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Simple and Convenient Synthetic Procedure Leading to Ruthenium Olefin Metathesis Catalysts Bearing the *N,N′*-Bis(mesityl)imidazol-2-ylidene (IMes) Ligand

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*Summary: The highly active olefin metathesis catalyst precursors $RuCl_2(=CHR')(IMes)(PR_3)_2$ ($R' = Ph$, $R = Cy$ (**4**), $R' = CH{=}CMe_2$, $R = Cpy$ (**5**)) can be conveniently synthesized from their phosphine analogues $RuCl_2(=CHR')(PR_3)_2$ ($R' = Ph$, $R = Cy$ (cyclohexyl) (**2**), $R' = CH{=}CMe_2$, $R = Cpy$ (cyclopentyl) (**3**)), imidazolium salts, and a base by a facile procedure. The ligand exchange reaction is performed in a "one-pot" procedure, and an easy workup leads to good yields of **4** and **5**.*

The formation of C−C bonds via olefin metathesis continues to be a powerful technique in organic synthesis and polymer chemistry.[1] Many catalyst systems are active in olefin metathesis,[1b] but most of them are ill-defined, multicomponent mixtures consisting of transition-metal compounds, cocatalysts, and promoters.[2] Recently, well-defined single-component metal carbene complexes have been utilized as catalyst precursors in olefin metathesis. Among these systems, the ruthenium carbene complexes $RuCl_2(=CHR')(PR_3)_2$ ($R = Ph$, $CH{=}CMe_2$, $CH{=}CPh_2$ and $R' = Ph$, Cy, Cpy) developed by Grubbs et al. have been the most widely used.[3] These compounds not only exhibit high reactivity in a variety of olefin metathesis reactions but also are highly tolerant of many different organic functional groups.[3i] However, these exhibit low thermal stability and readily decompose when subjected to elevated temperatures.[4]

Nucleophilic carbene ligands of the type imidazol-2-ylidene are phosphine mimics and have been used in various catalytic reactions.[5] Replacement of one of the phosphine ligands in the Grubbs system with a sterically demanding *N,N′*-disubstituted imidazol-2-ylidene such as *N,N′*-bis(mesityl)imidazol-2-ylidene (IMes, **1**) or their fully saturated analogues leads to increased thermal stability of the resulting ruthenium complexes.[4] Because of this increased thermal stability, these

