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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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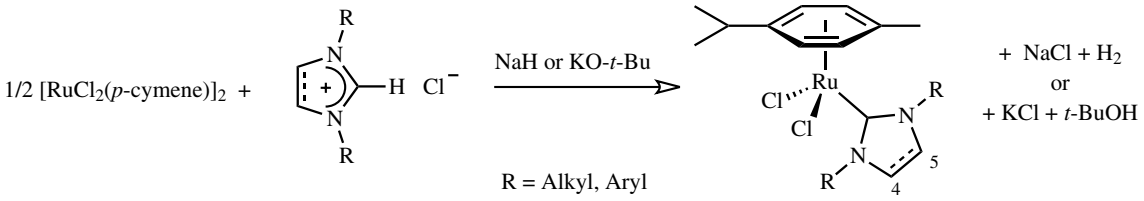


Scheme 1. Preparation of ruthenium–arene complexes bearing NHC ligands from $[RuCl_2(p\text{-cymene})]_2$, an imidazol(in)ium salt, and a base.

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].

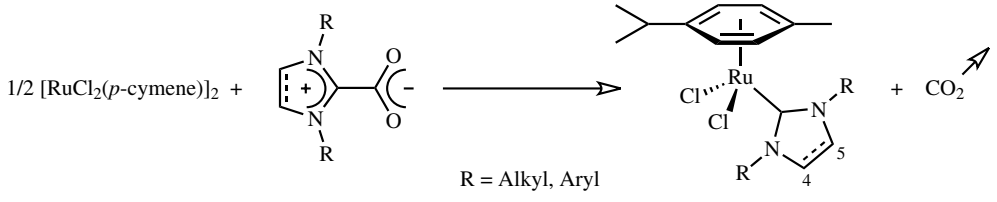
In this contribution, we report on the synthesis and characterization of five imidazol(in)ium-2-carboxylates bearing alkyl and aryl substituents on their nitrogen atoms. We also disclose the results obtained for the visible light induced ROMP of cyclooctene and for the cyclopropanation of styrene catalyzed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

autosampler liquid chromatograph equipped with a SFD 2000 refractive index detector and a battery of 4 PL gel columns fitted in series (particle size: 5 μm; pore sizes: 10^5, 10^4, 10^3, and 10^2 Å; flow rate: 1 mL/min). The molecular weights (not corrected) are reported versus monodisperse polystyrene standards used to calibrate the instrument. Melting points were recorded on an Electrothermal OSI 9100 apparatus and are not corrected.

2.2. Preparation of imidazol(in)ium-2-carboxylates

An oven-dried 100 mL round-bottom flask equipped with a magnetic stirring bar and capped with a three-way stopcock was charged with an imidazol(in)ium chloride (5 mmol) and 95% potassium bis(trimethylsilyl)amide (1.25 g, 6 mmol). The reactor was purged of air by applying three vacuum/argon cycles before dry THF (50 mL) was added. The resulting suspension was stirred 4 h at room temperature, it was then allowed to settle for 2 h. The supernatant solution was filtered through Celite and transferred with a cannula under inert atmosphere into a two-neck 100 mL round-bottom flask equipped with a magnetic stirring bar and capped with a three-way stopcock. Dry CO_2 gas was bubbled into the solution for 1 h. A white precipitate appeared within a few min. After 1 h, the solvent was evaporated under vacuum and the residue was washed with 10 mL of diethyl ether. It was dried under high vacuum.

2.2.1. 1,3-Bis(2,4,6-trimethylphenyl)imidazolium-2-carboxylate (*IMes · CO_2*)

White powder: yield 1.52 g (87%). ^{1}H NMR (DMSO-d_6, δ ppm): 2.09 (s, 12H, *ortho*-CH_3), 2.33 (s, 6H, *para*-CH_3), 7.08 (s, 4H, *meta*-CH), 7.86 (s, 2H, =CHN). ^{13}C NMR (DMSO-d_6, δ ppm): 16.8 (*ortho*-CH_3), 20.6 (*para*-CH_3), 121.6, 128.8 (*meta*-CH), 131.9, 134.6, 139.5, 146.4, 152.8 (CO_2). IR (KBr, $\bar{\nu}$ cm^{-1}): 3160, 3084, 2954, 2921, 2861, 1675 (CO_2), 1489, 1298, 1077. Mp: 240–241 °C (dec.), lit. mp: 315 °C [19].

2.2.2. 1,3-Bis(2,6-diisopropylphenyl)imidazolium-2-carboxylate (*IPR · CO_2*)

White powder: yield 1.27 g (58%). ^{1}H NMR (CD_2Cl_2, δ ppm): 1.21 (d, $^3J_{HH} = 6.8$ Hz, 24H, CH(CH_3)$_2$), 2.50 (sept, 4H, CH(CH$_3$)$_2$), 7.16 (s, 2H, =CHN), 7.32 (d, $^3J_{HH} = 7.6$ Hz, 4H, *meta*-CH), 7.52 (t, $^3J_{HH} = 7.6$ Hz, 2H, *para*-CH). ^{13}C NMR (CD_2Cl_2, δ ppm): 23.3 (CH_3), 24.2 (CH_3), 29.3 ((CH$_3$)$_2$CH), 122.6, 124.3, 130.9, 132.6, 145.1, 147.8, 152.3 (CO_2). IR (KBr, $\bar{\nu}$ cm^{-1}): 3152, 3073, 2963, 2871, 1679 (CO_2), 1489, 1322, 1305. Mp: 196–198 °C (dec.), lit. mp: 216 °C [19].

