DOI: 10.1002/ejic.200700665

Ruthenium-Based NHC-Arene Systems as Ring-Opening Metathesis Polymerisation Catalysts

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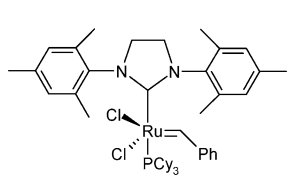
Keywords: Carbene ligands / Homogeneous catalysis / Olefin polymerisation / Ruthenium

The availability of starting materials, the complexity of the preparative routes and the cost to make the catalyst are key in the development of industrially relevant olefin metathesis catalysts. With this in mind, new synthetic routes, which lead to alternatives for the classic ruthenium benzylidene complexes and circumvent the need for patented Grubbs intermediates were explored. The research presented herein focuses on the coordination of "saturated" N-heterocyclic carbene (NHC) ligands to Ru dimer [(*p*-cymene)$RuCl_2$]$_2$. As the coordination of the standard NHC ligand H_2IMes (1,3-dimesityl-4,5-dihydroimidazol-2-ylidene) was found to be unattainable, bidentate NHC analogues were synthesized instead. These are *O*-hydroxyaryl-substituted NHCs, capable of binding with the metal centre through the oxygen atom as well as through the carbene carbon atom. Their chelating properties improved the stability of the corresponding ruthenium arene complexes, which allowed more successful isolation.

Introduction

Olefin metathesis is a fundamental catalytic process and stands among the most prominent ways to build carbon–carbon bonds.[1–6] The reaction consists of the cleavage and reformation of alkene double bonds with a simultaneous exchange of substituents. Cross metathesis (CM),[7,8] ring-closing metathesis (RCM),[9] ring-opening metathesis polymerisation (ROMP)[10] and acyclic diene metathesis polymerisation (ADMET),[11] illustrate the versatility of the olefin metathesis reaction. Thanks to the continuous improvement of its initiators and a sharpened comprehension of its reaction mechanism,[12–30] the olefin metathesis transformation has been upgraded to a very practical, efficient and flexible synthetic methodology. Olefin metathesis now allows cleaner, more efficient and less expensive industrial production of polymers, fine chemicals, pesticides and pharmaceutical intermediates. Despite the recent advances, the search for commercially relevant catalyst systems remains challenging. When thinking of commercial applications, one should not only focus on catalyst activity, selectivity or stability, as highly developed initiators are sometimes too expensive for applications on an industrial scale. Other important aspects are the availability of the starting materials, the complexity of the preparative routes and the cost to make the catalyst. In addition, it is often relevant to search for patent-free synthetic strategies. Up to now, most synthetic pathways toward Grubbs 2nd generation complexes, of which catalyst **1** is the most popular, proceed through bis(phosphane) benzylidene systems.[31,32] A more direct pathway with the use of moderate reaction conditions and readily available starting materials is quite desirable. This also involves the need for alternative means to introduce the alkylidene moiety, which avoid the quite cumbersome preparative routes by diazo compounds.[33] In this context, the Ru dimer [(*p*-cymene)$RuCl_2$]$_2$ (**2**) is air and moisture stable, and it is an easy to handle precursor that is an ideal starting material for the synthesis of allenylidene or vinylidene catalysts to be used for metathesis.[34–44] In order to find a resembling alternative for the classic Grubbs catalyst **1**, it would be necessary to coordinate H_2IMes (1,3-dimesityl-4,5-dihydroimidazol-2-ylidene) to Ru dimer **2**. Whereas several groups claim to have synthesized [(*p*-cy-



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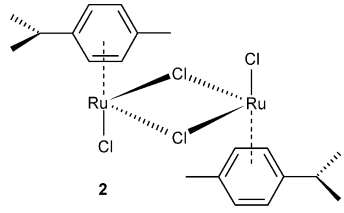

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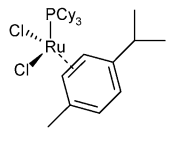

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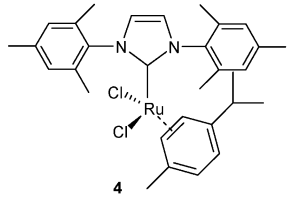

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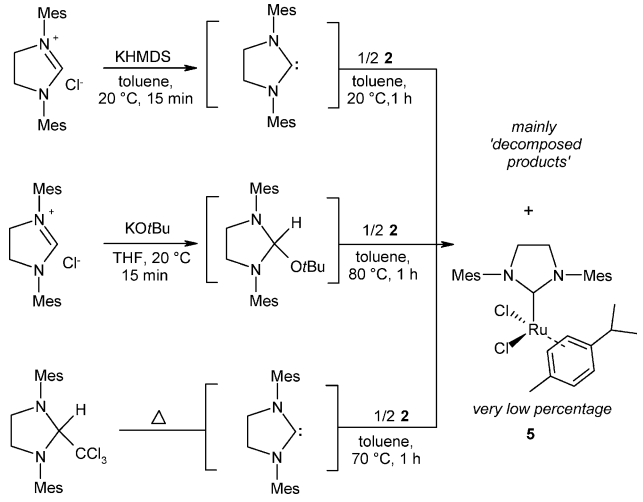
mene)(H_2IMes)RuCl_2] in situ, it was never isolated, nor fully characterized.[45,46] Driven by the fascinating challenge to find alternative synthetic strategies, we herein describe the endeavour we undertook to contribute to this quest.

