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N,N'-Dialkyl- and *N*-Alkyl-*N*-mesityl-Substituted *N*-Heterocyclic Carbenes as Ligands in Grubbs Catalysts

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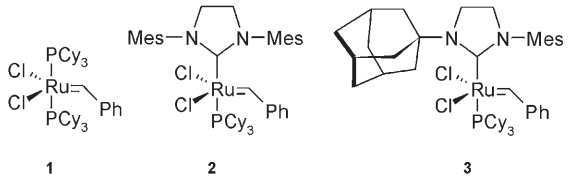
Abstract: Various symmetrically and asymmetrically substituted *N*-heterocyclic carbene (NHC) ligands bearing aliphatic nitrogen-containing side groups have been synthesised. In our attempts to isolate the corresponding second-generation Grubbs catalysts, we were unsuccessful when using the symmetrical aliphatic NHC ligands. For the asymmetrical ligands bearing an aliphatic moiety on one side and an aromatic mesityl group on the other side, substitution of a phosphine ligand was achieved. The performance of a so-formed series of Ru-based metathesis initiators has been evaluated for the ring-opening metathesis polymerisation (ROMP) of cycloocta-1,5-diene and the ring-closing metathesis (RCM) of diethyl diallylmalonate.

Keywords: carbene ligands · metathesis · ruthenium

Introduction

Olefin metathesis has evolved towards a powerful tool for the formation of carbon–carbon bonds, resulting in the recent Nobel Prize awarding of Y. Chauvin, R. R. Schrock and R. H. Grubbs, who made groundbreaking contributions to the development of olefin metathesis reactions and introduced a large number of catalytic initiators.[1,2] The intensive research effort has culminated in the discovery of well-defined ruthenium–carbene catalysts, such as the Grubbs first-generation catalyst **1**.[3] An important breakthrough in catalyst design was the substitution of one phosphine ligand by a bulky *N*-heterocyclic carbene (NHC) ligand, leading to increased activity and stability. The H_2IMes-substituted (H_2IMes = 1,3-bis-(mesityl)-4,5-dihydroimidazol-2-ylidene) complex **2** is nowadays widely known as the Grubbs second-generation catalyst.[4]



1 **2** **3**

In spite of their booming success, variation of NHC ligands has remained rather unexplored for Grubbs second-generation type catalysts, while it is evident that this variation could have a significant influence on the catalytic activity and selectivity.[5] Symmetrical dihydro NHC ligands seem to be limited to aromatic N-substituents (e.g., mesityl,[4] 2,6-diisopropylphenyl[6]). Aiming at further improvement of the application profile of Grubbs second-generation catalysts, we decided to pursue the coordination of dihydro NHC ligands bearing aliphatic groups with different steric bulk. However, a previous attempt towards coordination of an aliphatic NHC ligand by Mol et al. was not promising. They described the synthesis of 1,3-di(1-adamantyl)-4,5-dihydroimidazolinium chloride [H_2IAd(H)][Cl] and the unsymmetrical 1-(1-adamantyl)-3-mesityl-4,5-dihydroimidazolinium chloride [H_2IAdMes(H)][Cl].[7] It should be noted that only H_2IAdMes reacted in a favourable manner to give its second-generation analogue **3**. Failure of the reaction with H_2IAd was assigned to the bulkiness of the adamantyl moiety which could not take place directly over the benzylidene unit. The X-ray structure of **3** showed that the only isomer formed had the mesityl group above the benzylidene moiety. Surprisingly, complex **3** displayed only negligible metathesis activity, which was ascribed to steric blocking.

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Supporting information for this article is available on the WWW under http://www.chemeurj.org/ or from the author. The Supporting Information contains further synthetic details for all NHC precursors.

We were hoping that a reduced bulkiness of the N-substituents would allow easier NHC coordination and have a positive effect on the metathesis activity of the resulting catalysts. Higher electron density at the carbenic centre of saturated NHCs compared to their unsaturated analogues[8] in combination with even further enhancement of this electron donation caused by alkyl N-substituents[9] would allow an increase in catalyst activity. However this constitutes a subject of discussion, since Nolan et al. reported unexpected weaker Pd–C(NHC) bonds for electron-donating alkyl-substituted NHCs.[10] Even more noteworthy was their study of the CO stretching frequencies in $[Ni(CO)_3(NHC)]$ complexes.[11] Alkyl-substituted NHCs were found to be only marginally more electron donating than aryl-substituted ones. Furthermore saturated NHCs turned out slightly less electron donating than their unsaturated counterparts; this result is not in line with the common assumption that metal complexes bearing a saturated NHC perform better in catalytic reactions because of a higher electron donation. This demonstrates that considering only ligand basicity would be an oversimplification of the metal–NHC bonding properties.[12] In this respect, it is worth mentioning that Plenio et al. recently concluded from cyclic voltammetry experiments that the donor properties of aryl-substituted NHC ligands are characterised by σ-donation from the carbene carbon atom *and* by transfer of electron density between the aromatic NHC side groups and the Ru=CHPh unit.[13] It should also be noted that there is so far no straightforward explanation for the enhanced reactivity of Grubbs second-generation catalysts, although a lot of research is ongoing in this particular area.[14]