2.2.3. 1,3-Dicyclohexylimidazolium-2-carboxylate (*ICy · CO_2*)

White powder: yield 0.53 g (38%). ^{1}H NMR (DMSO-d_6, δ ppm): 1.13–1.24 (m, 2H, Cy), 1.26–1.40 (m, 4H, Cy), 1.61–1.73 (m, 6H, Cy), 1.78–1.85 (br d, 4H, Cy), 1.88–1.95 (br d, 4H, Cy), 4.82 (m, 2H, =CHN), 7.79 (s, 2H, =CHN). ^{13}C NMR (DMSO-d_6, δ ppm): 24.4 (CH_2), 24.9 (CH_2), 32.3 (CH_2), 57.2 (CHN), 117.6 (Im-C4,5), 143.0 (Im-C2), 154.3 (CO_2). IR (KBr, $\bar{\nu}$ cm^{-1}): 3142, 3100, 2938, 2857, 1663 (CO_2) 1405, 1316. Mp: 158–160 °C (dec.).

2.2.4. 1,3-Bis(2,4,6-trimethylphenyl)imidazolinium-2-carboxylate (*SIMes · CO_2*)

White powder: yield 1.39 g (79%). ^{1}H NMR (DMSO-d_6, δ ppm): 2.25 (s, 6H, *para*-CH_3), 2.36 (s, 12H, *ortho*-CH_3), 4.25 (s, 4H, CH_2), 6.98 (s, 4H, *meta*-CH). ^{13}C NMR (DMSO-d_6, δ ppm): 17.0 (*ortho*-CH_3), 20.5 (*para*-CH_3), 49.3 (CH_2N), 129.0 (*meta*-CH), 131.1 (*ipso*-C), 136.2 (*ortho*-C), 138.9 (*para*-C), 153.6 (CO_2), 164.3 (Im-C2). IR (KBr, $\bar{\nu}$ cm^{-1}): 2974, 2919, 2861, 1684 (CO_2), 1609, 1557, 1483, 1296, 1267. Mp: 218–219 °C (dec.).

2.2.5. 1,3-Bis(2,6-diisopropylphenyl)imidazolinium-2-carboxylate (*SIPR · CO_2*)

White powder: yield 1.33 g (61%). ^{1}H NMR (acetone-d_6, δ ppm): 1.30 (d, $^3J_{HH} = 6.0$ Hz, 12H, CH(CH_3)$_2$), 1.40 (d, $^3J_{HH} = 5.6$ Hz, 12H, CH(CH_3)$_2$), 3.40 (m, 4H, CH(CH$_3$)$_2$), 4.43 (s, 4H, CH_2), 7.28 (d, $^3J_{HH} = 6.8$ Hz, 4H, *meta*-CH), 7.41 (t, $^3J_{HH} = 6.8$ Hz, 2H, *para*-CH). IR (KBr, $\bar{\nu}$ cm^{-1}): 3063, 2964, 2930, 2869, 1683 (CO_2), 1661, 1549, 1466, 1327, 1278. Mp: 188–189 °C (dec.).

2.3. Typical procedure for the ROMP of cyclooctene

A 25 mL round-bottom flask equipped with a magnetic stirring bar and capped with a three-way stopcock was charged with [RuCl$_2$(*p*-cymene)]$_2$ (9.2 mg, 0.015 mmol) and an imidazol(in)ium-2-carboxylate (0.03 mmol). The reactor was purged of air by applying three vacuum/argon cycles before dry chlorobenzene (5 mL) was added. The solution was stirred for a few min at room temperature (r.t.) or in an oil bath thermostated at 60 °C. Cyclooctene (1 mL, 7.5 mmol) was added with a syringe and the reaction mixture was stirred for 2 h at r.t. or at 60 °C. It was irradiated by a 40 W "cold white" fluorescent tube placed 10 cm away from the Pyrex reaction flask. The conversion was monitored by gas chromatography using the cyclooctane impurity of cyclooctene as an internal standard. The resulting gel was diluted with $CHCl_3$ (20 mL) and slowly poured into CH_3OH (500 mL) under vigorous stirring. The precipitated polyoctenamer was dried under dynamic vacuum and characterized by GPC and NMR spectroscopy.

