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[(NHC)(NHC$_{ewg}$)RuCl$_2$(CHPh)] Complexes with Modified NHC$_{ewg}$ Ligands for Efficient Ring-Closing Metathesis Leading to Tetrasubstituted Olefins**

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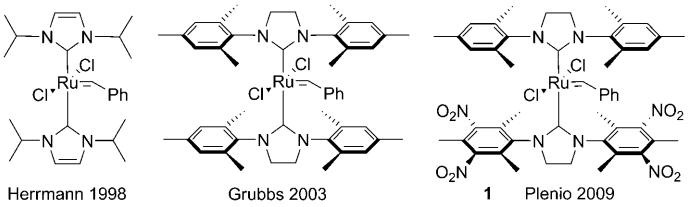
Abstract: Imidazolium salts (NHC$_{ewg}$·HCl) with electronically variable substituents in the 4,5-position (H,H or Cl,Cl or H,NO$_2$ or CN,CN) and sterically variable substituents in the 1,3-position (Me,Me or Et,Et or *i*Pr,*i*Pr or Me,*i*Pr) were synthesized and converted into the respective [AgI(NHC)$_{ewg}$] complexes. The reactions of [(NHC)RuCl$_2$(CHPh)(py)$_2$] with the [AgI(NHC$_{ewg}$)] complexes provide the respective [(NHC)(NHC$_{ewg}$)RuCl$_2$(CHPh)] complexes in excellent yields. The catalytic activity of such complexes in ring-closing metathesis (RCM) reactions leading to tetrasubstituted olefins was studied. To obtain quantitative substrate conversion, catalyst loadings of 0.2–0.5 mol% at 80 °C in toluene are sufficient. The complex with the best catalytic activity in such RCM reactions and the fastest initiation rate has an NHC$_{ewg}$ group with 1,3-Me,*i*Pr and 4,5-Cl,Cl substituents and can be synthesized in 95% isolated yield from the ruthenium precursor. To learn which one of the two NHC ligands acts as the leaving group in olefin metathesis reactions two complexes, [(FL-NHC)(NHC$_{ewg}$)RuCl$_2$(CHPh)] and [(FL-NHC$_{ewg}$)(NHC)RuCl$_2$(CHPh)], with a dansyl fluorophore (FL)-tagged electron-rich NHC ligand (FL-NHC) and an electron-deficient NHC ligand (FL-NHC$_{ewg}$) were prepared. The fluorescence of the dansyl fluorophore is quenched as long as it is in close vicinity to ruthenium, but increases strongly upon dissociation of the respective fluorophore-tagged ligand. In this manner, it was shown for ring-opening metathesis ploymerization (ROMP) reactions at room temperature that the NHC$_{ewg}$ ligand normally acts as the leaving group, whereas the other NHC ligand remains ligated to ruthenium.

Keywords: fluorescence · N-heterocyclic carbenes · olefin metathesis · ring-closing metathesis · ruthenium

Introduction

Ruthenium complexes bearing two identical N-heterocyclic carbenes (NHC) were first reported by Herrmann et al.[1] and later by Grubbs et al.[2] and found to display modest activities in olefin metathesis reactions.[3] In hindsight, this is not surprising as NHC ligands are now renowned for their ability to bind strongly to metal centers.[4] In the related Grubbs 2nd-generation complexes, the initiation reaction proceeds by dissociative substitution of PCy$_3$ with an olefin; the analogous pathway is likely for complexes with two NHC ligands.[5] Consequently, the presence of a second NHC ligand in [(NHC)$_2$RuCl$_2$(CHPh)] can be expected to slow down the initiation reaction.[3a,6] As a consequence, this class of complexes was considered to be less attractive for olefin metathesis and thus rarely studied.[6–7] However, Verpoort et al. showed that the second NHC ligand in [(NHC)$_2$RuCl$_2$(CHPh)] complexes appears to be more labile than expected and can be replaced by isopropoxystyrene to produce a Grubbs–Hoveyda-type complex.[8] Recently Sijbesma et al. also demonstrated for closely related complexes that a polymer-tagged NHC dissociates from ruthenium under the influence of ultrasound irradiation.[9]



We recently reported that attaching strongly electron-withdrawing groups to NHCs provides ligands (termed

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[**] NHC = N-heterocyclic carbene