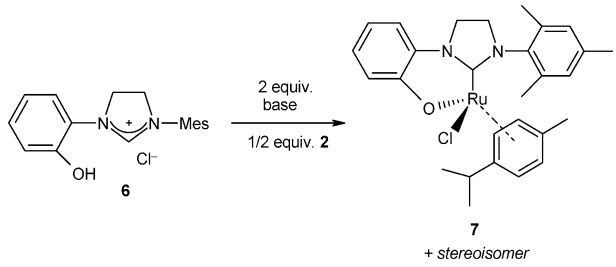
Results and Discussion

Whereas the coordination of IMes (1,3-dimesitylimidazol-2-ylidene) to Ru dimer **2** proceeds readily by standard synthetic strategies (complex **4**),[38,47] analogous binding of H_2IMes was found to be more problematic. Regardless of the reaction conditions applied, a mixture of Ru complexes was obtained (Scheme 1). Only when the chloroform adduct H_2IMes(H)(CCl_3) was used as a carbene precursor could a small rate of N-heterocyclic carbene (NHC) coordination be evidenced through ^{13}C NMR spectroscopy. A ^{13}C NMR resonance was found at δ = 202.5 ppm, which is characteristic for the carbene carbon atom coordinated to the metal centre. However, ^{1}H NMR spectroscopic analysis of the reaction products revealed that desired complex **5** was only formed as a minor product together with undefined hydridic species. ^{1}H NMR spectroscopic resonances were found at δ = –3.64, –3.98, –5.09 and –5.62 ppm.



Scheme 1. Synthesis of [(*p*-cymene)(H_2IMes)RuCl_2].

Because the failure in our efforts to isolate **5** was assigned to a lack of stability of the complex, a bidentate analogue of the NHC ligand was synthesized. The chelating properties of a bidentate NHC were expected to ameliorate the complex stability through a "chelate effect". The synthesis of 1-(mesityl)-3-(2-hydroxyphenyl)-4,5-dihydroimidazolium chloride salt (**6**) was straightforward following a procedure outlined by Grubbs et al.[48] In order to effectuate ligand coordination, the NHC precursor was treated with 2 equiv. of base; that is, 1 equiv. to liberate the free carbene and 1 equiv. to deprotonate the phenolic group. After 15 min of reaction time, Ru dimer **2** was added to the reaction mixture. As expected, the ligand bound to the metal centre in a chelating manner (Scheme 2). Because of the pseudotetrahedral arrangement of the ligands, a stereogenic centre was created at the Ru centre, leading to the existence of two stereoisomers. Complex **7** shows high stability and can be handled in air without any sign of decomposition. To explore its thermal stability, a solution of **7** (16.5 mg, 0.030 mmol) and coronene (internal standard, 9.0 mg, 0.030 mmol) in deuterated chlorobenzene (C_6D_5Cl, 0.50 mL) was followed over time at 100 °C by using ^{1}H NMR spectroscopy. After 48 h, no sign of decomposition was observed. At 120 °C, the complex fully decomposed within 4 h.



Scheme 2. Synthesis of NHC-arene complex **7**.

Dark-red crystals of **7** suitable for X-ray structure analysis were grown by slow evaporation of a toluene/CH_2Cl_2 solution, and its molecular structure is represented in Figure 1. The molecular species consists of a *p*-cymene ligand showing η^6-bonding, an anionic chloride ligand and a bidentate (C,O) chelating NHC ligand. The isopropyl group on the arene ligand is a little distorted away from the metal centre as a result of steric factors.

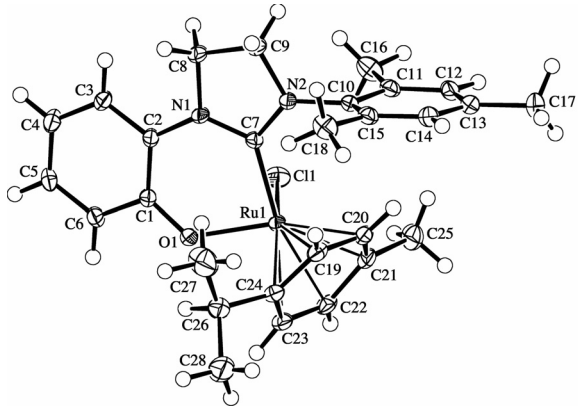


Figure 1. The molecular structure of **7**; ellipsoids show 50% probability.

The catalytic activity of **7** was evaluated in the ROMP of the highly strained monomer norbornene and compared to the activity of Ru dimer **2**, complex **3** and **4** (Table 1). Our results reveal that **7** displays very poor activity in metathesis reactions; only 20% of norbornene polymerised during a reaction time of 3 h at 85 °C (Table 1, Entry 4). It has been described in the literature that for this catalyst type decomplexation of the arene ligand is the prior requirement for the generation of catalytic activity.[49–52] The complex must be coordinatively unsaturated for a substrate to enter the coordination sphere of the metal. In other words, for the catalyst to become active, a ligand has to dissociate to generate a vacant site. However, the high stability of complex **7** indicates that arene ligand dissociation is greatly restrained.

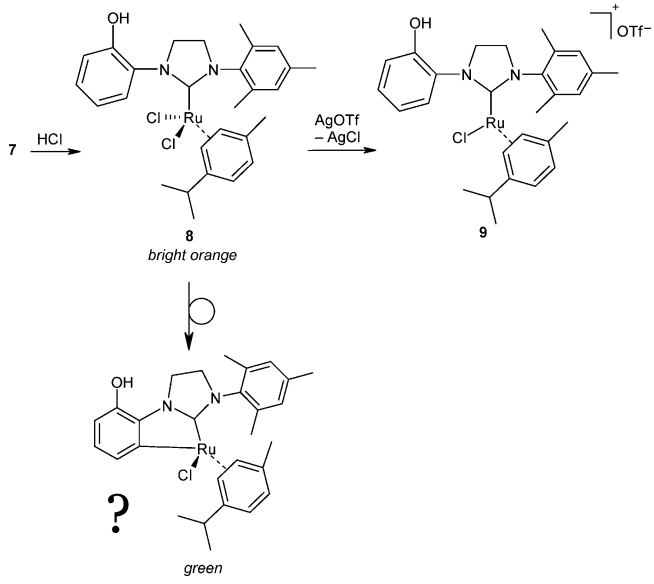
Table 1. ROMP of 2-norbornene.[a]