2.4. Typical procedure for the cyclopropanation of styrene with ethyl diazoacetate

A 10 mL two-neck flask equipped with a magnetic stirring bar and capped with a three-way stopcock was charged with [RuCl$_2$(*p*-cymene)]$_2$ (3.1 mg, 0.005 mmol) and an imidazol(in)ium-2-carboxylate (0.01 mmol). The reactor was purged of air by applying three vacuum/nitro-

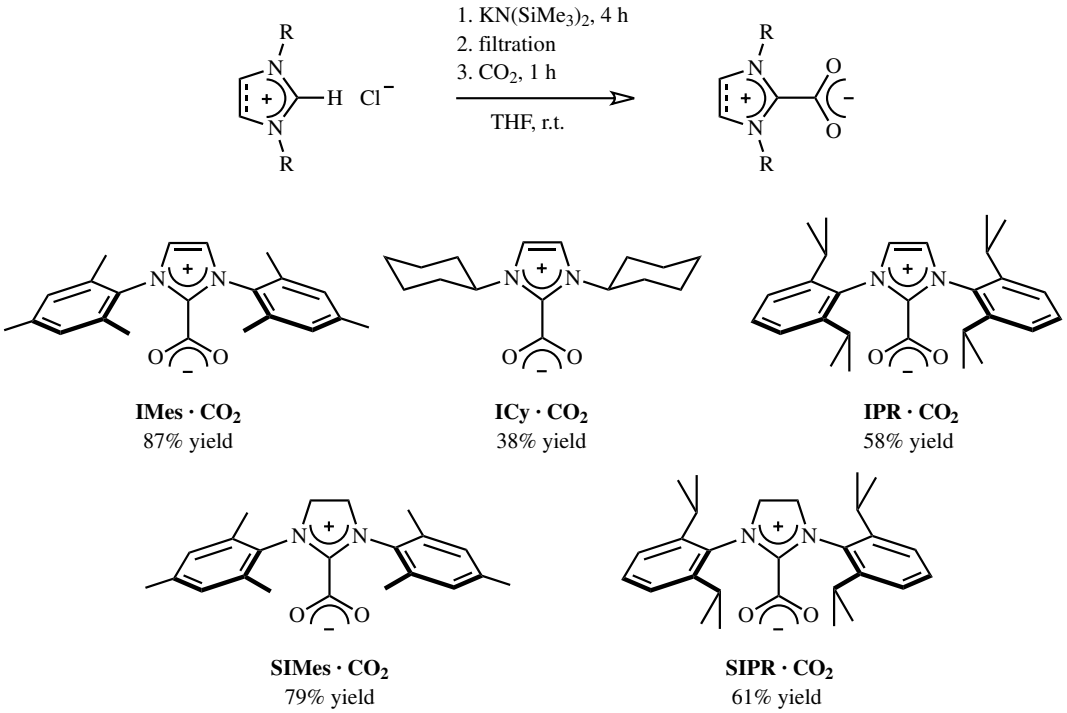
gen cycles before dry chlorobenzene (2 mL) and styrene (5 mL) were added. The solution was stirred for a few min at room temperature (r.t.) or in an oil bath thermostated at 60 °C. Ethyl diazoacetate (0.25 g, 2.2 mmol) was weighted and diluted up to 1 mL with styrene in a 1 mL syringe. This diazoester solution was slowly added to the reaction mixture with a syringe pump over a 4 h period. Stirring was maintained for an additional 20 h at r.t. or 60 °C. The rate of nitrogen evolution was monitored by a water column connected to the reaction flask via the three-way stopcock and a metallic cannula. After 24 h, the reaction mixture was analyzed by gas chromatography and its composition established by comparison with authentic samples.

3. Results and discussion

3.1. Synthesis and characterization of imidazol(in)ium-2-carboxylates

There are only a few precedents in the literature concerning imidazol(in)ium-2-carboxylates. The first report describing the synthesis and characterization of a NHC · CO_2 adduct appeared in 1974 when Schlösser and Regitz isolated 1,3-diphenylimidazolinium-2-carboxylate by hydrolysis of more complex zwitterionic carbamate derivatives [26]. In 1999, Kuhn et al. used gaseous CO_2 to trap 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene as a stable adduct [27]. The free carbene that served as a starting material was obtained by reduction of the corresponding 2-thioketone with potassium in refluxing THF [28]. In 2002, the group of Ishiguro and Sawaki identified 1,3-di-*tert*-butylimidazolium-2-carboxylate as a transfer product in reactions of the parent carbene with singlet oxygen [29]. In 2003, Tkatchenko and co-workers reported the unexpected formation of 1,3-dimethylimidazolium-2-carboxylate from 1-methylimidazole and dimethyl carbonate [30]. Tommasi and Sorrentino subsequently extended the procedure to the preparation of 1-butyl-3-methylimidazolium-2-carboxylate [31]. Last but not least, Louie and co-workers disclosed in 2004 the direct carboxylation of IMes and IPR by deprotonating the corresponding imidazolium chlorides with potassium *tert*-butoxide under a CO_2 atmosphere [19]. We have slightly modified this procedure to remove the KCl byproduct and any unreacted solid reagents prior to the precipitation of the organic carboxylates. We have also tested several strong bases to achieve the deprotonation step most efficiently. Potassium bis(trimethylsilyl)amide afforded reasonable reaction and filtration rates, yet potassium *tert*-butoxide or potassium hydride activated by a few drops of DMSO or *t*-BuOH were equally suitable in most cases. The revised reaction sequence is summarized in Scheme 3.