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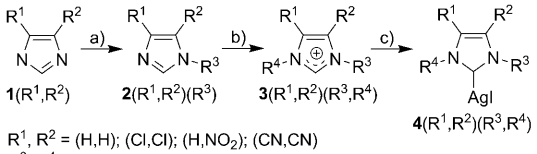
NHC_{ewg}) with significantly reduced donor abilities roughly comparable to PCy_3.[10] This led us to believe that NHC_{ewg} ligands could act as more facile leaving groups, just like PCy_3 in 2nd-generation Grubbs complexes. On testing such complexes in RCM reactions, it was discovered that [(NHC)-(NHC_{ewg})$RuCl_2$(CHPh)] **1** renders catalysts with unprecedented activities for RCM (ring-closing metathesis) reactions leading to tetrasubstituted olefins.[11] The synthesis of such olefin-metathesis products still poses significant problems with Grubbs-type complexes and until recently 2.5–5 mol% of catalyst and elevated temperatures were required for such reactions.[12] More recently, some improvements were reported and attributed to a reduced bulk of the NHC ligand,[13] to the use of NHC ligands with restricted-conformational freedom,[14] and by applying low polarity, perfluorinated solvents.[15] In 2009, work from Grubbs focused on the optimization of catalytic conditions for a single substrate (diethyl dimethallylmalonate) and reported impressive catalytic efficiencies at 0.2 mol% loading for this substrate.[16]

Following our initial report, we have now facilitated and generalized synthetic access to [(NHC)(NHC_{ewg})$RuCl_2$-(CHPh)] complexes. The easy availability of such compounds enables us to modify the steric and the electronic nature of the NHC_{ewg} groups, leading to further improved performance in RCM reactions of sterically hindered substrates and to perform mechanistic studies aimed at elucidating the basic mechanism of olefin metathesis reactions with such complexes.

Results and Discussions

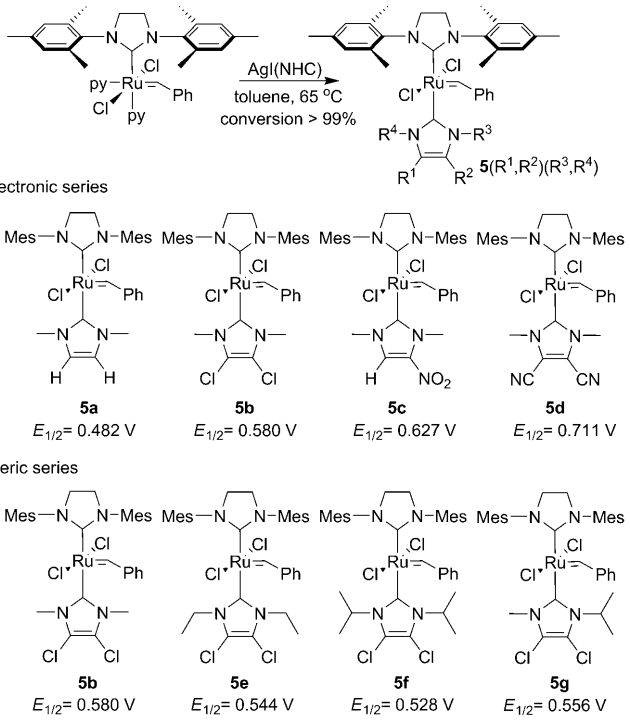
Synthesis of [(NHC)(NHC_{ewg})$RuCl_2$(CHPh)] complexes: To understand which properties of the NHC_{ewg} ligand influence the performance of [(NHC)(NHC_{ewg})$RuCl_2$(CHPh)] complexes in various RCM reactions, we systematically varied the nature of the R^1, R^2, R^3, and R^4 substituents in imidazolinium salts to allow the fine-tuning of the steric and electronic properties of the respective NHC_{ewg} ligand. The respective imidazoles **1** (R^1,R^2 = H,H; Cl,Cl; H,NO_2, and CN,CN) are commercially available. Imidazole **1** and the resulting 1-alkylimidazoles **2** are reacted with the respective alkyl iodides to produce the imidazolium salts **3** in excellent yields. The reaction of the dialkylimidazolium salts with Ag_2O (following a synthesis by Bielawski et al. for R^3,R^4 = Me,Me)[17] results in the facile formation of the respective [AgI(NHC_{ewg})] complexes (Scheme 1), which are excellent NHC-transfer reagents.[18]