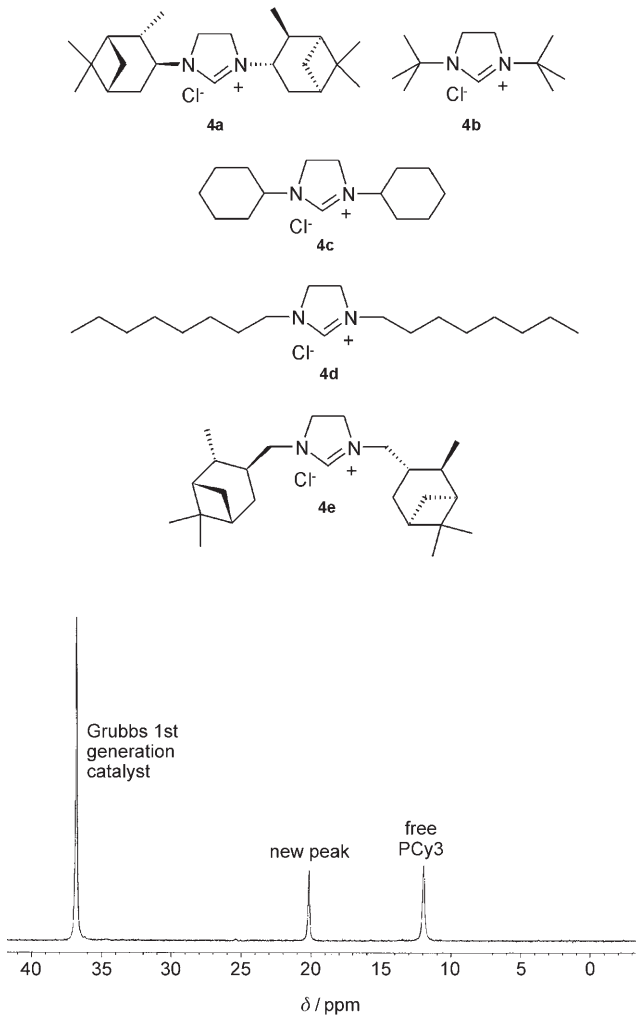


Figure 1. ^{31}P spectrum showing partial reaction of **1** with ligand **4a**.

Results and Discussion

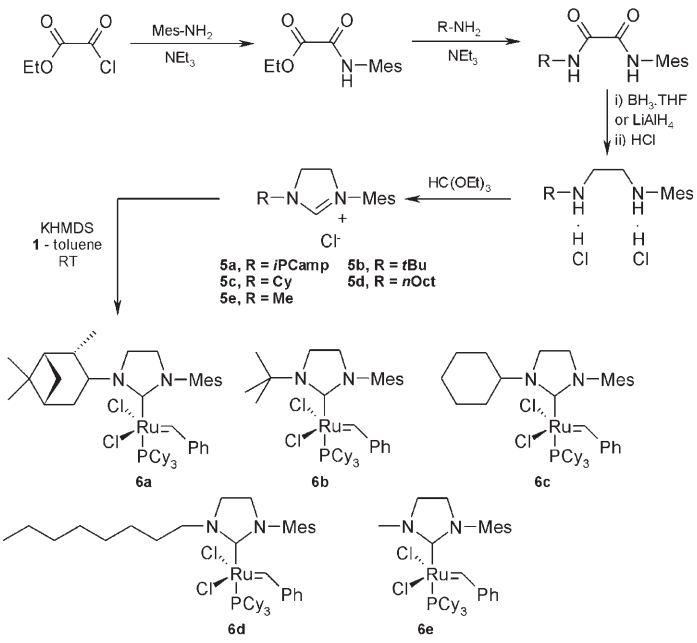
The synthesised NHC precursors include 1,3-diisopinocampheyl-4,5-dihydroimidazolinium chloride (**4a**), 1,3-di-*tert*-butyl-4,5-dihydroimidazolinium chloride (**4b**), 1,3-dicyclohexyl-4,5-dihydroimidazolinium chloride (**4c**), 1,3-di-*n*-octyl-4,5-dihydroimidazolinium chloride (**4d**) and the pinane-based imidazolinium chloride **4e**. Ligands **4a** and **4e** could induce some enantioselectivity,[15] which might be driven to a higher extent by modification of the pinane-derived moiety. As a base to deprotonate the imidazolium chloride, we used potassium bis(trimethylsilyl)amide (KHMDS). This base liberates the free carbene at room temperature and its steric bulk is high enough to prevent fast reaction with Grubbs catalyst **1**.[16]

Reaction of one equivalent of **4a** with one equivalent of base and **1** in dry toluene did not allow substitution of the phosphine, even when the reaction mixture was heated or stirred for several hours. An excess of NHC ligand (1.5 equiv) led to the observation of a new benzylidene α-proton at $\delta = 20.61$ ppm with a conversion of approximately 25%. The ^{31}P NMR spectrum showed a new signal at $\delta = 20.14$ ppm as well as a signal corresponding to free PCy_3 (Figure 1). This was assigned to NHC coordination. However, the downfield shift of the benzylidene signal surprised us, since generally for Grubbs second-generation complexes this peak is situated more upfield. The addition of more than a twofold excess of ligand allowed full conversion, but at this point difficulties to remove the ligand excess and free phosphine arose. Effort to isolate pure compound by precipitation remained unsuccessful due to high solubility in all common organic solvents. The complex decomposed upon chromatography on silica gel.

Several attempts to exchange one phosphine with H_2ItBu **4b**, applying an excess of ligand as well as prolonged reaction times, were unsuccessful. Hahn et al. recently reported the synthesis of a H_2ItBu substituted rhodium(I) complex, which showed low stability in solution. This was rationalised by the steric demand of the *N-tert*-butyl substituents, resulting in a weak bond between the metal and the carbene carbon atom.[17] Likewise we assume to have encountered steric obstruction, and we decided to synthesise **4c**–**4e**, hoping that their different geometry would allow coordination. Our endeavour involving ligand precursor **4c** led to the observation of a new ^1H benzylidene resonance at $\delta =$

20.28 ppm, and a new ^{31}P signal at $\delta = 27.49$ ppm. The ^{13}C NMR spectrum of the crude mixture showed a small doublet at $\delta = 210.2$ ppm, which corresponds to the NHC carbene carbon atom coordinated to ruthenium. Various attempts were undertaken to achieve isolation in order to get full characterisation, but the new complex was found to be too unstable. Reaction involving **4e** gave rise to a new small ^1H peak at $\delta = 20.08$ ppm; this is a little downfield to the original benzylidene signal. Efforts to obtain full conversion of **1** by applying longer reaction times led to decomposition of most of the catalytic species, which made it impossible to obtain pure product. Also ligand **4d** derived from a primary amine, did not allow the isolation of a NHC-substituted complex and induced decomposition of the catalytic system.