In addition to IMes · CO_2 and IPR · CO_2, we have prepared their saturated heterocycle analogues SIMes · CO_2 and SIPR · CO_2 in 79% and 61% yield, respectively. To further enlarge the scope of our catalytic studies with imidazol(in)ium-2-carboxylates, we also chose to include a representative adduct bearing alkyl groups instead of aryl substituents on its nitrogen atoms. Thus, we elected 1,3-dicyclohexylimidazolium-2-carboxylate (ICy · CO_2) to complement our set of NHC adducts. The 38% isolated



Scheme 3. Synthesis of imidazol(in)ium-2-carboxylates used in this work.

yield obtained for this inner salt was the lowest of the series and the only one that did not exceed the 50% mark. A recalcitrant deprotonation step was the main cause for this poor result.

The five adducts were characterized by IR and NMR spectroscopies. ^{1}H NMR spectra revealed mainly the disappearance of the strongly deshielded (9–11 ppm) imidazol(in)ium H2 signals characteristic of the starting materials, while ^{13}C NMR showed the emergence of a new resonance at ca. 150–155 ppm due to the incorporation of a carboxylate group in the products. Although they remained stable in the solid state at room temperature, we observed that the zwitterionic compounds progressively decomposed in solution. This phenomenon occurred more rapidly in highly polar solvents, such as DMSO-d_6, especially in the presence of air and moisture. It made the recording and interpretation of ^{13}C NMR spectra that required long acquisition times more difficult and prevented us from unambiguously distinguishing the ^{13}C signals of SIPR · CO_2 and its degradation products.

The FT-IR spectra of the five adducts were recorded in KBr pellets. Symmetric stretching vibration bands for the carboxylate group could not be assigned with certainty, due to the complexity of the spectra in the 1300–1500 cm^{-1} region. Yet, strong absorption bands due to the CO_2^- asymmetric stretching vibration were clearly identified in all spectra. Their wavenumbers followed the order:

$\bar{\nu}$ (cm^{-1}): 1663 (ICy · CO_2) < 1675 (IMes · CO_2) ≈ 1679 (IPR · CO_2) < 1683 (SIPR · CO_2) ≈ 1684 (SIMes · CO_2).

Previous studies from the literature had shown that 1,3-diisopropyl-4,5-dimethylimidazolium-2-carboxylate and 1,3-diphenylimidazolinium-2-carboxylate displayed similar absorption bands at 1666 [27] and 1688 cm^{-1} [26], respectively. Thus, a significant frequency shift was observed, whether alkyl or aryl groups were present on the nitrogen atoms and whether the central heterocycle was saturated or not. Conversely, limited structural variations in the alkyl (cyclohexyl or isopropyl) or aryl (phenyl, mesityl or 2,6-diisopropylphenyl) substituents on the nitrogen atoms had only little influence on the $\bar{\nu}(CO_2)$ value.

Carboxylate asymmetric stretching vibrations usually fall in the 1540–1640 cm^{-1} range [32,33]. However, a shift to higher frequencies is observed when the CO_2^- unit is adjacent to strongly electron-attracting groups. For instance, the trifluoroacetate anion absorbs at 1680 cm^{-1} [34]. Obviously, the presence of a positively charged heterocycle next to the carboxylate has a similar influence. This effect is more pronounced with a saturated imidazolinium ring than with its unsaturated counterpart, where further aromatic delocalization takes place.

To complete their characterization and to probe their thermal stability, we have carried out thermogravimetric analyses (TGA) of our five NHC · CO_2 adducts. The results are depicted in Fig. 1. The presence or the absence of a heterocyclic C4–C5 double bond did not significantly alter the onset of the decomposition that was chiefly determined by the nature of the substituents on the nitrogen atoms. ICy · CO_2 began loosing weight at ca. 80 °C, IPR · CO_2 and SIPR · CO_2 followed at ca. 120 °C, while IMes · CO_2 and SIMes · CO_2 resisted degradation up to 160 °C. This sequence parallels the melting points recorded (see Section 2). Evidence for a clean decarboxylative step was detected

