**. The reactivity and recyclability of the newly synthesized complex have been studied in detail for olefin cross-metathesis reactions in ionic liquid/organic solvent biphasic media. Usually in Ru-catalyzed metathesis, the catalytic activity of IMes-bearing complexes is found to be less efficient than that displayed by their SIMes counterparts, particularly at room temperature; only a slight activity difference was observed in the present pair studied. Our studies also provide some insights

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Table 3. Influence of Olefin Ratio[a]

	1 equiv		2 equiv		5 equiv	
run	isolated yield (%)	*E*/*Z*[b]	isolated yield (%)	*E*/*Z*[b]	isolated yield (%)	*E*/*Z*[b]
1	78	> 99/1	79	> 99/1	98	> 99/1
2	50	> 99/1	86	> 99/1	85	> 99/1
3	24	> 99/1	65	> 99/1	88	> 99/1
4			42	> 99/1	55	> 99/1
5			19	> 99/1	26	> 99/1
6					9	> 99/1

[a] Reaction conditions: precatalyst **11**, toluene as cosolvent, room temperature, $t = 3$ h. [b] Determined by ^{1}H NMR.

Table 4. Cosolvent Effect[a]

	toluene ($t = 3$ h)		benzene ($t = 2.5$ h)		MTBE ($t = 6$ h)	
run	isolated yield (%)	*E*/*Z*[a]	isolated yield (%)	*E*/*Z*[a]	isolated yield (%)	*E*/*Z*[a]
1	98	>99/1	93	>99/1	56	94/6
2	85	>99/1	73	>99/1	16	94/6
3	88	>99/1	88	>99/1	0	
4	55	>99/1	12	>99/1		
5	26	>99/1				
6	9	>99/1				

[a] Reaction conditions: precatalyst **11**, 5 equiv of **14**, room temperature. [b] Determined by ^{1}H NMR.

into the use of biphasic reaction mixtures involving an ionic liquid. Use of aromatic solvents such as toluene with [Bmim][PF$_6$] leads to the formation of a clathrate phase which allows a lowering of the ionic liquid medium viscosity of therefore an improvement in precatalyst solubility. Consequently, since activity and recyclability are intimately related, the present system presents an excellent case study where both activity and recyclability have been increased by this clathrate effect.

Experimental Section

General Considerations. All reagents were used as received. [Bmim][PF$_6$] was prepared and purified as reported previously[26] and dried overnight at 70 °C under high vacuum to remove traces of water.[1] Dichloromethane (DCM) and toluene were dispensed from a solvent purification system from Innovative Technology. Catalyst syntheses were performed in a MBraun glovebox containing dry argon and less than 1 ppm of oxygen. Flash column chromatography was performed on silica gel 60 (230–400 mesh). ^{1}H, ^{13}C, and ^{19}F nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance 400 Ultrashield NMR spectrometer. High resolution mass spectroscopy (HRMS) analyses were performed at the Centre Régionale de Mesures Physiques de l'Ouest (CRMPO), Université de Rennes I, on a Micromass ZABSpecTOF, or at the ICIQ on a Waters LCT Premier spectrometer or a Waters GCT spectrometer. Elemental analysis was performed at the Institut de Chimie des Substances Naturelles (ICSN), Gif-sur-Yvette, France. Compounds **10**,[3] **13**,[4] and **15**[5] have been previously described.