Given these observations, we decided to synthesise the unsymmetrical analogues of our NHC precursors, that is, 1-mesityl-3-isopinocampheyl-4,5-dihydroimidazolium chloride (**5a**), 1-mesityl-3-*tert*-butyl-4,5-dihydroimidazolium chloride (**5b**), 1-mesityl-3-cyclohexyl-4,5-dihydroimidazolium chloride (**5c**), 1-mesityl-3-*n*-octyl-4,5-dihydroimidazolium chloride (**5d**) and 1-mesityl-3-methyl-4,5-dihydroimidazolium chloride (**5e**), and to react them with **1**. Preparation of these NHCs was straightforward following a synthetic pathway described by Grubbs et al.[18] Condensation of ethyl chlorooxoacetate and 2,4,6-trimethylaniline affords the desired oxanilic ethylester, which is then treated with the aliphatic amine to provide the corresponding oxalamide. Reduction and subsequent addition of HCl results in the dihydrochloride salt, which undergoes cyclisation to the desired 4,5-dihydroimidazolium chloride in reaction with triethyl orthoformate. Exposure of the Grubbs catalyst **1** to these asymmetrically substituted NHC precursors and KHMDS as a base afforded the complexes **6a**–**6e** under mild reaction conditions (Scheme 1)



Scheme 1. Synthetic pathway towards complexes **6a**–**6e**.

Compared to the unsymmetrical ligands bearing one mesityl moiety, the symmetrical ligands **4a**–**4e** were much more difficult to coordinate to the Grubbs parent complex **1**. We observed coordination of ligands **4a, 4c** and **4e**, but ligand excesses were required and the so-formed complexes showed limited stability, which prevented their isolation. Therefore, we assume that π interactions between the benzylidene and the amino side group might be of significant importance. This is confirmed by the observation that the carbene derived from **5c** coordinates in such a way that the mesityl group is oriented towards the benzylidene moiety (single-crystal X-ray analysis of complex **6c**: Figure 2,

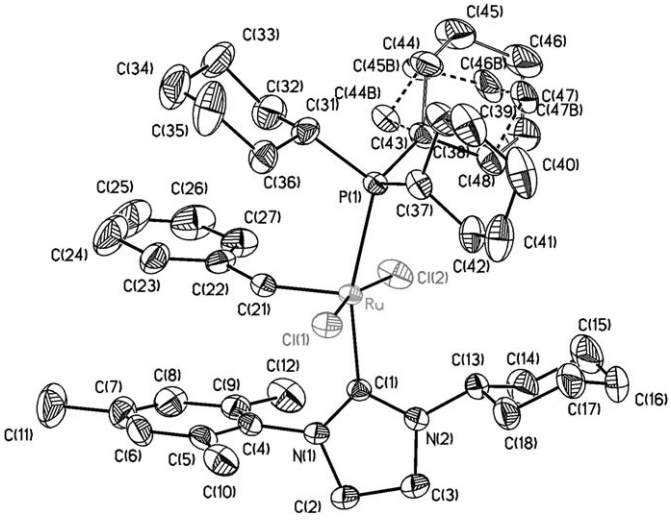


Figure 2. ORTEP diagram of **6c**. For clarity hydrogen atoms have been omitted.

Table 1) Both aromatic rings are nearly coplanar, allowing π–π interactions. The observation that intramolecular π–π stacking between the benzylidene carbene unit and the *N*-aryl substituents on the NHC residue might constitute a strong structural element in second-generation metathesis

Table 1. Selected bond lengths [Å] and angles [°] and sructural comparison of **6c, 2** and **3**.

	6c[a]	**2**[b]	**3**[c]
Ru=C	1.830(6)	1.835(2)	1.851(5)
Ru–CNN	2.060(5)	2.085(2)	2.083(5)
Ru–Cl(1)	2.419(3)	2.3988(5)	2.427(1)
Ru–Cl(2)	2.376(3)	2.3912(5)	2.398(1)
Ru–P	2.481(3)	2.4245(5)	2.521(1)
Cl–Ru–Cl	167.73(6)	167.71(2)	167.98(5)
N_2C–Ru–P	162.42(14)	163.73(6)	171.1(1)
N_2C–Ru=C	98.9(2)	100.24(8)	96.9(2)
P–Ru=C	98.63(18)	95.98(6)	91.5(2)
N_2C–Ru–Cl(1)	85.58(15)	83.26(5)	84.7(1)
N_2C–Ru–Cl(2)	89.18(16)	94.55(5)	88.1(1)
Ru=C–Ph	137.2(4)	136.98(16)	137.0(4)

[a] This work. [b] Reference [20]. [c] Reference [7].

catalysts was previously reported by Fürstner et al. for *unsaturated* NHC entities.[5,19]

In contrast to the Mol's complex **3**, most of our complexes showed nice olefin metathesis activities. Their catalytic performance in the ring-opening metathesis polymerisation (ROMP) of cycloocta-1,5-diene (COD) was compared with the reactivity of Grubbs catalysts **1** and **2**, using different solvents and monomer/catalyst ratios (Figures 3 and 4). Coordination of the NHC ligand led to a positive effect on the ROMP actvity for complexes **2, 6a, 6c, 6d** and **6e**. In contrast, for complexes **3** and **6b**, NHC coordination induced activity loss. These last two complexes required heating and low COD/catalyst ratio in order to obtain high conversion. (Table 2, entries 14 and 15)