Entry	Catalyst	Conversion [%]	Mn (*103)	PDI	*cis* [%]
1	**2**	84	198	2.1	45
2	**3**	≈100	85	2.9	16
3	**4**	≈100	339	2.8	49
4	**7**	20	108	3.8	57
5	**7** + phenylacetylene	33	228	3.0	52
6	**7** + TMSD	21	588	3.0	75
7	**8**	17	1954	2.0	81
8	**9**	16	1112	2.6	78
9	**10**	4	–	–	–
10	**10** + phenylacetylene	7	32	3.1	42
11	**10** + TMSD	10	65	4.5	65
12	**11**	14	932	2.1	61

[a] Catalyst/norbornene, 1:2500, cat. conc. = 0.41 mM, 85 °C, solvent = 0.5 mL of CH_2Cl_2 to dissolve the catalyst + 10 mL of toluene, reaction time = 3 h. A correction factor of 0.5*Mn was applied for characterizing the PNBs by gel permeation chromatography.[53] The *cis* fraction was determined by ^{1}H NMR spectroscopy: δ = 5.36 CH=CH *trans*, 5.22 CH=CH *cis*.

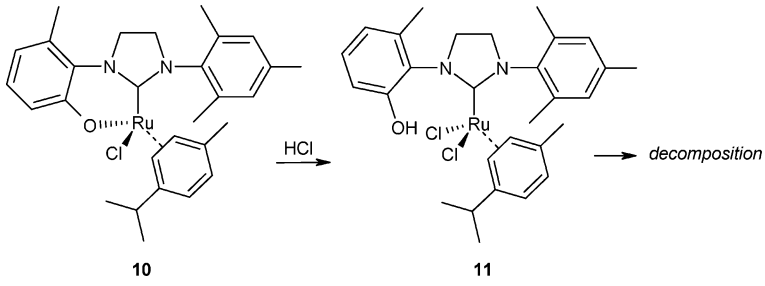
With the aim to generate the vinylidene moiety in situ, an excess amount of phenylacetylene (20 equiv.) was added to the catalyst (Table 1, Entry 5). Only a minor activity enhancement was observed. Also, the addition of (trimethylsilyl)diazomethane (TMSD), which is known to activate [(*p*-cymene)(PCy_3)$RuCl_2$] (**3**) with the in situ formation of [$RuCl_2$(=$CHSiMe_3$)(PCy_3)][49,54] did not significantly enhance the catalytic activity (Table 1, Entry 6). In a dissociative ligand substitution pathway, dissociation of the *p*-cymene moiety is a prerequisite for the generation of an empty coordination site where the alkylidene moiety can be introduced. As a result of the exceptional stability of the complex, which is accompanied by a low dissociation tendency of the arene ligand, the addition of a terminal alkyne or a diazo compound was found to have only a minor effect. Furthermore, we observed that in contrast to complexes of type **3** or **4**, which become more active towards metathesis upon UV irradiation,[35,51,55] the ROMP-catalyzed by **7** is not photoinduced, as no change in the outcome was seen when reactions were carried out in the dark or under constant irradiation with UV light (shortwave UV: 254 nm, longwave UV: 365 nm).

The addition of an excess amount of ethereal HCl to **7** caused protonation of the phenolic oxygen atom, therefrom affording complex **8** as a bright orange solid (Scheme 3). The OH proton was found at δ = 10.08 ppm as a broad ^{1}H NMR (C_6D_6) spectroscopic signal. Through breaking of the chelate, the complex was expected to lose part of its extreme stability and become more reactive. Entry 7 in Table 1 shows that a loss of catalytic activity was observed instead! Also, cationic counterpart **9** exhibited poor ROMP activity (Table 1, Entry 8). As expected, losing the chelate effect induced a significantly decreased stability of complex **8**. The complex was found to decompose rapidly in solution. Even as a solid stored under inert atmosphere the complex was unstable and slowly changed colour from orange to green (time course of two weeks). NMR spectroscopic analysis of the decomposition product indicated that both NHC and *p*-cymene ligand were still coordinated to the Ru centre. Therefore, we suggest that **8** suffers from a tendency to undergo *ortho* metallation with the 2-hydroxyphenyl amino side group.[46,56–58]



Scheme 3. Losing the chelate effect.

Anticipating that this *ortho* metallation might be avoided by a small modification in the NHC framework, a methyl unit was introduced at the carbon atom in the *ortho* position of the 2-hydroxyphenyl group. Coordination of the new bidentate NHC afforded air- and moisture-stable complex **10**. Also, this complex is a poor initiator for metathesis and the addition of a terminal alkyne or TMSD group only slightly increases the polymer yield (Table 1, Entries 9–11).



Scheme 4. Modified complexes **10** and **11**.

Again, HCl was added to "break" the chelate to afford complex **11**. Thereupon the catalytic activity in the ROMP of 2-norbornene was slightly enhanced (Table 1, Entry 12). In spite of the small ligand modification (*ortho* methylation), also this complex was found to slowly decompose. A solution of **11** in CH_2Cl_2 changed colour from orange to dark green during a time course of 1 h. Unfortunately, a complex mixture of products was obtained, and we were not able to identify the decomposition products (Scheme 4).