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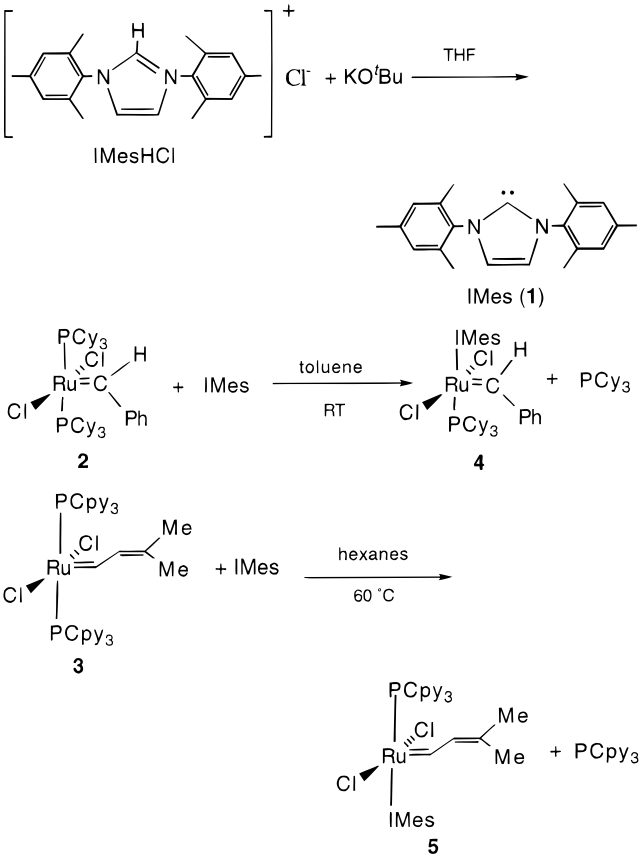
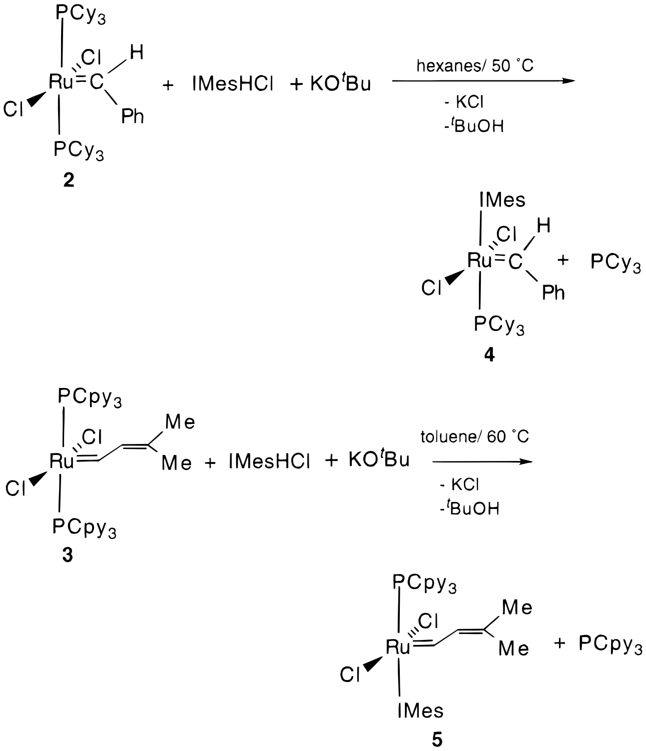
Scheme 1



Scheme 2



complexes exhibit increased ring closing activity toward tri- and tetrasubstituted substrates.[6]

The previously reported synthetic procedure for the thermally stable complexes was based on the observation that one carbene ligand (**1**) can be substituted for one phosphine ligand in RuCl$_2$(=CHR′)(PR$_3$)$_2$ (R′ = Ph, R = Cy (cyclohexyl), **2**; R′ = CH=CMe$_2$, R = Cpy (cyclopentyl), **3**) to yield RuCl$_2$(=CHR′)(IMes)(PR$_3$)$_2$ (R′ = Ph, R = Cy, **4**; R′ = CH=CMe$_2$, R = Cpy, **5**), respectively.[4] The synthetic procedure is shown in Scheme 1. Imidazol-2-ylidene ligands (neutral carbene moieties) are generated by reacting the appropriate imidazolium salt (e.g., IMesHCl) with a base (NaH or KO^{t}Bu).[7] The imidazolium salts can be synthesized by a method developed by Arduengo[8] et al. or by a novel route developed in our group.[9] These carbenes are air- and moisture-sensitive. Their synthesis requires handling under an inert atmosphere and the use of dry solvents.

Since the reactivity profile of **4** and **5** is so attractive, it would prove beneficial to develop a synthetic procedure that would circumvent the independent isolation of the nucleophilic carbenes. We now report easy, one-pot synthetic protocols leading to catalyst precursors **4** and **5**.

Results and Discussion. Ruthenium phosphine complexes **2** and **3** react with excess imidazolium salt IMesHCl in the presence of base (KO^{t}Bu) at moderate temperatures (50−60 °C) to afford respectively the mixed carbene−phosphine complexes **4** and **5** in good yields (Scheme 2). The proper solvent selection is critical in the formation of the products; the ligand substitution reactions are carried out in nonpolar solvents such as hexane and toluene. In the case of compound **4**, the heterogeneous reaction proceeds in hexane at 60 °C. The advantage of this method is provided by the lower solubility of product **4** compared to its precursor **2**. The workup procedure is simple and involves removal of the liquid phase by filtration, followed by washing the precipitate with degassed water to eliminate KCl and excess IMesHCl. The microcrystalline precipitate is then rinsed with hexane to remove any free phosphine and is dried in vacuo to afford a very pure product (by NMR spectroscopy and elemental analysis) in 78% yield.