Finally, the respective [(NHC)(NHC_{ewg})$RuCl_2$(CHPh)] complexes **5** (for numbering see Scheme 1 or Table 1) were obtained from the reaction of [(NHC)$RuCl_2$(CHPh)($py)_2$] with [AgI(NHC_{ewg})] **4** (Scheme 2). The conversions for this final step are nearly quantitative, whereas the isolated yields of the complexes **5** range between 70–95%. Complex **5g** is available in an isolated yield of 95%. This is important as this complex later turns out to be the most active precatalyst



R^1, R^2 = (H,H); (Cl,Cl); (H,NO_2); (CN,CN)
R^3, R^4= (Me,Me); (Et,Et); (*i*Pr,*i*Pr), (Me,*i*Pr)
3a, **4a** (H,H)(Me,Me); **3b**, **4b** (Cl,Cl)(Me, Me); **3c**, **4c** (H,NO_2)(Me,Me); **3d**, **4d** (CN,CN)(Me,Me); **3e**, **4e** (Cl, Cl)(Et,Et), **3f**, **4f** (Cl, Cl)(*i*Pr,*i*Pr); **3g**, **4g** (Cl,Cl)(Me,*i*Pr); **3h**, **4h** (H,NO_2)(Me,*i*Pr); **4i** (H,H)(Me,*i*Pr)

Scheme 1. Synthesis of [AgI(NHC)] complexes. a) R^3-I, DMSO, KOH, 5 h, RT; b) R^4-I (neat), 48 h, 85 °C; c) Ag_2O, CH_2Cl_2, 50 °C.



Scheme 2. Synthesis of new [(NHC)($NHC)_{ewg}$$RuCl_2$(CHPh)] complexes **5a**–**g** and the cyclic voltammetry-derived $Ru^{II/III}$ redox potentials $E_{1/2}$.

(see Table 1–3). With the exception of the 4,5-H,H-substituted complex **5a**, all complexes are air- and moisture-stable and can be purified by simple chromatography. Alternatively, it is also possible to synthesize complexes **5** directly from [(NHC)$RuCl_2$(CHPh)($py)_2$] and the respective imidazolium salt by utilizing Cs_2CO_3 as the base. However, the yields of **5** are significantly lower when using this direct route.

Electrochemistry of [(NHC)(NHC_{ewg})$RuCl_2$(CHPh)] complexes 5: To obtain information on the donation of the respective NHC ligands, the $Ru^{II/III}$ redox potentials of complexes **5** in the electronic and steric series were determined (listed in Scheme 2).[19] The cyclic voltammetry derived redox potentials range from $E_{1/2}$ = +0.482 V for **5a** to $E_{1/2}$ = +0.711 V for **5d** and display a reversible electrochemistry for all complexes. Within the electronic series, the increase in the redox potentials is correlated with the presence of more electron-withdrawing groups at the NHC_{ewg} ligand,

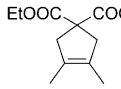
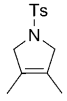
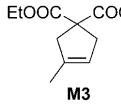
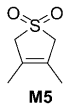
which provides evidence for a decreased donor ability of the respective NHC_{ewg} ligand.[10a,20] This is qualitatively in accord with observations by Bielawski et al. who studied in detail the electron donation in [(NHC)RhCl(cod)] (cod = 1,5-cyclooctadiene) and [(NHC)Rh(CO)$_2$Cl] by using the same NHC ligands as in the electronic series described here.

The steric properties of the NHC_{ewg} ligands (steric series, Scheme 2) were modified (with constant R^3,R^4 = Cl, Cl) in a systematic manner by introducing various *N*-alkyl substituents with variable bulk, ranging from R^1,R^2 = Me to R^1,R^2 = *i*Pr. The minor changes in the redox potentials of complexes **5** demonstrate that the variable bulk of the *N*,*N*-dialkyl groups exerts only a minor effect on the donating properties of NHC_{ewg} in the respective ruthenium complexes. The subtle changes in the redox potentials nicely reflect the increased donor capacity of secondary versus primary alkyl groups and the usefulness of redox potentials for the evaluation of NHC donation.[10a] Based on the present data, we conclude that the steric and electronic properties of NHC_{ewg} ligands can be manipulated almost independently from each other.

RCM reactions utilizing [(NHC)(NHC_{ewg})$RuCl_2$(CHPh)]: With a broad range of available complexes, we first evaluated the influence of variable NHC_{ewg} donor strength on the performance of the [(NHC)(NHC_{ewg})$RuCl_2$(CHPh)] complexes **5a**–**d** in the difficult ring-closing metathesis reaction of diethyl dimethallylmalonate at 80 °C (Table 1, entry 1). With a 0.5 mol % loading, the desired product is formed in 74–81 % yield, which is significantly better than the yields observed with complex **1** (48 %) recently reported by us.[11] Somewhat unexpectedly, the performance of complexes **5a**–**d** in the RCM of diethyl dimethallylmalonate is comparable, despite significant differences in the electron donation of the respective NHC_{ewg} ligands.