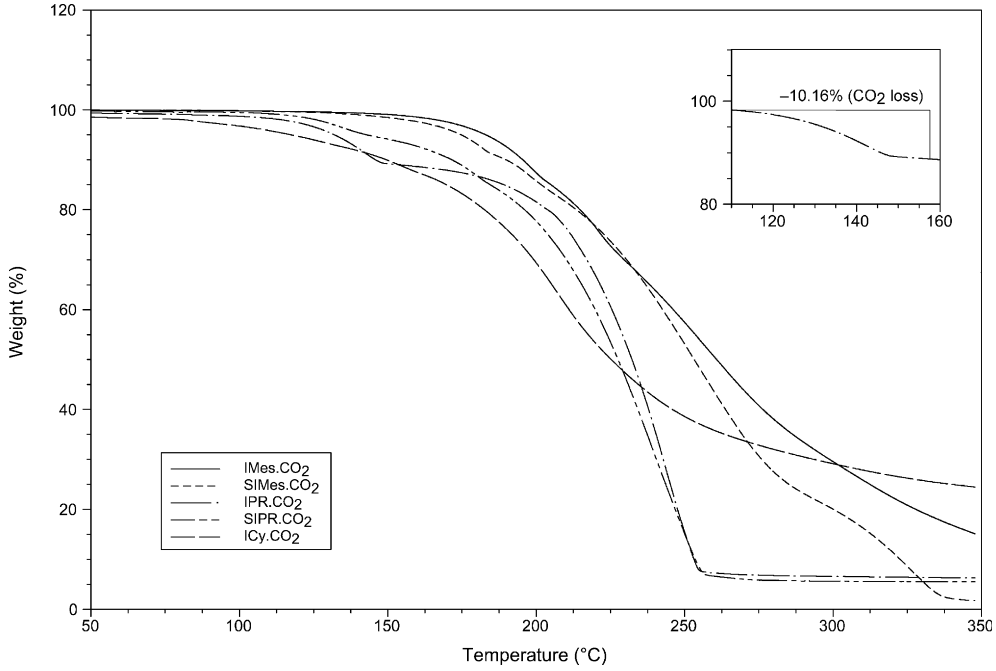


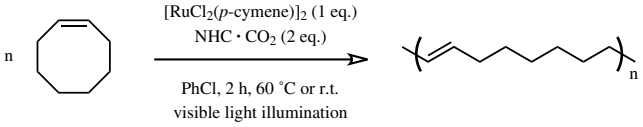
Fig. 1. TGA curves of the imidazol(in)ium-2-carboxylates used in this work.

only for IPR · CO_2 (theoretical weight loss for CO_2: 10.17%, found: 10.16%, see Fig. 1 inset), as previously observed by Louie and co-workers [19].

3.2. Ring-opening metathesis polymerization of cyclooctene

The ability of imidazol(in)ium-2-carboxylates to serve as NHC precursors for generating ruthenium–arene catalysts in situ was first investigated in the ROMP of cyclooctene (Scheme 4). In our laboratory, this reaction constitutes a benchmark test to assess the metathetical activity of new catalyst precursors [10,12,35,36]. Polymerizations were carried out in chlorobenzene at 60 °C or at room temperature using a stoichiometric mixture of $[RuCl_2(p\text{-cymene})]_2$ dimer and NHC · CO_2 adducts to release the active species in situ (cf. Scheme 2). The monomer-to-ruthenium ratio was 250 and an ordinary neon tube placed 10 cm away from the Pyrex reaction flasks complemented the experimental setup. This device ensured a strong, reproducible visible illumination required to trigger the catalytic process. Indeed, earlier studies had shown that visible light induced the ROMP of cycloolefins catalyzed by ruthenium–arene complexes bearing NHC ligands [11]. A photoactivation step was held responsible for the decoordination of the η^6-arene ligand, thereby affording highly unsaturated ruthenium centers that evolve into propagating alkylidene species, although the intimate details of the mechanism are still elusive.

In a first series of experiments, the ROMP of cyclooctene was carried out at 60 °C with the five NHC · CO_2 adducts and $[RuCl_2(p\text{-cymene})]_2$. The results are gathered in Table 1. Almost quantitative conversions of the starting material and high yields of polyoctenamer were attained within 2 h with all four mesityl- or 2,6-diisopropylphenyl-substituted carbene precursors, whereas the cyclohexyl-bearing imidazolium-2-carboxylate led to a 30% conversion and afforded only soluble oligomers and no high molecular weight polymer. The patent superiority of NHCs bearing aryl groups over their *N*-alkyl counterparts did not come as a surprise. It was already recognized when $RuCl_2$(*p*-cymene)(NHC) complexes, either preformed or generated in situ from imidazol(in)ium chlorides and a base were investigated [11]. Earlier studies had also shown that the C4–C5 double bond in the imidazole ring was not crucial to achieve high catalytic efficiencies [12].



Scheme 4. ROMP of cyclooctene with ruthenium–NHC complexes generated in situ from $[RuCl_2(p\text{-cymene})]_2$ and an imidazol(in)ium-2 carboxylate.

The similarity of behavior between the catalytic systems generated from NHC · CO_2 adducts or from NHC · HCl salts and a base at 60 °C was further evidenced by comparing the physico-chemical parameters of the polymers obtained in both cases (Table 1). No significant differences were observed in chain length distributions and *cis*/*trans* ratios. Most of the reactions led to high molecular weight polymers with a polydispersity index comprised between 2 and 3 and a sizable proportion (ca. 80%) of *trans* double bonds within the unsaturated backbones. Fluctuations in the molecular weights should not be overconsidered. Unlike related cationic ruthenium [37,38] or osmium [39] complexes possessing an alkylidene, vinylidene, allenylidene, or indenylidene moiety in their coordination sphere, the ruthenium-(*p*-cymene) catalyst precursors examined in this study lack a suitable metal–carbene fragment to initiate olefin metathesis. Ill-defined mechanisms involving arene disengagement and monomer coordination are held responsible for their transformation into active species during the course of the reaction [40,41]. The main drawback of this system is a poor control of the initiation step that results in high molecular weights and rather broad polydispersities. Because only a small number of propagating centers are present in solution, slight changes in the initiation efficiency from one experiment to another lead to significant variations in the molecular weights attained.

