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Imidazol(in)ium-2-carboxylates as N-heterocyclic carbene precursors in ruthenium–arene catalysts for olefin metathesis and cyclopropanation

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Abstract

Five imidazol(in)ium-2-carboxylates bearing cyclohexyl, mesityl, or 2,6-diisopropylphenyl substituents on their nitrogen atoms were prepared from the corresponding N-heterocyclic carbenes (NHCs) by reaction with carbon dioxide. They were characterized by IR and NMR spectroscopies, and by TGA. Their ability to act as NHC precursors for in situ catalytic applications was probed in ruthenium-promoted olefin metathesis and cyclopropanation reactions. When visible light induced ring-opening metathesis polymerization of cyclooctene or cyclopropanation of styrene with ethyl diazoacetate were carried out at 60 °C in the presence of $[RuCl_2(p\text{-cymene})]_2$, the NHC · CO_2 adducts and their NHC · HX counterparts (X = Cl, BF_4) displayed similar activities. When metathesis polymerizations were performed at room temperature, the carboxylates proved far superior to the corresponding imidazol(in)ium acid salts. They displayed the same level of activity as the preformed $RuCl_2$(*p*-cymene)(IMes) complex, whereas the combination of NHC · HX and KO-*t*-Bu were almost totally inactive. Results obtained for cyclopropanation reactions at room temperature did not show such a large discrepancy of behavior between the two types of adducts.

Keywords: Cyclooctene; Styrene; Ring-opening metathesis polymerization; Cyclopropanation; Homogeneous catalysis

1. Introduction

Stable N-heterocyclic carbenes (NHCs) have become ubiquitous ligands in organometallic chemistry and catalysis [1–4]. They have also acquired a place on their own as reagents and catalysts in organic synthesis, since they behave as powerful nucleophilic agents [5–7]. Currently, the NHCs most commonly encountered are based on the imidazole ring system. This electron-rich heterocycle provides a suitable framework that stabilizes the carbene center located between two nitrogen atoms [8]. Depending on the presence or the absence of a double bond between C4 and C5, imidazol-2-ylidene and imidazolin-2-ylidene species are obtained. They are usually prepared by deprotonating the corresponding imidazol(in)ium salts with a strong base, such as potassium *tert*-butoxide or sodium hydride [9]. We have applied this procedure to synthesize a wide range of ruthenium–arene complexes bearing NHC ligands (Scheme 1). The catalytic activity of these species, either preformed or generated in situ, was investigated in a number of transformations [10]. Fine tuning the steric and electronic properties of the substituents on the nitrogen atoms afforded highly efficient catalytic systems for the ring-opening metathesis polymerization (ROMP) of strained and low-strain cycloolefins [11,12], for olefin cyclopropanation with diazoesters [10], and for atom transfer radical addition (ATRA) or polymerization (ATRP) of vinyl monomers [13,14].

As part of our continuous endeavor to develop convenient synthetic methods based on the association of carbene ligands and transition-metal catalysts, we became interested in alternative sources to imidazol(in)ium salts

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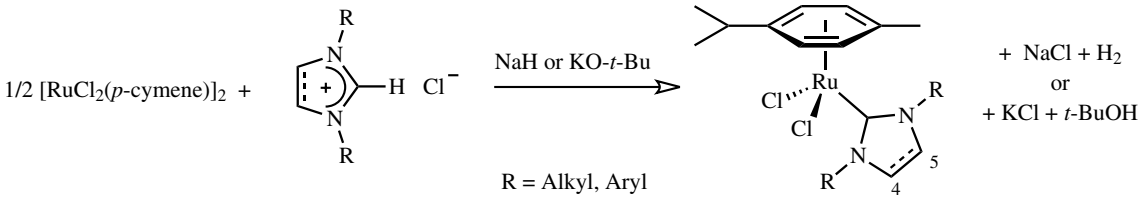


Scheme 1. Preparation of ruthenium–arene complexes bearing NHC ligands from $[RuCl_2(p\text{-cymene})]_2$, an imidazol(in)ium salt, and a base.