We next decided to expand the Cl,Cl-substituted NHC_{ewg} complexes derived from **5b** to probe the influence of steric bulk in the NHC_{ewg} on the catalytic performance for the same RCM reaction (Table 1, entry 1).[21] In the series of complexes **5b**, **5e**, **5f**, and **5g**, the methyl groups in **5b** are successively replaced by the more bulky ethyl and isopropyl units. The effect of steric modifications on the performance of the respective ruthenium complexes is more pronounced than the electronic effect. The RCM yields when using the [(NHC)(NHC_{ewg})$RuCl_2$(CHPh)] complexes **5b**, **5e**, **5f**, and **5g** range from 56–84 % (Table 1, entry 1 and Figure 1). All of the newly synthesized complexes are characterized by superior performance relative to complex **1** and even the least efficient one of the new complexes gives better yields than complex **1** for this test reaction.[11] The best results in terms of final yield and rate of the RCM reaction are obtained for complex **5g** with an unsymmetrical NHC_{ewg} ligand (R^1 = Me, R^2 = *i*Pr). This complex is characterized by a combination of high activity and relatively fast initiation. Whereas some ruthenium complexes reported here require up to 24 h at 80 °C to reach full conversion of the substrates, RCM reactions that utilize **5g** are normally finished within 6–8 h at 80 °C. At this point, we also tried to further improve the performance of complexes **5**. This was based on the assumption that the main decomposition pathway of the RCM catalysts

Table 1. RCM reactions leading to tetrasubstituted, five-membered cyclic olefins.[a]

Entry	Product	Catalyst loading [mol %]	Yield [%] **1**	Me,Me H,H **5a**	Me,Me Cl,Cl **5b**	Me,Me H,NO_2 **5c**	Me,Me CN,CN **5d**	Et,Et Cl,Cl **5e**	*i*Pr,*i*Pr Cl,Cl **5f**	Me,*i*Pr Cl,Cl **5g**	Me,*i*Pr H,NO_2 **5h**
1	 **M1**	0.5	48	74	78	81	74	56	58	84	75
		0.5		30	37	41	97[b]			50[b]	
		0.2					34, 77[b]			36	
2	 **M2**	0.5	98	96	98	94	88		98	99	
		0.2					36[b]			65	
3	 **M3**	0.05		93	97	99	94			98	
4	 **M4**	0.2		99	99	99	99			99	
		0.1								68	
5	 **M5**	0.5		91	99		99			99	

[a] General procedure for metathesis screen: 0.2 mmol olefinic substrate in toluene (10 mL, 0.02 M), T = 80 °C, 20 h, Ru complexes **5a**–**h** were added as a stock solution (3 mmol L^{-1} in toluene). Substrate conversion determined by GC. [b] T = 100 °C.

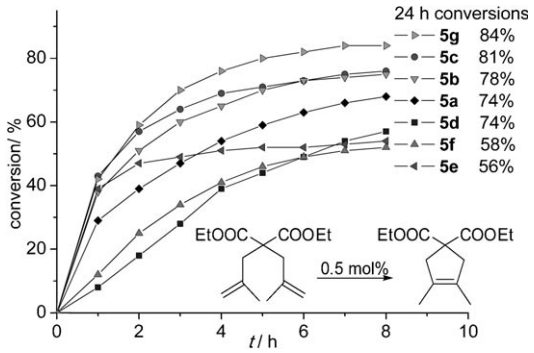
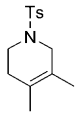
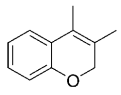
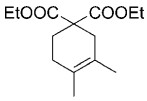
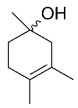
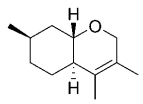


Figure 1. Time–conversion curves for the RCM of diethyl dimethallylmalonate by using the complexes **5a**–**g**.

under the present conditions occurs via the unstable {(NHC)$RuCl_2(CH_2)$} intermediate.[22] This species obviously forms more easily in the presence of the reaction product ethene. Analogous to our previous ADMET (acyclic diene metathesis) experiments,[23] we carried out the RCM reaction of diethyl dimethallylmalonate in a high-boiling solvent (1,2-dichlorobenzene) at 80 °C under a dynamic vacuum of 100 mbar. However, this led to no improvement as with a 0.2 mol % loading of **5d** product **M1** was formed in 45 % yield under standard conditions, but in only 25 % yield with applied dynamic vacuum. It appears that the complete and fast removal of ethene is unfavorable. This came as a surprise as the presence of ethene in closed-vessel reactions is not favorable for RCM reactions.[24]