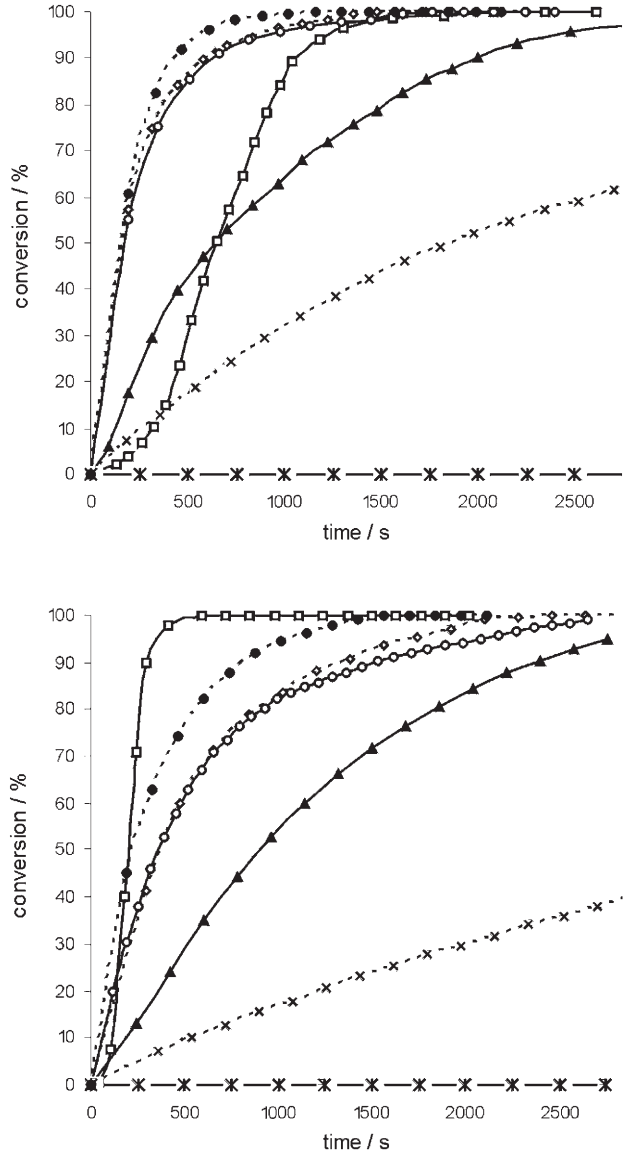


Figure 3. Monitoring ROMP of COD by ^{1}H NMR spectroscopy (20 °C). Conditions: monomer/catalyst = 300, catalyst concentration = 4.52 mM. Top: solvent = $CDCl_3$. Bottom: solvent = C_6D_6. **1**: ×; **2**: □; **6a**: ◇; **6b**: *; **6c**: ▲; **6d**: ○; **6e**: ●.

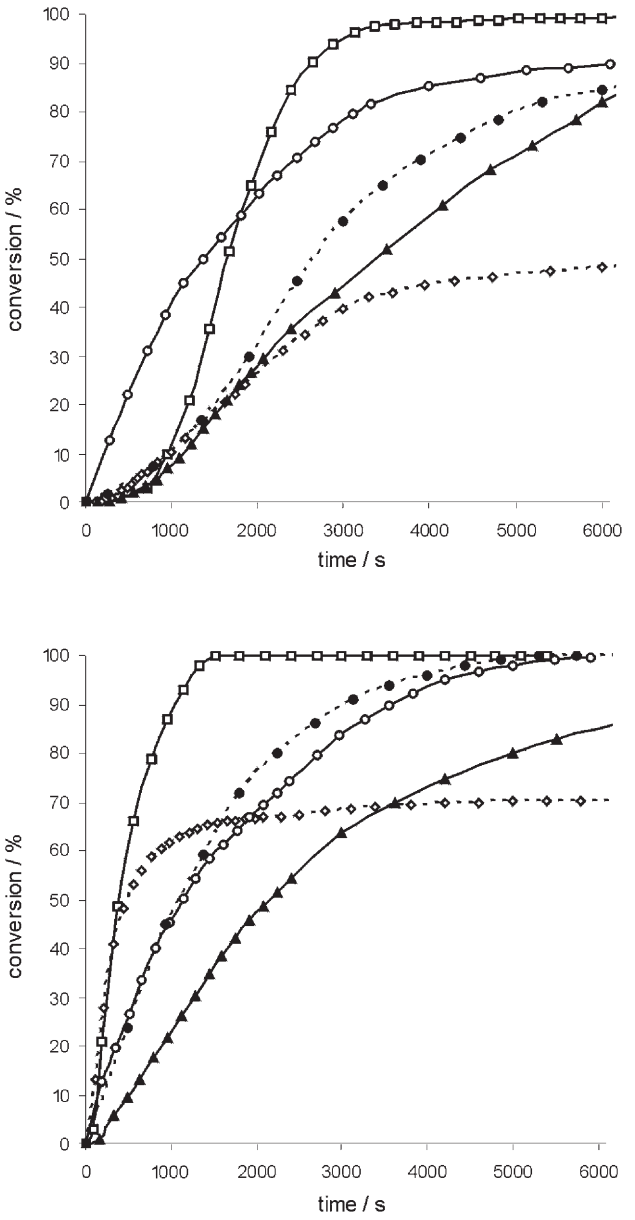


Figure 4. Monitoring ROMP of COD by ^{1}H NMR spectroscopy (20 °C). Conditions: monomer/catalyst = 3000, catalyst concentration = 0.452 mM. Top: solvent = $CDCl_3$. Bottom: solvent = C_6D_6. **2**: □; **6a**: ◇; **6c**: ▲; **6d**: ○; **6e**: ●.