for generating active species in situ. Stable adducts resulting from the insertion of NHCs into acidic C–H bonds have already been successfully employed to generate various ruthenium–NHC complexes. For instance, Grubbs and co-workers used either chloroform or *tert*-butanol adducts of 1,3-dimesitylimidazolin-2-ylidene (nicknamed SIMes) to prepare their second generation ruthenium–alkylidene metathesis catalyst $RuCl_2(=CHPh)(PCy_3)(SIMes)$ [15,16]. Blechert and co-workers followed a similar pathway to substitute SIMes for a triphenylphosphine ligand in a ruthenium–indenylidene complex, starting from the *t*-BuOH adduct [17]. Although highly effective, these strategies are suitable only for introducing saturated imidazolin-2-ylidene ligands, since the clean formation of insertion products could not be achieved with unsaturated imidazol-2-ylidene species [18]. Moreover, the experimental procedures require thermal activation to induce the decomposition of the NHC adducts. They also imply the release of a stoichiometric amount of chloroform or alcohol in the reaction mixtures. Hence, they have not been used so far for in situ catalytic applications with ruthenium complexes.

We reasoned that the use of carbon dioxide to reversibly convert air- and moisture-sensitive carbenes into more stable adducts would alleviate most concerns of interference with catalytic systems. Indeed, Louie and co-workers reported in 2004 that the CO_2 adducts of 1,3-dimesitylimidazol-2-ylidene (IMes) and 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IPR) were labile zwitterionic compounds that readily exchanged their carboxylate groups in solution [19]. These observations prompted us to investigate the recourse to imidazol(in)ium-2-carboxylates as NHC precursors in ruthenium–arene complexes for in situ catalytic applications (Scheme 2). The validity of this approach was strengthened by a 2005 report from Crabtree and co-workers published while our work was in progress. The Yale group showed that 1,3-dimethylimidazolium-2-carboxylate efficiently transferred its carbene fragment to various transition-metal complexes, including the $[RuCl_2(p\text{-cymene})]_2$ dimer, to afford the corresponding NHC complexes in high yields [20].

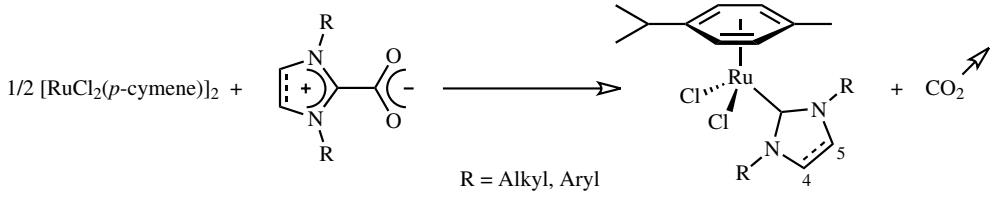
In this contribution, we report on the synthesis and characterization of five imidazol(in)ium-2-carboxylates bearing alkyl and aryl substituents on their nitrogen atoms. We also disclose the results obtained for the visible light induced ROMP of cyclooctene and for the cyclopropanation of styrene catalyzed by ruthenium complexes generated in situ with these NHC precursors.

2. Experimental

2.1. General information

All syntheses were carried out under a dry argon atmosphere using standard Schlenk techniques. Solvents and monomers were distilled from appropriate drying agents and deoxygenated prior to use. The $[RuCl_2(p\text{-cymene})]_2$ dimer was purchased from Strem. Imidazol(in)ium salts IMes · HCl [21], IMes · HBF_4 [22], IPR · HCl [21], ICy · HCl [23], SIMes · HCl [21], SIMes · HBF_4 [24], SIPR · HCl [21], and the $RuCl_2(p\text{-cymene})(IMes)$ complex [25] were synthesized according to published procedures.

^1H and ^{13}C NMR spectra were recorded at 298 K on a Bruker DRX 400 spectrometer operating at 400.13 and 100.62 MHz, respectively. Chemical shifts are listed in parts per million downfield from TMS and are referenced from the solvent peaks or TMS. Infrared spectra were recorded on a Perkin Elmer Spectrum One FT-IR spectrometer. Thermogravimetric analyses were performed on a TA Q500 instrument with a 5 °C/min ramp. Gas chromatography was carried out on a Varian 3900 instrument equipped with a flame ionization detector and a WCOT fused silica column (stationary phase: CP-Sil 5CB; column length: 15 m; inside diameter: 0.25 mm; outside diameter: 0.39 mm; film thickness: 0.25 μm). Gel permeation chromatography was performed in THF at 45 °C on a SFD S5200



Scheme 2. Preparation of ruthenium–arene complexes bearing NHC ligands from $[RuCl_2(p\text{-cymene})]_2$ and an imidazol(in)ium-2 carboxylate.