Table 1
ROMP of cyclooctene in chlorobenzene at 60 °C for 2 h catalyzed by various ruthenium–NHC complexes generated in situ from $[RuCl_2(p\text{-cymene})]_2$ and an imidazol(in)ium-2 carboxylate or an imidazol(in)ium salt and a base

NHC Precursor	Conversion (%)	Isolated yield (%)	M_n (kg mol^{-1})[a]	M_w/M_n[a]	σ_{cis}[b]
IMes · CO_2	100	91	632	2.32	0.21
IPR · CO_2	79	64	798	2.70	0.29
ICy · CO_2	30	0	–	–	–
SIMes · CO_2	100	85	692	2.87	0.19
SIPR · CO_2	89	77	383	2.11	0.24
IMes · HCl + KO-*t*-Bu[c]	99	92	659	2.02	0.20
IPR · HCl + KO-*t*-Bu[c]	99	60	398	3.09	0.20
SIMes · HCl + KO-*t*-Bu[c]	99	93	512	2.19	0.23
SIPR · HCl + KO-*t*-Bu[c]	57	44	838	2.13	0.51

[a] Determined by GPC in THF vs. monodisperse polystyrene standards.
[b] Fraction of *cis* double bonds within the polyoctenamer, determined by ^{13}C NMR.
[c] Data from Ref. [12].

The good results obtained with the 1,3-diarylimidazol(in)ium-2-carboxylates at 60 °C encouraged us to launch a second series of ROMP experiments at room temperature. All the other parameters were kept unchanged. Within the 2 h allowed for the polymerization to proceed, three out of the four adducts led to high conversions, now in the 80–90% range, while polyoctenamer was isolated in 70–80% yield (Table 2). The macromolecular chains still had a very high molecular weight but their polydispersity was significantly narrowed compared to the reactions performed at 60 °C. The *cis*/*trans* distribution of the double bonds in the metathesis products was also noticeably altered by the temperature change. Working at a lower temperature gave rise to higher *cis* content. In other words, increasing the temperature favored the formation of thermodynamically more stable *trans* double bonds, as it could have been anticipated. Only the SIPR · CO_2 adduct displayed a considerable drop in activity when reacted at room temperature instead of 60 °C. Furthermore, it led to a much higher proportion of *cis* double bonds. Although we have no rational explanation for these anomalies, a similar trend was already observed for the corresponding hydrochloride salt at 60 °C (cf. Table 1).

To put the results obtained with the NHC · CO_2 adducts in perspective, we carried out the ROMP of cyclooctene at room temperature using the preformed $RuCl_2$(*p*-cymene)(IMes) complex or mesityl-based catalysts generated in situ from imidazol(in)ium salts and potassium *tert*-butoxide (Table 2). The former path did not show any superiority, while the latter systems were almost completely devoid of catalytic activity. A polymer sample was only isolated in low yield with the combination of IMes · HCl and KO-*t*-Bu. Substitution of the chloride counter-ions by tetrafluoroborate anions or attempts to use a SIMes precursor did not lead to any macromolecular products. A poor solubility of the ionic components in chlorobenzene at room temperature was invoked to account for this lack of initiation [11]. Thus, recourse to the labile carboxylates proved a successful strategy to maintain the high activity of the preformed ruthenium–NHC complex under mild conditions, while enabling the use of easily available, air-stable catalyst precursors.

3.3. Cyclopropanation of styrene with ethyl diazoacetate

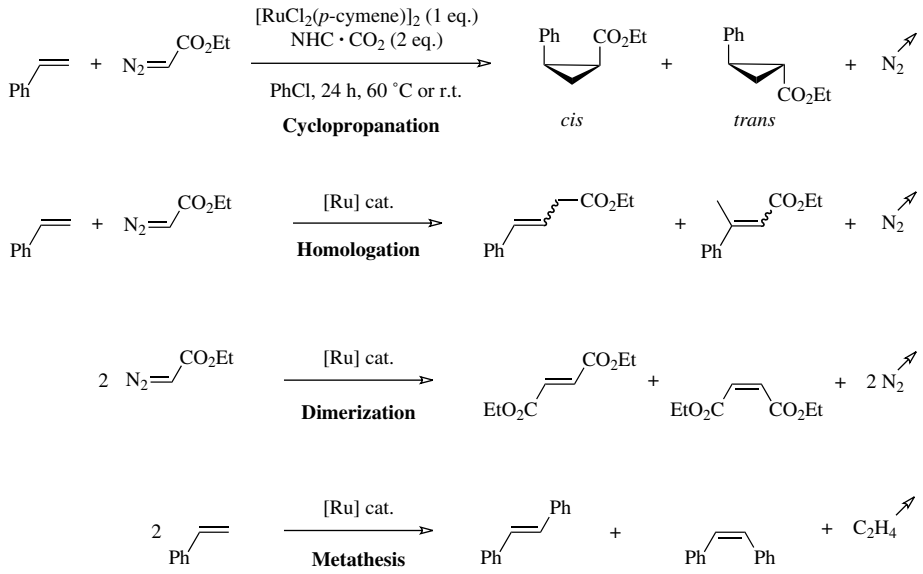
Ruthenium catalysts active in olefin metathesis are frequently also highly efficient for olefin cyclopropanation with diazo compounds [42]. Recourse to the first generation Grubbs' alkylidene complex $RuCl_2$(=CHPh)$(PCy_3)_2$ even allowed to combine enyne metathesis and cyclopropanation in a single tandem process [43]. The possible common intermediacy of metallacyclobutanes in both transformations has been proposed to rationalize the dual activity observed, although this hypothesis has not received an experimental confirmation yet. As a matter of fact, we have already shown that ruthenium–NHC complexes generated in situ from $[RuCl_2(p\text{-cymene})]_2$, an imidazol(in)ium salt, and a base were versatile catalysts for C=C bond transformations, since they were able to induce either ROMP or cyclopropanation depending on the experimental conditions adopted [10].