The formation of complex **5** requires the use of toluene as solvent. The reaction does not proceed in hexane and longer reaction time at elevated temperatures only result in the decomposition of the ruthenium precursor **3** in this solvent. When the reaction is carried out in toluene, the progress of the reaction can be monitored

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by $^{31}P\{^1H\}$ NMR spectroscopy. After the reaction mixture is heated in toluene for 3 h, the signal at 30.4 ppm assigned to the starting material **3** disappears and only two resonances at 28.4 and 5.4 ppm for the product **5** and free phosphine, respectively, are observed. The mixture is filtered to remove KCl, and the filtrate is dried in vacuo. The residue is then extracted with cold pentane (−78 °C), and the precipitate formed is collected on a collection frit and dried in vacuo. The isolated yield of pure **5** (by NMR spectroscopy and elemental analysis) is 61%. The complexes synthesized using this simple methodology display catalytic behavior identical with those previously synthesized using the ligand exchange protocol with the isolated nucleophilic carbene.

Conclusions. The highly active olefin metathesis catalyst precursors **4** and **5** can be conveniently synthesized from their phosphine analogues (**2** and **3**), imidazolium salts, and a base by a facile procedure. The isolation of the highly air- and moisture-sensitive carbene ligand IMes (**1**) is avoided by generating the ligand in situ, and the ligand exchange is performed in the same reaction flask. An easy workup leads to good yields of **4** and **5**.

Experimental Section. General Considerations. All reactions were carried out under an atmosphere of dry argon with standard Schlenk tube techniques or in a MBraun glovebox containing less than 1 ppm of oxygen and water. Anhydrous solvents were purchased from Aldrich and used as received. The imidazolium salt was prepared according to the literature procedure.[8,9] NMR spectra were recorded using a Varian Oxford 400 MHz spectrometer, and elemental analyses were performed by Desert Analysis, Tucson, AZ.

Synthesis of $RuCl_2(=CHPh)(IMes)(PCy_3)_2$ (4). A 200 mL Schlenk flask was charged with **2** (5.0 g, 6.05 mmol), IMesHCl (now conveniently available from Strem; 3.1 g, 9.1 mmol), KO^{t}Bu (1.55 g, 13.65 mmol), and hexane (50 mL). The reaction mixture was then heated to 50 °C for 5 h and allowed to cool to room temperature. The suspension was filtered with the help of a collection frit; the precipitate was then washed with degassed water and rinsed with hexane. The precipitate was dried in vacuo to yield a pink-brown solid in 78% yield (4.0 g). The ^1H and $^{31}P\{^1H\}$ NMR data are in agreement with the literature values.[4]

Synthesis of $RuCl_2(=CH-CMe_2)(IMes)(PCpy_3)_2$ (5). A 200 mL Schlenk flask was charged with **3** (5.0 g, 7.0 mmol), IMesHCl (4.77 g, 14.0 mmol), KO^{t}Bu (2.36 g, 21.0 mmol), and toluene (50 mL). The reaction mixture was heated to 60 °C for 3 h, during which time all ruthenium starting material was consumed. The mixture was stirred at room temperature for 2 h and filtered through Celite. The filtrate was then evaporated to dryness, and the residue was extracted with cold (−78 °C) pentane. The suspension was filtered and dried in vacuo to yield a brown solid in 61% yield (3.33 g). The ^1H and $^{31}P\{^1H\}$ NMR data are in agreement with the literature values.[4]

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