[1,3-Bis(2,4,6-trimethylphenyl)imidazol-2-ylidene][2-(1-methylethoxy)-5-(3-(3-methyl-1*H*-imidazolium-1-yl)propyl)benzylidene]ruthenium(II) Dichloride Hexafluorophosphate (11). In a glovebox, a 50 mL Schlenk flask was charged with catalyst **9** (423 mg, 0.5 mmol), ligand **10**[14a] (140 mg, 0.33 mmol), copper(I) chloride (66 mg, 0.66 mmol), and 20 mL of DCM; the resulting reaction mixture was heated to 40 °C for 24 h. The solvent was then evaporated under vacuum, the residue was dissolved in dry acetone (10 mL), and the insoluble materials were removed by filtration and washed with acetone (2 × 5 mL). The filtrate was evaporated under vacuum, and this residue was then dissolved in a minimum amount of DCM (1 mL). An equal amount of toluene (1 mL) was added, and the solution was cooled to –10 °C over 10 h. The resulting green crystals were filtered and washed with cold toluene and dried under vacuum to afford the catalyst as a green microcrystalline solid (220 mg, 75%). ^{1}H NMR (400 MHz, CD$_2$Cl$_2$, 25 °C, TMS): δ 16.61 (s, 1H, C*H*═Ru), 8.25 (s, 1H, NC*H*N), 7.39 (dd, *J*(H,H) = 8.5 and 2.0 Hz, 1H, H^{Ar}), 7.25–7.21 (m, 2H, H^{Im}), 7.19–7.13 (m, 4H, H^{Mes}), 7.03 (s, 1H, H^{NHC}), 6.91 (s, 1H, H^{NHC}), 6.77 (d, *J*(H,H) = 8.5 Hz, 1H, H^{Ar}), 6.70 (d, *J*(H,H) = 1.7 Hz, 1H, H^{Ar}), 4.84 (sept, *J*(H,H) = 5.9 Hz, 1H, C*H*(CH$_3$)$_2$), 4.16 (t, *J*(H,H) = 6.9 Hz, 2H, C*H*$_2$N), 3.68 (s, 3H, CH_3^{Im}), 2.79 (t, *J*(H,H) = 6.9 Hz, 2H, C*H*$_2$C), 2.46 (s, 6H, CH_3^{Mes}), 2.24 (s, 12H, CH_3^{Mes}), 2.10 (quint, *J*(H,H) = 6.9 Hz, 2H, CH$_2$C*H*$_2$CH$_2$), 1.28 (d, *J*(H,H) = 5.9 Hz, 6H, CH(C*H*$_3$)$_2$). ^{13}C NMR (100 MHz, CD$_2$Cl$_2$, 25 °C, TMS): δ 296.7 (d, *J*(C,Ru) = 26.9 Hz, *C*H═Ru), 182.7 (C, N*C*N), 151.0 (C, C^{Ar}), 145.4 (C, C^{Ar}), 140.0 (C, C^{Ar}), 138.2 (CH, CH^{NHC}), 136.1 (CH, CH^{Ar}), 134.0 (CH, CH^{Ar}), 129.3 (CH, CH^{Ar}), 129.2 (CH, CH^{Ar}), 128.4 (C, C^{Ar}), 125.5 (C, C^{Ar}), 124.0 (CH, CH^{Im}), 122.0 (CH, CH^{Im}), 121.0 (CH, CH^{Im}), 113.3 (CH, CH^{Ar}), 75.7 (CH, *C*H(CH$_3$)$_2$), 50.3 (CH$_2$, *C*H$_2$N), 36.7 (CH$_3$, CH_3^{Im}), 31.6 (CH$_2$, *C*H$_2$C), 30.9 (CH$_2$, CH$_2$*C*H$_2$CH$_2$), 21.4 (CH$_3$, CH(*C*H$_3$)$_2$), 21.2 (CH$_3$, CH_3^{Mes}), 19.0 (CH$_3$, CH_3^{Mes}). ^{31}P NMR (162 MHz, CD$_2$Cl$_2$, 25 °C, TMS): δ –143.1 (d, *J*(P,F)= 711 Hz, 1P, *P*F$_6$). ^{19}F NMR (376 MHz, CD$_2$Cl$_2$, 25 °C, TMS): δ –72.8 (d, *J*(F,P)= 711 Hz, 6F, P*F*$_6$). HRMS (MAB): *m*/*z* calcd for $C_{38}H_{49}Cl_2N_4ORu$ (cation), 747.2170 [C^+]; found, 747.2161. Anal. Calcd for $C_{38}H_{49}Cl_2F_6N_4OPRu$: C, 51.12; H, 5.31; N, 6.28. Found: C, 51.41; H, 5.41; N, 5.75.

Pent-4-enyl Benzoate 13.[27] To a solution of 4-penten-1-ol (2 mL, 19.4 mmol) and pyridine (2.7 mL, 23.3 mmol) in dry DCM (50 mL) was added benzoyl chloride dropwise at 0 °C. The reaction mixture was stirred for 1 h at room temperature before 50 mL of 1 M HCl was added. The reaction mixture was extracted with DCM (3 × 50 mL), the combined organic layers were dried over magnesium sulfate, and the volatiles were removed in vacuo. The crude mixture was purified by flash chromatography on silica gel (pentane/diethyl ether, 95/5) to afford the title compound as a colorless oil (3.14 g, 85% yield). ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C, TMS): δ 8.07 (dd, ^3J(H,H) = 7.5 Hz, ^4J(H,H) = 1.4 Hz, 2H, CH^{Ar}), 7.56 (t, ^3J(H,H) = 7.7 Hz, 2H, CH^{Ar}), 7.45 (t, ^3J(H,H) = 7.7 Hz, 2H, CH^{Ar}), 5.92–5.82 (m, 1H, C*H*═CH$_2$), 5.09 (dd, ^3J(H,H) = 17.1 Hz, ^3J(H,H) = 1.6 Hz, 1H, CH═C*H*$_2$), 5.03 (d, ^3J(H,H) = 10.2 Hz, 1H, CH═C*H*$_2$), 4.36 (t, ^3J(H,H) = 6.6 Hz, 2H, C*H*$_2$O), 2.24 (q, ^3J(H,H) = 7.2 Hz, 2H, C*H*$_2$CH═CH$_2$), 1.93–1.86 (m, 2H, CH$_2$C*H*$_2$CH$_2$). ^{13}C NMR (100 MHz, CDCl$_3$, 25 °C, TMS): δ 166.6 (C, Ph*C*═O), 137.5 (CH, *C*H═CH$_2$), 132.8 (CH, C^{Ar}), 130.5 (C,