To complement this study, we probed the activity of imidazol(in)ium-2-carboxylates in the ruthenium-promoted cyclopropanation of styrene with ethyl diazoacetate (EDA). Our first investigations were carried out at 60 °C under standard conditions. The diazoester was slowly added to the olefin over a 4 h period of time and the release of nitrogen was monitored with a gas burette. After 24 h, the reaction mixtures were analyzed by gas chromatography. *cis*- and *trans*-Cyclopropane adducts were the major products (Scheme 5). In most cases, however, limited albeit significant amounts of homologation products were also detected. Formally, they result from carbene insertion in either vinylic C–H bond of styrene, but the mechanistic pathway leading to their formation remains uncertain [44]. We also searched systematically for the presence of *cis*- and *trans*-stilbene peaks in the chromatograms, as they were indicative of styrene metathesis. Other possible side-products, which were identified by GC–MS analysis in previous studies, include ethyl acrylate, ethyl cinnamate,

Table 2
ROMP of cyclooctene in chlorobenzene at room temperature for 2 h catalyzed by various ruthenium–NHC complexes preformed or generated in situ from $[RuCl_2(p\text{-cymene})]_2$ and an imidazol(in)ium-2 carboxylate or an imidazol(in)ium salt and a base

NHC Precursor	Conversion (%)	Isolated yield (%)	M_n (kg mol^{-1})[a]	M_w/M_n[a]	σ_{cis}[b]
IMes · CO_2	78	70	502	1.48	0.33
IPR · CO_2	80	72	1017	1.58	0.31
SIMes · CO_2	88	78	706	1.51	0.33
SIPR · CO_2	33	28	699	1.53	0.55
$RuCl_2$(*p*-cym)(IMes)	85	78	899	1.51	0.30
IMes · HCl + KO-*t*-Bu	25	11	1014	1.46	0.37
IMes · HBF_4 + KO-*t*-Bu	8	0	–	–	–
SIMes · HCl + KO-*t*-Bu	2	1	–	–	–
SIMes · HBF_4 + KO-*t*-Bu	2	0	–	–	–

[a] Determined by GPC in THF vs. monodisperse polystyrene standards.
[b] Fraction of *cis* double bonds within the polyoctenamer, determined by ^{13}C NMR.



Scheme 5. Reactions of styrene and ethyl diazoacetate catalyzed by ruthenium–NHC complexes generated in situ from $[RuCl_2(p\text{-cymene})]_2$ and an imidazol(in)ium carboxylate.

phenylcyclopropane, and 1,2-diphenylcyclopropane [45]. Since they were formed only in trace amounts in the present work, their contribution was neglected. Last but not least, the formal carbene dimers, diethyl maleate and diethyl fumarate accounted for the mass balance.

Experimental results obtained with the five NHC · CO_2 adducts at 60 °C are gathered in Table 3. Varying the nature of the substituents or removing the C4–C5 unsaturation in the N-heterocyclic moiety did not significantly alter the product distribution. In all cases, cyclopropane adducts were produced in high yields (ca. 80% based on ethyl diazoacetate). The stereoselectivity of the carbenoid fragment insertion remained also relatively unaffected by structural variations in the NHC precursors. Indeed, the proportion of *cis* isomer stayed within the 35–40% bounds for the whole series of catalysts under examination. Homologation contributed to the consumption of diazoester only to a small extent (4–6%), whereas dimerization gave rise to the formation of diester byproducts in larger quantities (up to 20% with SIPR · CO_2), despite the slow addition of the diazo compound to the reaction medium. Stilbenes, out of which the *trans* isomer was largely predominant, were also formed, except when ICy · CO_2 was employed as NHC precursor. The absence of metathesis products with this N-alkylated carbene source is in line with the trends previously discussed for the ROMP of cyclooctene (see Section 3.2). When comparing the yields for stilbene and ester derivatives, it should be kept in mind that styrene was the limiting reagent in the former case, while EDA determined the formation of the other products. Taking into consideration the large excess of olefin used, one can conclude that cyclopropanation and related reactions occur much faster than styrene metathesis under the experimental conditions adopted.

Once again, the results acquired at 60 °C with the imidazol(in)ium-2-carboxylates did not show major deviation from those obtained previously starting from imidazol(in)ium chlorides and potassium *tert*-butoxide (Table

Table 3
Reaction of styrene with ethyl diazoacetate in chlorobenzene at 60 °C for 24 h catalyzed by various ruthenium–NHC complexes generated in situ from $[RuCl_2(p\text{-cymene})]_2$ and an imidazol(in)ium-2 carboxylate or an imidazol(in)ium salt and a base

NHC Precursor	Cyclopropanation yield (%)[a]	*cis*/*trans* ratio	Homologation yield (%)[a]	Dimerization yield (%)[a]	Metathesis yield (%)[b]
IMes · CO_2	83	0.53	4	13	3
IPR · CO_2	86	0.67	4	11	5
ICy · CO_2	80	0.56	6	14	0
SIMes · CO_2	83	0.59	5	12	4
SIPR · CO_2	75	0.63	5	20	5
IMes · HCl + KO-*t*-Bu[c]	81	0.59	15	4	3
IPR · HCl + KO-*t*-Bu[c]	77	0.77	11	12	<1
SIMes · HCl + KO-*t*-Bu[c]	81	0.56	9	10	<1
SIPR · HCl + KO-*t*-Bu[c]	80	0.56	14	6	<1

[a] Determined by GC, based on ethyl diazoacetate.
[b] Determined by GC, based on styrene.
[c] Data from Ref. [10].