Conclusions

From these results, it is clear that complexes of the type [(*p*-cymene)(L)$RuCl_2$] (with L = H_2IMes or resembling NHC) are not very reactive, and they too unstable for practical use. Likely due to stability problems, we were unable to isolate complex [(*p*-cymene)(H_2IMes)$RuCl_2$] (**5**). Similar complexes **8** and **11** were successfully isolated, but only when an uncommon synthetic strategy was followed. The NHCs were first introduced as bidentate ligands, which greatly enhanced the stability of the complex through the chelate effect. Subsequent treatment with hydrochloric acid caused a breaking of the chelate O–Ru bond and formation of complexes [(*p*-cymene)(NHC)$RuCl_2$] bearing monodentate NHCs. Upon loss of the chelate effect, a dramatic decrease in the stability of the complex was observed; as a result, complexes **8** and **11** could not be kept for more than a few days even when stored as a solid under an inert atmosphere. In solution, both complexes decomposed very rapidly, which drastically restricted their catalytic value. To adequately compete with the Grubbs catalysts, it is unquestionable that better activity and stability levels have to be reached. Therefore, our attention has now been drawn to other synthetic methods that first introduce an alkylidene moiety and then, in a second reaction step, realize the coordination of an NHC ligand. We hope to be able to report on these results in the near future.

Experimental Section

General: All reactions and manipulations involving organometallic compounds were conducted in oven-dried glassware under an argon atmosphere by using standard Schlenk techniques. Solvents were dried with appropriate drying agents and distilled prior to use. ^{1}H and ^{13}C NMR spectroscopic measurements were performed with a Varian Unity-300 spectrometer. Ru dimer **2**,[59] H_2IMes(H)(CCl_3),[60] the bidentate NHC salts[47] and complex **3**[35] were prepared according to literature procedures. (Trimethylsilyl)diazomethane (TMSD) was purchased from Aldrich as a solution in hexane. We were unable to do elemental analysis on complexes **9** and **11** because of the lack of stability of these compounds. For these two complexes, we hope that characterisation through ^{1}H NMR and ^{13}C NMR spectroscopy is sufficient.

Synthesis of the Complexed

[(*p*-cymene)$RuCl_2$(IMes)] (4): The synthesis of complex **4** was previously reported by Nolan et al. to result from the reaction of Ru dimer with free IMes carbene.[38] We herein describe a slightly altered synthetic strategy, which avoids the isolation and handling of the air- and moisture-sensitive free carbene. To a dry Schlenk flask charged with 1,3-bis(2,4,6-trimethylphenyl)imidazolium chloride (0.490 g, 1.44 mmol) and dry toluene (5 mL) was added LiHMDS (0.5 M in toluene, 2.88 mL, 1 equiv.). The resulting suspension was stirred at room temperature for 15 min. Ru dimer **2** (0.43 g, 0.70 mmol) was then added as a solid, and the mixture was stirred at room temperature for an additional 45 min. The solution was filtered to remove residual salts, and the filtrate was concentrated under vacuum. The residue was dissolved in a small amount of CH_2Cl_2 (1 mL) and precipitated upon addition of hexane (25 mL). The orange solid was filtered off and vacuum dried. Yield: 0.67 g, 78%. NMR spectroscopic data are similar to those reported by Nolan et al.: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.95 (s, 4 H, Mes-3,5-H), 6.90 (s, 2 H, NC*H*C*H*N), 5.03 (d, J = 5.5 Hz, 2 H, *p*-cymene aryl-H), 4.63 (d, J = 5.5 Hz, 2 H, *p*-cymene aryl-H), 2.51 (m, 1 H, *p*-cymene C*H*(CH_3)$_2$), 2.35 (s, 6 H, mesityl *p*-CH_3), 2.23 (s, 6 H, mesityl *o*-CH_3), 1.79 (s, 3 H, *p*-cymene CH_3), 1.07 [d, J = 6.8 Hz, 6 H, *p*-cymene CH(CH_3)$_2$] ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 6.95 172.0 (N*C*N), 139.0, 138.9, 130.1, 128.9, 125.4, 103.1, 96.0, 87.0, 85.9, 30.4 [*p*-cymene *C*H(CH_3)$_2$], 22.9, 22.7, 21.4, 19.3, 18.24, 18.0 ppm.