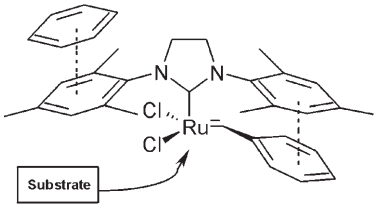
It is worth noting that the catalytic activity of complex **2** strongly depends on the solvent used, while a solvent effect is less significant for complexes **6a–6e**. The catalysts **6a, 6c, 6d** and **6e** show a slightly higher ROMP-activity in $CDCl_3$ than in C_6D_6 when a monomer/catalyst ratio of 300 is used. Their activity is somewhat higher in C_6D_6 when the monomer/catalyst ratio equals 3000, which is due to an induction period and loss of activity in the $CDCl_3$ polymerisation. Complex **2** is unambiguously more active in C_6D_6. Such an increased reactivity in aromatic solvents was also observed by Fürstner et al. for $[RuCl_2(=CHPh)(IMes)(PCy_3)]$. This was assigned to competing interactions of the *N*-mesityl

Table 2. ROMP of COD.

Entry	Catalyst	T [°C]	COD/cat.	t [min]	Conversion [%]	*cis* [%][a]
1	**1**	RT	3000	30	23	75
				60	55	71
2	**2**	RT	3000	30	100	9
3	**3**	RT	3000	30	0	–
4	**6a**	RT	3000	30	100	17
5	**6b**	RT	3000	30	0	–
6	**6c**	RT	3000	30	100	37
7	**6d**	RT	3000	30	100	51
8	**6e**	RT	3000	30	100	46
9	**2**	RT	30000	30	86	12
				[b]	100	13
10	**6a**	RT	30000	30	7	–
				[b]	30	80
11	**6c**	RT	30000	30	48	78
				[b]	71	76
12	**6d**	RT	30000	30	74	82
				[b]	94	83
13	**6e**	RT	30000	60	10	–
				120	26	80
				[b]	34	80
14	**3**	70	300	120	69	75
15	**6b**	70	300	120	72	77

[a] Percent olefin with *cis* configuration in the polymer backbone; ratio based on data from ^{1}H and ^{13}C NMR spectra (^{13}C NMR spectroscopy: $\delta = 32.9$ ppm allylic carbon *trans*; $\delta = 27.6$ ppm allylic carbon *cis*). [b] Overnight.

group with the solvent molecules, which reduce the intramolecular π–π interactions with the benzylidene moiety.[5] As mentioned earlier, we expect **6a, 6c, 6d** and **6e** to have similar π–π interactions, but when lower COD/catalyst ratios were applied, we did not observe such a *competition* effect. The increased activity of **2** in aromatic solvents might be assigned to a π–π interaction between the mesityl group that is not coplanar with the benzylidene moiety and the aromatic solvent. (Scheme 2) An alternative explanation for the



Scheme 2. Increased activity of **2** in aromatic solvents.

different response of complex **2** on the solvent change might be that a rotation of the NHC ligand allows two populations to be stabilised by π–π interactions, compared to only one for catalysts **6a**–**6e**. This would also explain its longer induction period and high reactivity after the retarding π–π stacking effect is lost. It is, however, taken for granted that for **6a**–**6e**, no rotation of the NHC ligand is possible due to the high steric demand of the *N*-alkyl substituents.

Furthermore it is evident that when high substrate/catalyst ratios are used, decomposition of the catalyst system is not negligible, leading to incomplete conversion as observed for catalyst **6a**.

^{13}C NMR spectroscopy allowed the determination of the *cis* fraction of the newly formed double bonds in the polymer chains (Table 2).[21] The *cis*/*trans* ratio can be seen as the primary microstructural characteristic, having a well-established relationship with the solid state and solution properties of the ROMP polymer.[1a] Grubbs second-generation catalyst **2** gave rise to a ROMP polymer with a predominately *trans*-olefin content, while other catalyst systems generally led to a higher *cis* value. A high *trans* content for **2** was also observed by Grubbs et al., as it could be expected for an equilibrium-controlled polymerisation in which secondary chain transfer occurs.[22] Entries 1–8 in Table 2 demonstrate that all NHC-bearing complexes (except **6b**) show a significantly higher *trans*-content than the first-generation Grubbs complex **1**. For a higher COD/catalyst ratio (entries 9–13) all catalysts but **2** show a predominately *cis*-olefin content; these results indicate that for **6a, 6c, 6d** and **6e** considerably less chain transfer occurred, probably caused by a quicker decomposition of the catalyst systems.

It's worth pointing out that complexes **6b** and **3** are both bright green complexes, while the more active complexes **2, 6a, 6c, 6d** and **6e** are all pinkish. We assume this is the result of higher steric requirements of the *tert*-butyl and adamantyl groups. These NHCs are the only ones in the series in which the first carbon atom adjacent to the amino group is bonded to three other carbon atoms. Whereas the other NHC entities can orient their side groups perpendicularly to the imidazoline plane in order to minimise steric interactions, such an orientation cannot be obtained for the adamantyl- and *tert*-butyl-bearing ligands.[11] Mol et al. reported the possibility of an interaction of a β-carbon atom of the adamantyl group with the metal centre.[7] Analogously **6b** might show a similar interaction resulting in the green colour and reduced activity of the catalyst.

The RCM activity of the new complexes was tested on the standard RCM substrate diethyl diallylmalonate. (Figure 5) A significant dependence of the reactivity on the bulkiness of the NHC entities was observed. The most crowded NHCs correspond to the lowest RCM activity, while activity increases considerably for complexes bearing less bulky NHCs. The most active catalyst system was found to be complex **6e**, bearing an NHC ligand with a small methyl amino moiety. This complex was substantially more active than the Grubbs complex **2**. It is therefore undeniable that the steric bulk of the amino side group is of great importance. (Scheme 3) During the course of our investigation, Blechert et al. preceded us with a report on the synthesis of complex **6e**. Complex **6e** was found to give a better diastereoselective RCM and significantly different *E*/*Z* ratios in cross metathesis.[23] This study constitues more evidence of the interesting characteristics of these novel metathesis ini-