Table 4
Reaction of styrene with ethyl diazoacetate in chlorobenzene at room temperature for 24 h catalyzed by various ruthenium–NHC complexes generated in situ from $[RuCl_2(p\text{-cymene})]_2$ and an imidazol(in)ium-2 carboxylate or an imidazol(in)ium salt and a base

NHC Precursor	Cyclopropanation yield (%)[a]	*cis*/*trans* ratio	Homologation yield (%)[a]	Dimerization yield (%)[a]	Metathesis yield (%)[b]
IMes · CO_2	61	0.34	1	38	3
SIMes · CO_2	56	0.34	2	41	2
IMes · HCl + KO-*t*-Bu	67	0.31	2	31	3
SIMes · HCl + KO-*t*-Bu	60	0.39	1	39	<1

[a] Determined by GC, based on ethyl diazoacetate.
[b] Determined by GC, based on styrene.

3). The method used to generate the NHC ligands in situ had no significant impact on the yield of cyclopropanation nor on its stereoselectivity. However, homologation took the precedence over dimerization as a side-reaction with a number of NHC · HCl adducts, while styrene metathesis was almost completely repressed. Yet, for both NHC · CO_2 and NHC · HCl adducts, the exact nature of the carbene moiety seemed to have very little influence on the outcome of the cyclopropanation. This observation corroborates earlier reports from the literature showing that the influence of the catalyst structure on diastereoselectivity is generally small [46]. This was rationalized by assuming that the high reactivity of the metal–carbene complex results in an early transition state in which the olefin is still at a significant distance from the metal center. Because of that, steric influences are usually not decisive in the induction of diastereomeric excesses, unless very bulky reagents (the diazoester and the olefin) are employed. Accordingly, most catalytic systems lead to *cis*/*trans* ratios in the 50/50 to 25/75 range for the cyclopropanation of styrene with ethyl diazoacetate [46].

To complete this study, we have carried out the cyclopropanation of styrene with EDA at room temperature instead of 60 °C. The IMes and SIMes ligands were selected as representative NHCs for these runs. They were generated in situ from their CO_2 or HCl adducts. Potassium *tert*-butoxide was employed to perform the deprotonation in the latter case. The experimental results are listed in Table 4. Contrary to what happened in the ROMP of cyclooctene, the carboxylates did not outperform the corresponding hydrochlorides. They led to somewhat reduced yields of ethyl 2-phenylcyclopropanecarboxylate and a concomitant increase in the formation of ethyl maleate and fumarate. With both types of NHC precursors, homologation and metathesis processes were kept at a low level and the aromatic heterocycles turned out to be slightly more active toward cyclopropanation than their imidazolinium counterparts. The stereoselectivity of the reaction was affected by the temperature change. The proportion of *cis* diastereomers dropped from 35–40% at 60 °C to 25–28% at room temperature.

4. Conclusion

A range of N-heterocyclic carbenes bearing alkyl or aryl substituents on their nitrogen atoms were converted into the corresponding imidazol(in)ium-2-carboxylates by reaction with carbon dioxide. Compared to the free carbenes, the zwitterionic adducts displayed a much greater stability toward air and moisture in the solid state. Thus, they could be easily handled with no particular precautions. Upon heating or dissolution, however, they readily lost the CO_2 moiety, thereby providing a convenient method to generate NHC ligands in situ. Contrary to the deprotonation of imidazol(in)ium salts, the decomposition of betaine adducts did not require the use of a strong base and was accompanied only by the evolution of carbon dioxide.

The aptitude of imidazol(in)ium-2-carboxylates to act as NHC precursors for in situ catalytic applications was investigated in ruthenium-promoted olefin metathesis and cyclopropanation reactions. When visible light induced ROMP of cyclooctene or cyclopropanation of styrene with EDA were carried out at 60 °C, the NHC · CO_2 adducts and their NHC · HX counterparts (X = Cl, BF_4) displayed similar high activities. When metathesis polymerizations were performed at room temperature, however, the carboxylates proved far superior to the corresponding imidazol(in)ium acid salts. Indeed, 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 as ROMP initiators. Results obtained for the cyclopropanation reactions at room temperature did not show such a large discrepancy of behavior between the two types of adducts.

Numerous other systems could benefit from the use of imidazol(in)ium-2-carboxylates as NHC precursors, either alone for organocatalytic transformations, or associated with transition metals for organometallic synthesis and catalysis. We are presently investigating the replacement of NHC · HX adducts by their NHC · CO_2 counterparts in palladium-catalyzed Suzuki–Miyaura cross-coupling reactions. The preliminary results are promising.

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