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Scheme 4. Cross-Metathesis Reaction without Ionic Liquid

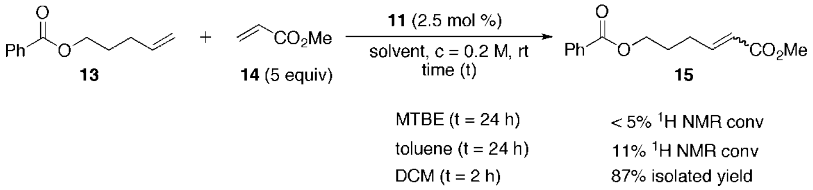

Table 5. Temperature Influence[a]

	room temp (t = 3 h)		50 °C (t = 0.5 h)	
run	isolated yield (%)	E/Z[b]	isolated yield (%)	E/Z[b]
1	98	>99/1	97	99/1
2	85	>99/1	95	93/7
3	88	>99/1	90	90/10
4	55	>99/1	77	95/5
5	26	>99/1	32	92/8
6	9	>99/1	0	

[a] Reaction conditions: precatalyst **11**, toluene as cosolvent, 5 equiv of **15**. [b] Determined by ^{1}H NMR.

C^{Ar}), 129.6 (CH, C^{Ar}), 128.3 (CH, C^{Ar}), 115.4 (CH, CH_2=CH), 64.3 (CH_2, -CH_2), 30.2 (CH_2, $CH_2CH{=}CH_2$), 27.9 (CH_2, $CH_2CH_2CH_2$). HRMS (ESI): *m/z* calcd for $C_{12}H_{14}O_2$ + Na, 213.0891 [M^+ + Na]; found, 213.0896.

Procedure for Cross-Metathesis Reactions. A Schlenk flask under argon was charged with BMI·PF_6 (0.5 mL) and heated to 80 °C for 2 h. The catalyst was added and the reaction mixture stirred at room temperature for 1 h to dissolve the catalyst. The olefin **13** (0.5 mmol), the cosolvent (2 mL, c = 0.2 M), and then methyl acrylate (**14**) were added to the reaction mixture. The progress of the reaction was monitored by TLC or ^{1}H NMR by integrating the characteristic allylic proton resonances. The product was extracted from the reaction mixture with the cosolvent (4 × 5 mL). The combined extracted layers were evaporated in vacuo, and the crude residue was purified by flash column chromatography to yield the pure product.

(*E*)-6-Methoxy-6-oxohex-4-enyl Benzoate (15).[28] The general procedure yielded after flash chromatography on silica gel (pentane/diethyl ether, 95/5) the title compound as an yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ 8.03 (dd, ^3J(H,H) = 7.9 Hz, ^4J(H,H) = 1.1 Hz, 2H, CH^{Ar}), 7.55 (tt, ^3J(H,H) = 7.4 Hz, ^4J(H,H) = 1.1 Hz, 1H, CH^{Ar}), 7.43 (t, ^3J(H,H) = 7.5 Hz, 2H, CH^{Ar}), 7.01 (dt, ^3J(H,H) = 15.7 Hz, ^4J(H,H) = 6.9 Hz, 1H, $CHCO_2Me$), 5.88 (dt, ^3J(H,H) = 15.7 Hz, ^4J(H,H) = 1.4 Hz, 1H, $CHCH_2$), 4.35 (t, ^3J(H,H) = 6.4 Hz, 2H, OCH_2), 3.71 (s, 3H, CH_3), 2.38 (dq, ^3J(H,H) = 7.2 Hz, ^3J(H,H) = 1.4 Hz, 2H, CH_2CH), 1.98–1.91 (m, 2H, $CH_2CH_2CH_2$). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ 166.8 (C, CHC=O), 166.5 (C, PhC=O), 147.9 (CH, $CH{=}CH_2$), 133.0 (CH, C^{Ar}), 130.2 (C, C^{Ar}), 129.6 (CH, C^{Ar}), 128.4 (CH, C^{Ar}), 121.7 (CH, $CHCO_2Me$), 64.0 (CH_2, OCH_2), 51.4 (CH_3, CO_2CH_3), 28.8 (CH_2, $CHCH_2$), 27.2 (CH_2, $CH_2CH_2CH_2$). HRMS (ESI): *m/z* calcd for $C_{14}H_{16}O_4$ + Na, 271.0946 [M^+ + Na]; found, 271.0946.

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Supporting Information Available: CIF files giving crystallographic data for complexes **6** and **11**. This material is available free of charge via the Internet at http://pubs.acs.org. The CIF files of complexes **6** and **11** have also been deposited with the CCDC as, respectively, No. CCDC-670925 and CCDC-670926. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K.: fax, +44 1223 336 033; web, http://www.ccdc.cam.ac.uk; e-mail, deposit@ccdc.cam.ac.uk.

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