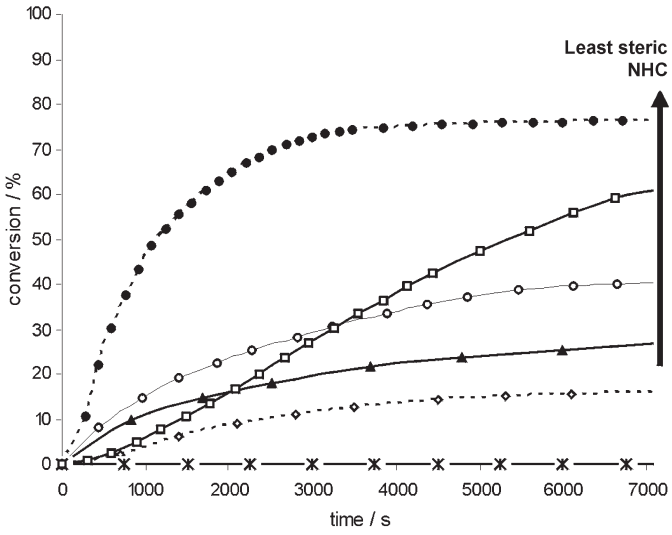
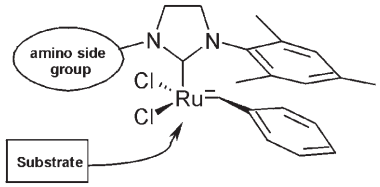


Figure 5. Monitoring RCM of diethyl diallylmalonate by ^{1}H NMR spectroscopy (20 °C). Conditions: diethyl diallylmalonate/catalyst = 200, catalyst concentration = 4.52 mM, solvent = CD_2Cl_2. **2**: □; **6a**: ◇; **6b**: *; **6c**: ▲; **6d**: ○; **6e**: ●.



Scheme 3. Importance of the steric bulk of the amino side groups.

tiators and we agree with Blechert et al. that further investigation to gain a better understanding of the selectivity effects is welcome.

Conclusion

A series of NHC ligands bearing aliphatic amino side groups were synthesised and reacted with the Grubbs first-generation catalyst. Reactions involving symmetrical NHCs did not allow us to isolate any pure NHC-substituted complexes due to their instability. Unsymmetrical NHCs with a planar mesityl group on one amino side chain reacted in a favourable manner, and the resulting complexes were stable enough to be isolated. X-ray crystallographic analysis demonstrated that the mesityl group is coplanar with the phenyl ring of the benzylidene; this result indicates that π–π interaction between the mesityl arm and the benzylidene moiety might constitute an important structural element and that this needs to be considered in future catalyst design of Grubbs second-generation analogues. Catalysts **6a, 6c, 6d** and **6e** were found to surpass the parent complex **1** for the ROMP of cycloocta-1,5-diene. Catalyst **6b**, substituted with an NHC derived from *t*Bu-NH_2 was considerably less metathesis active than the catalysts derived from amines with primary or secondary groups on the nitrogen atom. Furthermore the observation that the least steric complex **6e** is the most active for RCM, clearly demonstrates that modification of the NHC ligand can induce substantial changes in the reactivity pattern of the corresponding catalysts and that systematic variation of the N-substituents may eventually allow fine tuning.

Experimental Section

All reactions and manipulations involving organometallic compounds were conducted in oven-dried glassware under argon atmosphere using standard Schlenk techniques and dried, distilled and degassed solvents. Starting chemicals were purchased from commercial sources and used as received. ^{1}H, ^{13}C and ^{31}P NMR measurements were performed with a Varian Unity-300 spectrometer.

One-pot procedure for synthesis of complexes 3, 6a and 6c: [$RuCl_2$(=CHPh)(PCy_3)$_2$] (1 equiv), NHC chloride salt (1.5 equiv) and KHMDS (1.5 equiv, 0.5 M in toluene) were dissolved in dry toluene and stirred at room temperature for 1 h. Toluene was evaporated under vacuum and a small amount of MeOH was added under vigorous stirring. The precipitate was filtered off, washed with MeOH, and dried. The spectroscopic and analytical data of the complexes prepared by this method are compiled below.

[$RuCl_2$(=CHPh)(IAdMesH_2)(PCy_3)] (3): Bright green solid; yield: 81%; NMR data equal those described by Mol et al.[11]

[$RuCl_2$(=CHPh)(I*i*PCampMesH_2)(PCy_3)] (6a): Pink solid; yield 79%; ^{1}H NMR ($CDCl_3$): δ = 19.20 (s, 1H; Ru=C*H*Ph), 8.91 (brs, 1H; *o*-C_5H_6), 7.42 (t, 1H; *p*-C_5H_6), 7.15 (m, 2H; *m*-H), 6.64 and 5.81 (2×brs, 2H; *o*-C_5H_6 and $C_6H_2Me_3$), 5.19 (s, 1H; $C_6H_2Me_3$), 4.09 (m, 1H; N-C_a*H*), 3.76 (m, 2H; *i*PCampNCH_2CH_2NMes), 3.63 (m, 2H; *i*PCampNCH_2CH_2NMes), 2.89 (brs, 1H), 2.52–1.05 ppm (several peaks); ^{31}P NMR ($CDCl_3$): δ = 22.41 ppm; ^{13}C NMR ($CDCl_3$): δ = 297.2 (Ru=*C*HPh), 217.1 (d, *J*(P,C) = 77.0 Hz, *i*PCampN*C*NMes), 151.1 (*i*C_6H_5), 137.8, 137.3, 131.8–126.8 (several peaks), 58.6 (C_a *i*PCamp), 50.9 (*i*PCampNCH_2CH_2NMes), 48.0 (*i*PCampN*C*H_2CH_2NMes), 44.3, 41.9, 40.7, 38.7, 35.9, 35.1, 33.8, 32.8, 28.3–26.5 (several peaks), 24.2, 21.2 (*p*-Me), 18.6 ppm (*o*-Me); elemental analysis calcd (%) for $C_{47}H_{71}N_2Cl_2PRu$ (867.04): C 65.11, H 8.25, N 3.23; found: C 64.73 H 8.25 N 3.19.