NHC-Arene Complex 7: The NHC precursor 1-mesityl-3-(2-hydroxyphenyl)-4,5-dihydroimidazolium chloride (0.765 g, 2.41 mmol) was treated with a solution of potassium hexamethyldisilazide (KHMDS; 0.5 M in toluene, 9.66 mL, 4.83 mmol, 2 equiv.) over 15 min at room temperature. A suspension of Ru dimer **2** (0.70 g, 1.14 mmol) in toluene was added, and the resulting mixture was stirred for an additional 1.5 h at room temperature. The toluene solution was filtered and washed with CH_2Cl_2 (2 × 10 mL). After evaporation of the filtrate, cold acetone was added while stirring. Subsequent filtration allowed the isolation of the pure red-pink catalyst, which was thoroughly dried. Yield: 0.58 g, 46%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.93–7.02 (m, 3 H, aryl CH), 6.79 (t, $^3J_{H,H}$ = 7.3 Hz, 1 H, aryl CH), 6.71 (d, $^3J_{H,H}$ = 7.9 Hz, 1 H, aryl CH), 6.43 (t, $^3J_{H,H}$ = 7.3 Hz, 1 H, aryl CH), 5.52 (d, J = 4.6 Hz, 1 H, *p*-cymene aryl-H), 5.26 (d, J = 4.6 Hz, 1 H, *p*-cymene aryl-H), 5.09 (d, J = 3.4 Hz, 1 H, *p*-cymene aryl-H), 4.43 (pseudo q, J_{app} = ca. 10.5 Hz, 1 H, NCH_2CH_2N), 4.18 (pseudo q, J_{app} = ca. 10.5 Hz, 1 H, NCH_2CH_2N), 4.02 (pseudo q, J_{app} = ca. 10.5 Hz, 1 H, NCH_2CH_2N), 3.92 (pseudo q, J_{app} = ca. 10.5 Hz, 1 H, NCH_2CH_2N), 3.69 (d, J = 3.2 Hz, 1 H, *p*-cymene aryl-H), 2.50 (s, 3 H, mesityl CH_3), 2.42 (s, 3 H, mesityl CH_3), 2.41 [m, 1 H, *p*-cymene C*H*(CH_3)$_2$], 2.33 (s, 3 H, mesityl CH_3), 1.58 (s, 3 H, *p*-cymene CH_3), 0.96 [d, $^3J_{H,H}$ = 6.7 Hz, 3 H, *p*-cymene CH(CH_3)$_2$], 0.83 [d, $^3J_{H,H}$ = 6.7 Hz, 3 H, *p*-cymene CH(CH_3)$_2$] ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 202.7 (N*C*N), 157.4 (*C*-O), 139.7 (NHC aryl-C), 139.0 (NHC aryl-C), 138.0 (NHC aryl-C), 136.2 (NHC aryl-C), 130.9 (NHC aryl-C), 130.5 and 130.3 (NHC aryl-C), 128.9 and 128.8 (NHC aryl-C), 124.92 and 124.86 (NHC aryl-C), 121.3 and 121.2 (NHC aryl-C), 116.3 and 116.2 (NHC aryl-C), 113.9 and 113.8 (NHC aryl-C), 101.1 (*p*-cymene aryl-C), 95.2 (*p*-cymene aryl-C), 94.7 (*p*-cymene aryl-C), 93.1 (*p*-cymene aryl-C), 83.8 (*p*-cymene aryl-C), 79.4 (*p*-cymene aryl-C), 51.1 (*C*H_2CH_2), 48.7 (CH$_2$*C*H$_2$), 30.2 and 30.1 [p-cymene *C*H(CH_3)$_2$], 23.3 (*C*H_3), 21.3 and 21.1 (*C*H_3), 20.0 and 19.8 (*C*H_3), 18.6 and 18.5 (*C*H_3), 18.3 and 18.1 (*C*H_3) ppm. *Some carbon atoms have a double peak in the spectrum, which indicates the presence of two diastereomers in roughly an equal ratio.* $C_{28}H_{33}ClN_2ORu$ (550.11): C 61.14, H 6.05, N 5.09; found C 61.39, H 6.08, N 5.12.

NHC-Arene Complex 8: Complex **7** (0.125 g, 0.227 mmol) was dissolved in CH_2Cl_2 (5 mL). An excess amount of HCl (1 N in Et_2O, 1 mL) was added, and the resulting mixture was stirred at room temperature for 5 min. Solvents were evaporated and hexane

(25 mL) was added to precipitate complex **8** as a bright orange solid. Yield: 0.12 g, 93%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.02 (d, J = 7.5 Hz, 1 H, aryl C*H*), 7.10 (s, 1 H, aryl C*H*), 7.03 (s, 1 H, aryl C*H*), 6.96 (m, 1 H, aryl C*H*), 6.89 (m, 2 H, aryl C*H*), 5.70 (br. s, 2 H, *p*-cymene aryl-*H*), 5.32 (br. s, 2 H, *p*-cymene aryl-*H*), 4.34 (m, 2 H, NCH_2CH_2N), 4.10 (m, 1 H, NCH_2CH_2N), 3.98 (m, 1 H, NCH_2CH_2N), 2.86 [sept, J = 5.5 Hz, 1 H, *p*-cymene C*H*(CH_3)$_2$], 2.58 (s, 3 H, mesityl CH_3), 2.38 (s, 3 H, mesityl CH_3), 2.35 (s, 3 H, mesityl CH_3), 1.75 (s, 3 H, *p*-cymene CH_3), 1.02 [m, 6 H, *p*-cymene CH(CH_3)$_2$] ppm. *Signals of the aromatic p-cymene protons appear as broad signals due to internal rotation of the ligand.* ^{1}H NMR (300 MHz, C_6D_6): δ = 10.08 (br. s, 1 H, O*H*) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 203.0 (N*C*N), 146.1 (*C*-OH), 139.8 (NHC aryl-C), 138.8 (NHC aryl-C), 137.4 (NHC aryl-C), 135.5 (NHC aryl-C), 130.4 (NHC aryl-C), 129.5 (NHC aryl-C), 129.2 (NHC aryl-C), 125.1 (NHC aryl-C), 121.7 (NHC aryl-C), 118.9 (NHC aryl-C), 117.7 (NHC aryl-C), 105.0 (br., *p*-cymene aryl-C), 97.3 (br., *p*-cymene aryl-C), 92.1 (br., *p*-cymene aryl-C), 82.3 (br., *p*-cymene aryl-C), 52.0 (N*C*H_2CH_2N), 49.7 (N*C*H_2CH_2N), 30.4 [*p*-cymene *C*H(CH_3)$_2$], 23.6 (*C*H_3), 21.3 (*C*H_3), 21.2 (*C*H_3), 19.8 (*C*H_3), 18.9 (*C*H_3), 18.5 (*C*H_3) ppm. $C_{28}H_{34}Cl_2N_2ORu$ (586.57): calcd. C 57.34, H 5.84, N 4.78; found C 56.62, H 5.79, N 4.54.