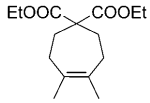
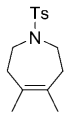
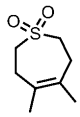
To demonstrate the broad applicability of these complexes for the synthesis of tetrasubstituted olefins, we tested a number of additional RCM transformations (Table 1, entries 2–5, Table 2, entries 1–6, and Table 3, entries 1–3). In almost all of the test reactions, complex **5g** with *N*,*N*′-Me,*i*Pr substituents shows the best catalytic performance. This is why we decided to also realize the *N*,*N*′-Me,*i*Pr pattern with (H,NO_2) substituents in the backbone of complex **5h**. But the performance of this complex cannot rival that of complex **5g** (Table 1–3). However, complex **5b** (**5**-(Me,Me), (Cl,Cl) is nearly as good as **5g**. In general, the differences in the series of complexes are less pronounced as anticipated and this is one reason why we refrained from screening all

Table 2. RCM reactions leading to tetrasubstituted, six-membered cyclic olefins.[a]

Entry	Product	Catalyst loading [mol %]	**1**	Yield [%] Me,Me H,H **5a**	Me,Me Cl,Cl **5b**	Me,Me H,NO_2 **5c**	Me,Me CN,CN **5d**	Et,Et Cl,Cl **5e**	*i*Pr,*i*Pr Cl,Cl **5f**	Me,*i*Pr Cl,Cl **5g**	Me,*i*Pr H,NO_2 **5h**
1	 **M6**	0.5	99	99	99	99	99				
		0.2		59	79	55	68			86	
		0.2					78[b]			79[b]	
2	 **M7**	0.5								99	
3	 **M8**	0.5	99								
		0.2	64	56	87	69	61	72	98	99	90
		0.2								75[b]	
4	 **M9**	0.5	98	99	99	99	99	94	87	95	
		0.2		81	95	81	69	63	53	93	65
		0.2					49[b]			69[b]	
5	 **M10**	0.5		82	95	84	78			99	
		0.2			32	43	55[b]			33	
6	 **M11**	0.5		84	86	85	79			94	

[a] General procedure for metathesis screen: 0.2 mmol olefinic substrate in toluene (10 mL, 0.02 M), $T = 80$ °C, 20 h, Ru complexes **5a**–**h** were added as a stock solution (3 mmol L^{-1} in toluene). Substrate conversion determined by GC. [b] $T = 100$ °C.

Table 3. RCM reactions leading to tetrasubstituted, seven-membered cyclic olefins.[a]

Entry	Product	Catalyst loading [mol%]	1	Yield [%] Me,Me H,H 5a	Me,Me Cl,Cl 5b	Me,Me H,NO_2 5c	Me,Me CN,CN 5d	Et,Et Cl,Cl 5e	*i*Pr,*i*Pr Cl,Cl 5f	Me,*i*Pr Cl,Cl 5g	Me,*i*Pr H,NO_2 5h
1	 M12	0.5	60	95	98	92	89	79	95		
		0.2		57	57	53	67		59		
		0.2					40[b]		33		
2	 M13	0.2		63	85	76	70		84		
3	 M14	0.5		46	59		63		46		

[a] General procedure for metathesis screen: 0.2 mmol olefinic substrate in toluene (10 mL, 0.02 M), $T=80\,^{\circ}C$, 20 h, Ru complexes **5a–h** were added as a stock solution (3 mmol L^{-1} in toluene). Substrate conversion determined by GC. [b] $T=100\,^{\circ}C$.

possible combinations of complexes **5a–h** and the various substrates.

The new complex **5g** requires a two-to-three times lower catalyst loading than complex **1** in RCM reactions, which in turn was already significantly more active than complexes reported by others.[12c,e,13–15] As an example, the formation of **M9** by RCM was reported to require 5 mol% for quantitative conversion,[25] whereas with complex **5g** as little as 0.5 mol% was sufficient. For a more detailed comparison of different ruthenium complexes (**1**, Grubbs 1st and 2nd-generation, Grubbs–Hoveyda) in RCM reactions leading to tetrasubstituted olefins, the reader is referred to our previous publication.[11] Here we are only going to discuss the work of others published in 2009 and the substrate conversions not studied previously.