[$RuCl_2$(=CHPh)(I*t*BuMesH_2)(PCy_3)] (6b): Since [I*t*BuMesH_2]Cl was found to be a sticky compound, which dissolved only slowly in toluene, it was treated with KHMDS before addition of **1**. A solution of KHMDS in toluene (0.5 M, 1.7 mL, 0.850 mmol) was added to [I*t*BuMesH_2]Cl (0.231 g, 0.823 mmol) in dry toluene (5 mL). The resulting suspension was stirred for 30 min. Complex **1** (0.34 g, 0.414 mmol) was added and the reaction mixture was stirred for another 1.5 h to reach full conversion of the Ru precursor. The solution was filtered and evaporated. Since the desired complex dissolved in MeOH and hexane, acetone was used to precipitate the catalyst. The desired complex was filtered off as a bright green powder in 56% yield. ^{1}H NMR ($CDCl_3$): δ = 19.09 (s, 1H; Ru=C*H*Ph), 9.16 (brs, 1H; *o*-C_5H_6), 7.38 (t, 1H; *p*-C_5H_6), 7.24 (m, 2H; *m*-C_6H_5), 6.95 (brs, 1H; *o*-C_6H_5), 6.71 (s, 1H; $C_6H_2Me_3$), 5.80 (s, 1H; $C_6H_2Me_3$), 3.91–3.64 (m, 4H; *t*BuNCH_2CH_2NMes), 2.42 (s, 6H; *o*-CH_3), 2.37 (s, 3H; *p*-CH_3), 2.06 (s, 9H; (CH_3)$_3$C), 2.09, 1.94, 1.90, 1.70, 1.56, 1.27, 1.10 ppm (all PCy_3 protons); ^{31}P NMR ($CDCl_3$): δ = 22.92 ppm; ^{13}C NMR ($CDCl_3$): δ = 300.3 (Ru=*C*HPh), 217.5 (d, *J*(P,C) = 77.3 Hz, *t*BuN*C*NMes), 152.4 (*i*C_6H_5), 138.2, 137.9, 137.8, 137.2, 132.7, 131.3, 129.5, 129.3, 128.8, 128.6, 127.2, 57.3 ((CH_3)$_3$*C*), 51.2 (*t*BuNCH_2CH_2NMes), 46.1 (*t*BuN*C*H_2CH_2NMes), 35.5, 33.2, 30.3, 28.9, 27.9, 27.2, 27.1, 26.7, 26.5, 21.1 (*p*-*C*H_3), 19.0, 18.6 ppm (*o*-*C*H_3); elemental analysis calcd (%) for $C_{41}H_{63}N_2Cl_2PRu$ (786.91): C 62.58, H 8.07, N 3.56; found C 62.09, H 7.77, N 3.40.

[$RuCl_2$(=CHPh)(ICyMesH_2)(PCy_3)] (6c): Pink solid; yield: 87%; ^{1}H NMR ($CDCl_3$): δ = 19.10 (s, 1H; Ru=C*H*Ph), 8.73 (brs, 1H; *o*-C_5H_6), 7.39 (t, 1H; *p*-C_5H_6), 7.12 (m, 2H; *m*-C_6H_5), 6.62 (brs, 1H; *o*-C_6H_5), 6.00

(brs, 2H; $C_6H_2Me_3$), 4.53 (m, 1H; N-C*H*), 3.89 (m, 2H; CyN-CH_2CH_2NMes), 3.72 (m, 2H; CyNC$H_2$$CH_2$NMes), 3.47 (s, 1H), 2.46 (brs, 1H), 2.22, 1.89, 1.60–1.11 ppm (several peaks); ^{31}P NMR ($CDCl_3$): $\delta = 28.13$; ^{13}C NMR ($CDCl_3$): $\delta = 295.7$ (Ru=CHPh), 215.5 (d, J(P,C) = 76.9 Hz, CyN*C*NMes), 151.2 (iC_6H_5), 137.7, 137.6, 136.7, 130.7–128.1 (several peaks), 58.2 (C_1 Cy), 50.7 (CyNCH$_2$*C*H$_2$NMes), 43.8 (CyN-*C*H$_2$CH$_2$NMes), 32.3, 31.1, 30.5, 29.4–25.0 (several peaks), 21.1 (*p*-Me), 18.7 ppm (*o*-Me); elemental analysis calcd (%) for $C_{43}H_{65}N_2Cl_2PRu$ (812.95): C 63.53, H 8.06, N 3.45; found C 63.20, H 7.99, N 3.40; single crystals suitable for X-ray analysis were grown by slow evaporation of a solution of **6c** in CH_2Cl_2 (Figure 2).