Cationic NHC-arene Complex 9: Silver triflate (0.049 g, 0.19 mmol) was added to a solution of **8** (0.109 g, 0.19 mmol) in CH_2Cl_2 (5 mL). The reaction mixture was stirred for 15 min at room temperature. The solution was filtered to remove AgCl, and the solvent was evaporated to almost complete dryness. The addition of hexane (10 mL) led to precipitation of the desired cationic complex as a bright orange solid, which was filtered off and dried in vacuo. Yield: 0.13 g, 96%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.51 (d, J = 5.1 Hz, 1 H, aryl C*H*), 7.08 (s, 1 H, aryl C*H*), 7.02 (m, 4 H), 5.75 (br. s, 2 H, *p*-cymene aryl-*H*), 5.43 (br. s, 2 H, *p*-cymene aryl-*H*), 4.53 (m, 1 H, NCH_2CH_2N), 4.28 (m, 1 H, NCH_2CH_2N), 4.09 (m, 2 H, NCH_2CH_2N), 2.59 (s, 3 H, mesityl CH_3), 2.47 [m, 1 H, *p*-cymene C*H*(CH_3)$_2$], 2.36 (s, 3 H, mesityl CH_3), 2.33 (s, 3 H, mesityl CH_3), 1.63 (s, 3 H, *p*-cymene CH_3), 0.95 [m, 6 H, *p*-cymene CH(CH_3)$_2$] ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 204.4 (N*C*N), 144.2 (*C*-OH), 139.9 (NHC aryl-C),138.8 (NHC aryl-C), 136.8 (NHC aryl-C), 135.5 (NHC aryl-C), 130.6 (NHC aryl-C), 129.4 (NHC aryl-C), 129.0 (NHC aryl-C), 125.7 (NHC aryl-C), 123.5 (NHC aryl-C), 118.4 (NHC aryl-C), 117.8 (NHC aryl-C), 91.8 (br., *p*-cymene aryl-C), 83.2 (br., *p*-cymene aryl-C), 52.1 (N*C*H_2CH_2N), 49.6 (N*C*H_2CH_2N), 30.6 [*p*-cymene *C*H(CH_3)$_2$], 23.0 (*C*H_3), 21.2 (*C*H_3), 21.1 (*C*H_3), 19.9 (*C*H_3), 18.7 (*C*H_3), 18.2 (*C*H_3) ppm.

NHC-Arene Complex 10: In an analogous procedure as for complex **7**, 1-mesityl-3-(2-hydroxy-6-methylphenyl)-4,5-dihydroimidazolium chloride (0.284 g, 0.86 mmol), KHMDS (0.5 M in toluene, 3.43 mL) and Ru dimer **2** (0.25 g, 0.41 mmol) afforded complex **10** as an orange-red solid. Yield: 0.15 g, 32%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.02 (m, 2 H, aryl C*H*), 6.84 (t, J = 6.9 Hz, 1 H, aryl C*H*), 6.73 (d, J = 7.3 Hz, 1 H, aryl C*H*), 6.46 (m, 1 H, aryl C*H*), 5.56 (d, J = 6.3 Hz, 1 H, *p*-cymene aryl-*H*), 5.29 (br. s, 1 H, *p*-cymene aryl-*H*), 5.11 (d, J = 5.0 Hz, 1 H, *p*-cymene aryl-*H*), 4.43 (pseudo q, J = 10.5 Hz, 1 H, NCH_2CH_2N), 4.18 (pseudo q, J = 10.1 Hz, 1 H, NCH_2CH_2N), 4.04–3.92 (m, 2 H, NCH_2CH_2N), 3.71 (br. s, 1 H, *p*-cymene aryl-*H*), 2.53 (s, 3 H, mesityl CH_3), 2.45 (s, 6 H, 2-hydroxy-6-methylphenyl and mesityl CH_3), 2.41 [m, 1 H, *p*-cymene C*H*(CH_3)$_2$], 2.36 (s, 3 H, mesityl CH_3), 1.61 (s, 3 H, *p*-cymene CH_3), 0.98 [d, J = 7.0 Hz, 3 H, *p*-cymene CH(CH_3)$_2$], 0.85 [d, J = 6.8 Hz, 3 H, *p*-cymene CH(CH_3)$_2$] ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 201.5 (N*C*N), 156.1 (*C*-OH), 138.6 (NHC aryl-C), 137.8 (NHC aryl-C), 136.8 (NHC aryl-C), 134.9 (NHC aryl-C), 129.5 (NHC aryl-C), 129.2 (NHC aryl-C), 127.5 (NHC aryl-C), 123.8 (NHC aryl-C), 120.0 (NHC aryl-C), 114.9 (NHC aryl-C), 112.6 (NHC aryl-C), 99.5 (br., *p*-cymene aryl-C), 97.6 (*p*-cymene aryl-C), 93.9 (br., *p*-cymene aryl-C), 91.9 (*p*-cymene aryl-C), 82.4 (br., *p*-cymene aryl-C), 78.0 (*p*-cymene aryl-C), 49.8 (N*C*H_2CH_2N), 47.4 (N*C*H_2CH_2N), 28.9 [*p*-cymene *C*H(CH_3)$_2$], 22.1 (*C*H_3), 20.0 (*C*H_3), 19.8 (*C*H_3), 18.6 (*C*H_3), 17.3 (*C*H_3), 16.9 (*C*H_3) ppm. $C_{29}H_{35}ClN_2ORu$ (564.14): calcd. C 61.74, H 6.25, N 4.97; found C 61.48, H 6.12, N 4.56.