The synthesis of **M10** (Table 2, entry 5) was studied by Grela et al. and found to require 5 mol% of a Grubbs–Hoveyda-type catalyst for quantitative product formation,[25] whereas with **5g** as little as 0.5 mol% produces a 99% yield. The formation of **M11** (Table 2, entry 6) requires 1 mol% in fluorinated solvents for 99% product formation,[15a] whereas 0.5 mol% of complex **5g** in toluene solvent was already sufficient for nearly quantitative conversion (94%). We also tested a few difficult RCM reactions leading to di- or trisubstituted cyclic olefins. Numerous groups studied the RCM reactions of $Ph_2Si(CH_2CH{=}CH_2)_2$ (Table 1, entry 4) and typically 5 mol% of ruthenium complex were needed for quantitative conversion.[26] In our experiments with complex **5g**, as little as 0.2 mol% were sufficient and even with 0.1 mol% catalyst loading a respectable 68% conversion is obtained.

An increase of the reaction temperature from 80 to 100 °C changes the ranking of complexes **5a–g** for the synthesis of **M1**. At such temperatures complex **5d** with the least electron-donating NHC_{ewg} ligand shows the best substrate conversions (Table 1, entry 1). With a 0.5 mol% loading of **5d** virtually quantitative conversion was observed and with 0.2 mol% loading 77% (Table 1, entry 1). This excellent performance is comparable to that of the best complexes recently reported in a careful optimization study by the Grubbs group for the same substrate.[16] Nonetheless, it appears that the least electron-donating NHC_{ewg} ligand with $R^3,R^4=CN$ is a less efficient leaving group, as complex **5d** requires significantly higher temperatures for reaction. For other RCM reactions higher reaction temperatures are not helpful and the peak performance is normally observed at 80 °C. For entry 2 (Table 1) and entries 1, 4, and 5 (Table 2) complex **5d** is less efficient than **5g** at the same temperature and when comparing to the 80 °C performance of **5g**. We therefore studied one RCM reaction (Table 3, entry 1) at a range of different temperatures, employing a 0.2 mol% loading of complex **5g** under standard conditions. The following RCM results were observed: $T=100\,^{\circ}C$, 33% conversion; 90 °C, 41%; 80 °C, 59%; and 70 °C, 30%. After lowering the reaction temperature to 60 °C, almost no conversion was observed.

This clearly shows that $[(NHC)(NHC_{ewg})RuCl_2(CHPh)]$ complexes are not rapidly initiating species. However, the slow initiation reaction appears coupled with a high stability of the precatalyst, since complexes **5** still show significant activity after being heated to 80 °C for 20 h. This property may very well be responsible for the high activity of complexes **5** in the conversion of otherwise difficult substrates: the high stability of the precatalysts appears to lead to the slow generation of active species at elevated temperatures, at a rate that appears to be required for the formation of

tetrasubstituted olefins. This explanation is compatible with the fact that following initiation and loss of one NHC ligand, [(NHC)(NHC_{ewg})$RuCl_2$(CHPh)] probably forms the same active species as Grubbs II or Grubbs–Hoveyda-type complexes.

Two sulfoxides (Table 1, entry 5 and Table 3, entry 3) and the respective thioethers and sulfoxides were tested in RCM reactions. Both the thioether and the sulfoxide could not be converted to the respective cyclic products by using the catalysts reported here, but we are not aware that this transformation is possible with other RCM catalysts. This failure is most likely attributed to the coordination of the sulfur lone pair to ruthenium resulting in catalyst inhibition. On the other hand, the reaction leading to the cyclic sulfone **M5** (Table 1, entry 5) was successful; with a 0.5 mol% loading a 99% conversion was observed. The synthesis of this sulfone had previously been reported by using 5 mol% Grubbs II complex,[27] whereas **M14** (Table 3, entry 3) was not obtained previously by RCM reactions.