[RuCl$_2$(=CHPh)(I^{n}octMesH$_2$)(PCy$_3$)] (6d): Imidazolinium chloride **5d** (0.29 g, 0.861 mmol) was stirred with an equimolar quantity of KHMDS in toluene (0.5 M, 1.722 mL) for 15 min. Complex **1** (0.4 g, 0.487 mmol) was added and the resulting solution was allowed to stir at room temperature for 1 h, during which the mixture changed colour from purple to dark red. The solution was filtered to remove salts and the solvent was evaporated. The crude mixture was loaded onto a column of silica gel and the product was eluted by flash chromatography (9:1 hexane/Et_2O). Complex **6d** was obtained as a pure pinkish compound with 49% yield. ^{1}H NMR ($CDCl_3$): $\delta = 18.99$ (s, 1H; Ru=C*H*Ph), 7.96 (brs, 1H; *o*-C_5H_6), 7.37 (m, 1H; *p*-C_6H_5), 7.09 (m, 2H; *m*-C_6H_5), 6.88 (brs, 1H; *o*-C_6H_5), 6.86 (brs, 1H; $C_6H_2Me_3$), 6.22 (brs, 1H; $C_6H_2Me_3$), 4.17 (t, 2H; NCH_2CH_2N-CH_2), 3.89 (t, 2H; *n*-octNCH$_2$CH_2NMes), 3.74 (t, 2H; *n*-octNCH_2CH$_2$NMes), 2.27, 2.16, 1.87, 1.61, 1.30, 1.11, 0.90 ppm (57H); ^{31}P NMR ($CDCl_3$): $\delta = 32.61$ ppm; ^{13}C NMR ($CDCl_3$): $\delta = 294.5$–293.3 (br, Ru=CHPh), 217.1 (d, J(P,C) = 75.2 Hz, *n*-octN*C*NMes), 149.9 (iC_6H_5), 136.5, 136.2, 135.4, 129.4 (br), 128.4, 127.8, 127.4, 127.0, 126.8, 125.5, 49.9, 49.7 (*n*-octNCH$_2$*C*H$_2$NMes and C_1-*n*-octyl), 47.3 (*n*-octN*C*H$_2$CH$_2$NMes), 34.8, 34.0, 30.9, 30.8, 30.5, 28.8, 28.3, 27.4, 26.8, 26.7, 26.1, 25.9, 25.5, 25.4, 25.2, 24.4, 21.7 (*p*-*C*H$_3$), 19.8, 17.4 (*o*-*C*H$_3$), 13.1 ppm (C_8-*n*-octyl); elemental analysis calcd (%) for $C_{45}H_{71}N_2Cl_2PRu$ (843.02): C 64.11, H 8.49, N 3.32; found: C 63.27 H 8.38 N 3.28.

[RuCl$_2$(=CHPh)(IMeMesH$_2$)(PCy$_3$)] (6e): Imidazolinium chloride **5e** (0.091 g, 0.381 mmol) was stirred with an equimolar quantity of KHMDS in toluene (0.5 M, 0.762 mL) for 30 min. Complex **1** (0.2 g, 0.24 mmol) was added and the resulting solution was allowed to stir at room temperature for 1 h. The solution was filtered to remove salts and evaporated in vacuo. Precipitation of pure pink product was achieved by addition of hexane to a concentrated solution of the complex in CH_2Cl_2. Yield: 77%; ^{1}H NMR ($CDCl_3$): $\delta = 18.89$ (s, 1H; Ru=C*H*Ph), 7.81 (brs, 1H; *o*-C_5H_6), 7.37 (t, 1H; *p*-C_6H_5), 7.10 (m, 2H; *m*-C_6H_5), 6.90 (s, 1H; *o*-C_6H_5), 6.82 (brs, 1H; $C_6H_2Me_3$), 6.28 (brs, 1H; $C_6H_2Me_3$), 3.95 (m, 2H; MeNCH$_2$CH_2NMes), 3.82 (s, 3H; NCH_3), 3.49 (m, 2H; MeNCH_2CH$_2$NMes), 2.32, 2.17, 1.89, 1.61, 1.27, 1.12, 0.88 ppm; ^{31}P NMR ($CDCl_3$): $\delta = 34.92$ ppm; ^{13}C NMR ($CDCl_3$): $\delta = 294.3$–239.4 (br, Ru=CHPh), 219.4 (d, J(P,C) = 74.4 Hz, MeN*C*NMes), 151.0 (iC_6H_5), 137.8, 137.2, 136.5, 130.5, 130.0 (br), 129.0, 128.3, 127.9, 52.4 (MeNCH$_2$*C*H$_2$NMes), 51.4 (MeN*C*H$_2$CH$_2$NMes), 37.6, 35.9, 35.1, 31.7, 31.5, 31.4, 30.6, 30.1, 29.6, 28.0, 27.1, 26.8, 22.8, 21.1 (*p*-*C*H$_3$), 18.4 ppm (*o*-*C*H$_3$); elemental analysis calcd (%) for $C_{38}H_{57}N_2Cl_2PRu$ (744.83): C 61.28, H 7.71, N 3.76; found C 60.98, H 7.55, N 3.60.

Note: For all of these complexes only one ^{31}P signal and one single ^{1}H α-benzylidene signal were found, suggesting that only one single isomer had been formed.

Monitoring ROMP of COD (Figures 3 and 4): After charging an NMR tube with the appropriate amount of catalyst dissolved in dry, deuterated solvent ($CDCl_3$ or C_6D_6), COD was injected into the tube. The polymerisation reaction was monitored as a function of time at 20°C by integrating olefinic ^{1}H signals of the formed polymer and the disappearing monomer.

Monitoring RCM of diethyl diallylmalonate (Figure 5): An NMR tube was charged with of a solution of the catalyst in CD_2Cl_2 (0.6 mL; 4.52 mM or 0.002712 mmol catalyst). Diethyl diallylmalonate (200 equiv or 0.13 mL) was added and the NMR tube was closed. The ethylene generated during the reaction process was not removed so that the RCM reactions were carried out under equilibrium conditions. The progress of the ring-closing reaction was monitored at 20°C by integration of ^{1}H signals of allylic protons of the ring-closed product and of the disappearing substrate.

Representative procedure for ROMP tests (Table 2): Small oven-dried glass vials with septum were charged with a stirring bar and the appropriate amount of catalyst taken from a CH_2Cl_2 stock solution. The dichloromethane was subsequently evaporated, and the glass vials with solid catalyst were kept under argon atmosphere. To start the ROMP test, toluene (200 μL) was added in order to dissolve the catalyst. The appropriate amount of COD monomer was then transferred to the vial by syringe under vigorous stirring at room temperature for **2, 6a, 6c, 6d** and **6e** and at 70°C for **3** and **6b**. After a certain time span, a small quantity of the reaction mixture, which had become viscous, was taken out of the vial and dissolved in $CDCl_3$. Conversion was then determined by ^{1}H NMR spectroscopy.

CCDC-295190 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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