NHC-Arene Complex 11: Analogous to **8**, complex **11** was obtained as an orange solid in good yield (83%). Characterisation through ^{1}H NMR spectroscopy was troublesome as the aromatic *p*-cymene protons and the backbone protons on the NHC appeared as very broad signals due to internal rotation of the ligands. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.19 (m, 1 H, aryl C*H*), 7.07 (br. s, 1 H, aryl C*H*), 7.03 (s, 1 H, aryl C*H*), 6.88 (m, 1 H, aryl C*H*), 6.58 (m, 2 H, aryl C*H*), 5.49–5.36 and 5.19 (br. signals, 4 H, *p*-cymene aryl-*H*), 4.26–3.92 (br. m, 4 H, NCH_2CH_2N), 2.69–0.88 (several signals) ppm. ^{1}H NMR (300 MHz, C_6D_6): δ = 10.14 (br. s, 1 H, O*H*) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 202.2 (N*C*N), 151.2 (*C*-OH), 138.2 (NHC aryl-C), 136.5 (NHC aryl-C), 134.9 (NHC aryl-C), 131.1 (NHC aryl-C), 129.4 (NHC aryl-C), 128.2 (NHC aryl-C), 124.3 (NHC aryl-C), 119.4 (NHC aryl-C), 118.1 (NHC aryl-C), 116.9 (NHC aryl-C), 98.1 (br., *p*-cymene aryl-C), 95.0 (br., *p*-cymene aryl-C), 93.4 (br., *p*-cymene aryl-C), 80.9 (br., *p*-cymene aryl-C), 53.8 (br., N*C*H_2CH_2N), 29.3 [*p*-cymene *C*H(CH_3)$_2$], 22.4 (*C*H_3), 21.7 (*C*H_3), 21.0 (*C*H_3), 20.4 (*C*H_3), 19.6 (*C*H_3), 19.1 (*C*H_3) ppm.

Catalytic Reactions

ROMP of 2-Norbornene: In a typical ROMP experiment (see Table 1), the catalyst (0.004248 mmol) in CH_2Cl_2 (0.5 mL) was transferred into a 15-mL vessel followed by the addition of 2-norbornene (1 g, 2500 equiv.) and toluene (10 mL). The reaction was then stirred at 85 °C for 3 h. To stop the polymerisation, a 2-ethyl vinyl ether/BHT(2,6-di-*tert*-butyl-4-methylphenol) solution in $CHCl_3$ was added. The reaction mixture was then poured into MeOH (50 mL) to precipitate the polymer. The polymer was isolated upon filtration and analysed gravimetrically by ^{1}H NMR spectroscopy and GPC (gel permeation chromatography).

CCDC-652147 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

The authors gratefully acknowledge the FWO-Flanders and the research Fund of Ghent University for generous financial support during the preparation of this manuscript. We wish to thank Olivier F. Grenelle and Dr. Marc G. Proot of Chevron Technology, Ghent, for elemental analyses and *dr* determination and Anthony Linden of the Institute of Organic Chemistry, University of Zürich, for collecting the crystallographic data set.

[1] R. H. Grubbs, *Tetrahedron* **2004**, *60*, 7117–7140.
[2] A. Fürstner, *Angew. Chem. Int. Ed.* **2000**, *39*, 3012–3043.
[3] M. Schuster, S. Blechert, *Angew. Chem. Int. Ed.* **1997**, *36*, 2036–2056.
[4] R. H. Grubbs, *Adv. Synth. Catal.* **2007**, *349*, 34–40.
[5] K. J. Ivin, J. C. Mol, *Olefin Metathesis and Metathesis Polymerizations*, Academic, San Diego, **1997**.
[6] R. H. Grubbs, *Handbook of Metathesis*, Wiley-VCH, Weinheim, **2003**.