Crystal structure analysis of 5d: We have determined the crystal structure of **5d** (Figure 2), but the structural features are unremarkable relative to Grubbs 2nd-generation com-

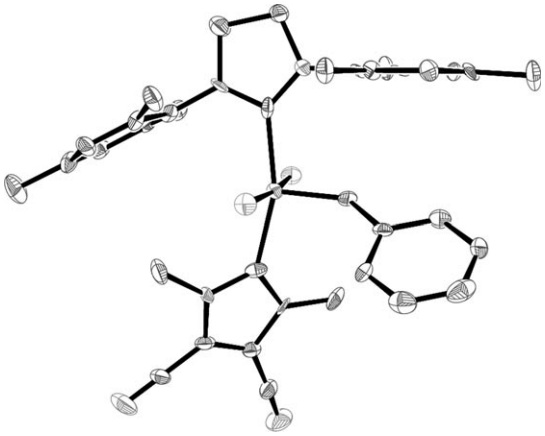


Figure 2. Crystal structure analysis of **5d**. Important bond lengths and angles: Ru–C(SiMes): 207.2(8), Ru–C(NHC_{ewg}): 207.8, Ru–Cl: 238.6(2), 240.94(18) pm; (NHC)C-Ru-C(NHC): 160.7(3), Cl-Ru-Cl 173.33(8)°.

plexes.[3b] Both NHC ligands are tilted away from the benzylidene to utilize the empty space *trans* to Ru=CHPh. The two Ru–C(NHC) bond lengths in **5d** are almost identical. This is consistent with the observation that variable electron donation of NHC ligands exerts only a subtle influence on structural parameters.[10a] Based on the evaluation of the steric shielding of the ruthenium atom by the five ligands, primarily by the two NHC units, it also appears unlikely that the substitution of NHC_{ewg} by pyridine or in the initiation reaction by olefins occur by an associative mechanism.

Leaving-group quality of NHC ligands in [(NHC)(NHC_{ewg})$RuCl_2$(CHPh)] complexes: Our initial and simple hypothesis was that NHC_{ewg} ligands with more strongly electron-withdrawing substituents are better leaving groups than NHC_{ewg} with weakly electron-withdrawing groups.[11] However, the detailed catalytic study undertaken now sheds some doubts on this simple mechanistic picture. We therefore decided to study in more detail the leaving group quality of different NHC_{ewg} ligands, which also concerns the initiation of the RCM reactions. Complexes **5a–d** were dissolved in [D_5]pyridine and the rate for the substitution of the NHC_{ewg} ligands by pyridine determined by ^{1}H NMR spectroscopy (by the respective integrals of the benzylidene C*H*Ph signals). Pyridine replaces the NHC_{ewg} group and [(NHC)$RuCl_2$(CHPh)$(py)_2$] is formed, as evidenced by the disappearance of the $\delta = 19.75$ ppm ^{1}H NMR spectroscopic shift of the benzylidene proton (C*H*Ph). Instead a signal at $\delta = 19.95$ ppm grows in, which corresponds to the benzylidene proton in [(NHC)$RuCl_2$(CHPh)$(py)_2$]. Based on the NMR spectroscopic experiments, the k_{obs} for the NHC_{ewg} substitution by pyridine for the electronic series were calculated (Table 4). There is no apparent correlation of these

Table 4. k_{obs} for NHC_{ewg}–pyridine exchange.

[(NHC)(NHC_{ewg})$RuCl_2$(CHPh)]	k_{obs} [s^{-1}]
steric series	
5f: R^1,R^2 = *i*Pr,*i*Pr; R^3,R^4 = Cl,Cl	378.0 ± 45.4
5g: R^1,R^2 = Me,*i*Pr; R^3,R^4 = Cl,Cl	113.4 ± 8.3
5b: R^1,R^2 = Me,Me; R^3,R^4 = Cl, Cl	106.2 ± 2.7
5e: R^1,R^2 = Et,Et; R^3,R^4 = Cl,Cl	67.0 ± 6.1
electronic series	
5c: R,R‘ = Me; R^3,R^4 = H,NO_2	547.2 ± 10.4
5d: R^1, R^2 = Me,Me; R^3,R^4 = CN,CN	255.6 ± 5.0[a]
5b: R^1, R^2 = Me,Me; R^3,R^4 = Cl,Cl	106.2 ± 2.7[a]

[a] Errors from curve fitting, the real error should be higher as the conversions for the reaction monitored are not quantitative.

rates with the rate of the initiation reaction for the RCM reactions. It is therefore likely that the NHC substitution by pyridine is not a good model reaction for the initiation reaction. Unfortunately, the rates obtained from the pyridine-exchange experiments are also not correlated with the electron donation or the sterics of the respective NHC_{ewg} ligand. However, as pointed out by Bielawski et al., the bonding of the NHC ligands used here is more complicated.[17] Apart from being good σ-donors (to a variable extent) the degree of π-back bonding is significant especially for the cyano-substituted NHC ligands,[17,28] which should influence the leaving-group properties of the respective NHC_{ewg} ligand.[29]