[7] S. J. Connon, S. Blechert, *Angew. Chem. Int. Ed.* **2003**, *42*, 1900–1923.
[8] A. K. Chatterjee, T.-L. Choi, D. P. Sanders, R. H. Grubbs, *J. Am. Chem. Soc.* **2003**, *125*, 11360–11370.
[9] R. H. Grubbs, S. J. Miller, G. C. Fu, *Acc. Chem. Res.* **1995**, *28*, 446–452.
[10] C. W. Bielawski, R. H. Grubbs, *Prog. Polym. Sci.* **2007**, *32*, 1–29.
[11] J. E. Schwendeman, A. C. Church, K. B. Wagener, *Adv. Synth. Catal.* **2002**, *344*, 597–613.
[12] E. L. Dias, S. T. Nguyen, R. H. Grubbs, *J. Am. Chem. Soc.* **1997**, *119*, 3887–3897.
[13] S. F. Vyboishchikov, M. Bühl, W. Thiel, *Chem. Eur. J.* **2002**, *8*, 3962–3975.
[14] S. Fomine, S. M. Vargas, M. A. Tlenkopatchev, *Organometallics* **2003**, *22*, 93–99.
[15] F. Bernardi, A. Bottoni, G. P. Miscione, *Organometallics* **2003**, *22*, 940–947.
[16] W. J. van Rensburg, P. J. Steynberg, W. H. Meyer, M. M. Kirk, G. S. Forman, *J. Am. Chem. Soc.* **2004**, *126*, 14332–14333.
[17] C. Adlhart, P. Chen, *J. Am. Chem. Soc.* **2004**, *126*, 3496–3510.
[18] M. Jordaan, P. van Helden, C. G. C. E. Sittert, H. C. M. Vosloo, *J. Mol. Catal. A* **2006**, *254*, 145–154.
[19] L. Cavallo, *J. Am. Chem. Soc.* **2002**, *124*, 8965–8973.
[20] B. F. Straub, *Adv. Synth. Catal.* **2007**, *349*, 204–214.
[21] M. Ulman, R. H. Grubbs, *Organometallics* **1998**, *17*, 2484–2489.
[22] M. S. Sanford, J. Love, R. H. Grubbs, *J. Am. Chem. Soc.* **2001**, *123*, 6543–6554.
[23] M. S. Sanford, M. Ulman, R. H. Grubbs, *J. Am. Chem. Soc.* **2001**, *123*, 749–750.
[24] B. F. Straub, *Angew. Chem. Int. Ed.* **2005**, *44*, 5974–5978.
[25] M. A. O. Volland, C. Adlhart, C. A. Kiener, P. Chen, P. Hofmann, *Chem. Eur. J.* **2001**, *7*, 4621–4632.
[26] P. E. Romero, W. E. Piers, *J. Am. Chem. Soc.* **2005**, *127*, 5032–5033.
[27] C. Adlhart, C. Hinderling, H. Baumann, P. Chen, *J. Am. Chem. Soc.* **2000**, *122*, 8204–8214.
[28] A. G. Wenzel, R. H. Grubbs, *J. Am. Chem. Soc.* **2006**, *128*, 16048–16049.
[29] A. Correa, L. Cavallo, *J. Am. Chem. Soc.* **2006**, *128*, 13352–13353.
[30] P. E. Romero, W. E. Piers, *J. Am. Chem. Soc.* **2007**, *129*, 1698–1704.
[31] M. Scholl, T. M. Trnka, J. P. Morgan, R. H. Grubbs, *Tetrahedron Lett.* **1999**, *40*, 2247–2250.
[32] J. Huang, E. D. Stevens, S. P. Nolan, J. L. Peterson, *J. Am. Chem. Soc.* **1999**, *121*, 2674–2678.
[33] P. Schwab, R. H. Grubbs, J. W. Ziller, *J. Am. Chem. Soc.* **1996**, *118*, 100–110.
[34] K. J. Harlow, A. F. Hill, J. D. E. T. Wilton-Eley, *J. Chem. Soc. Dalton Trans.* **1999**, 285–291.
[35] A. Fürstner, M. Liebl, C. W. Lehmann, M. Picquet, R. Kunz, C. Bruneau, D. Touchard, P. H. Dixneuf, *Chem. Eur. J.* **2000**, *6*, 1847–1857.
[36] M. Picquet, D. Touchard, C. Bruneau, P. H. Dixneuf, *New J. Chem.* **1999**, *23*, 141–143.
[37] A. Fürstner, M. Picquet, C. Bruneau, P. H. Dixneuf, *Chem. Commun.* **1998**, 1315–1316.
[38] L. Jafarpour, J. Huang, E. D. Stevens, S. P. Nolan, *Organometallics* **1999**, *18*, 3760–3763.
[39] L. Jafarpour, S. P. Nolan, *J. Organomet. Chem.* **2001**, *617–618*, 17–27.
[40] H. Katayama, F. Ozawa, *Coord. Chem. Rev.* **2004**, *248*, 1703–1715.
[41] H. Katayama, F. Ozawa, *Organometallics* **1998**, *17*, 5190–5196.
[42] H. Katayama, F. Ozawa, *Chem. Lett.* **1998**, 67–68.
[43] J. Louie, R. H. Grubbs, *Angew. Chem. Int. Ed.* **2001**, *40*, 247–249.
[44] I. Dragutan, V. Dragutan, *Platin. Met. Rev.* **2006**, *50*, 81–94.
[45] L. Delaude, A. Demonceau, A. F. Noels, *Chem. Commun.* **2001**, 986–987.
[46] L. Delaude, M. Szypa, A. Demonceau, A. F. Noels, *Adv. Synth. Catal.* **2002**, *344*, 749–756.
[47] C. Lo, R. Cariou, C. Fischmeister, P. H. Dixneuf, *Adv. Synth. Catal.* **2007**, *349*, 546–550.
[48] A. W. Waltman, R. H. Grubbs, *Organometallics* **2004**, *23*, 3105–3107.
[49] A. Demonceau, A. W. Stumpf, E. Saive, A. F. Noels, *Macromolecules* **1997**, *30*, 3127–3136.
[50] T. Karlen, A. Ludi, A. Mühlebach, P. Bernhard, C. Pharisa, *J. Polym. Sci. Part A: Polym. Chem.* **1995**, *33*, 1665–1674.
[51] A. Hafner, A. Mühlebach, P. A. van der Schaaf, *Angew. Chem. Int. Ed.* **1997**, *360*, 2121–2124.
[52] A. Fürstner, L. Ackermann, *Chem. Commun.* **1999**, 95–96.
[53] C. W. Bielawski, D. Benitez, T. Morita, R. H. Grubbs, *Macromolecules* **2001**, *34*, 8610–8618.
[54] R. Castarlenas, D. Sémeril, A. F. Noels, A. Demonceau, P. H. Dixneuf, *J. Organomet. Chem.* **2002**, *663*, 235–238.
[55] L. Delaude, A. Demonceau, A. F. Noels, *Chem. Commun.* **2001**, 986–987.
[56] P. B. Hitchcock, M. F. Lappert, P. L. Pye, S. Thomas, *J. Chem. Soc. Dalton Trans.* **1979**, 1929–1942.
[57] T. M. Trnka, J. P. Morgan, M. S. Sanford, T. E. Wilhelm, M. Scholl, T.-L. Choi, S. Ding, M. W. Day, R. H. Grubbs, *J. Am. Chem. Soc.* **2003**, *125*, 2546–2558.
[58] S. H. Hong, A. Chlenov, M. W. Day, R. H. Grubbs, *Angew. Chem. Int. Ed.* **2007**, *46*, 5148–5151.
[59] M. A. Bennett, T. N. Huang, T. W. Matheson, A. K. Smith, *Inorg. Synth.* **1985**, *21*, 75.
[60] H. Türkmen, B. Cetinkaya, *J. Organomet. Chem.* **2006**, *691*, 3749–3759.

Received: June 27, 2007
Published Online: October 19, 2007