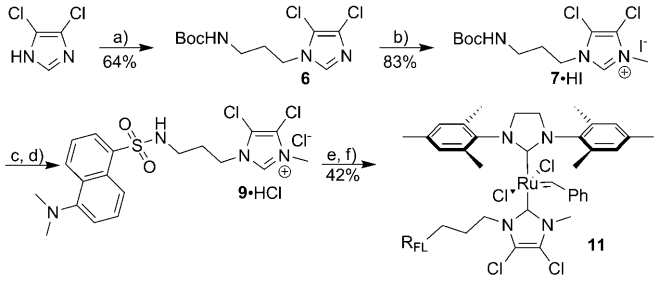
In the case of [(NHC)(NHC_{ewg})$RuCl_2$(CHPh)] **5a** the pyridine reaction produces a second (major) product (δ = 18.09 ppm) in addition to [(NHC)$RuCl_2$(CHPh)$(py)_2$] (ca. 60:40 ratio). To test whether this complex results from the exchange of the NHC ligand in **5a** instead of the expected NHC_{ewg} ligand, we synthesized the symmetrical bis-NHC complex by Herrmann et al.[1] However, the reaction of this complex in [D_5]pyridine is characterized by decomposition and no resonance at $\delta = 18.09$ ppm was observed.

Fluorophore-tagged NHC ligands and [(NHC)(NHC_{ewg})$RuCl_2$(CHPh)] complexes: The results from the

NHC–pyridine substitution reactions put our simple mechanistic hypothesis of NHC_{ewg} ligands as efficient leaving groups during olefin metathesis reactions in jeopardy. As it is doubtful whether the pyridine experiments serve as good models for the initiation step in olefin metathesis, we decided to study olefin metathesis reactions by using different [(NHC)(NHC_{ewg})$RuCl_2$(CHPh)] complexes. The main question in this respect was which NHC is liberated during an olefin metathesis reaction and which NHC remains ligated to ruthenium. We and others recently discovered that tagging of certain ligands in metal complexes with fluorescent dyes can provide valuable mechanistic information due to changes in the fluorescence intensity in the course of catalytic reactions.[30] Transition metals are able to quench the fluorescence of fluorescent dyes, depending on the distance between the fluorophore and the metal.[31] This is why ligand dissociation reactions can give rise to changes in the fluorescence properties. Consequently a new fluorophore-tagged FL-NHC_{ewg} **9**·HCl was synthesized (Scheme 3), whereas FL-NHC **12**·HCl was available from a previous study.[30a] The respective complexes [(FL-NHC_{ewg})-(NHC)$RuCl_2$(CHPh)] **11** and [(FL-NHC)(NHC_{ewg})$RuCl_2$-(CHPh)] **15** were synthesized according to our standard procedures (Schemes 3 and 4). In those complexes, either the NHC or the NHC_{ewg} ligand is tagged with a fluorescent dansyl group. For both complexes **11** and **15** the fluorescence intensity during the olefin metathesis reaction was probed. Since ruthenium in Grubbs-type complexes is known to quench the fluorescence of the dansyl dye,[30c] the dissociation of the fluorophore tag was expected to lead to a drastic increase in the fluorescence intensity.

Accordingly, solutions of **11** and **15** display only weak fluorescence, whereas the free NHC ligands **9** and **12** are characterized by strong fluorescence emission. It is important to realize that the high sensitivity of fluorescence detection allows the observation of ligand dissociation events under real catalytic conditions; that is, in the low-concentration regime.

We first tested the ruthenium complexes **11** and **15** in pure CH_2Cl_2 at room temperature, to learn more about the time-dependent fluorescence evolution resulting from adventitious decomposition of the ruthenium complexes in the absence of substrates (blind experiment). With **11** a significant increase in fluorescence was observed, which reflects the lower stability and decomposition of less-stable **11** (Figure 3, trace a). The fluorescence of a solution of **15** increases only slowly, indicative of the high stability of **15** (Figure 4, trace a). Next we probed the substitution of NHC ligands with pyridine. For complex **15**, virtually the same fluorescence–time curve as in the blind experiment is ob-



Scheme 3. Synthesis of the dansyl-tagged NHC ligand and [(NHC)(FL-NHC_{ewg})$RuCl_2$(CHPh)] complex. a) NaH, $Br(CH_2)_3NHBoc$, THF, 60 °C, 12 h; b) MeI, 40 °C, 24 h; c) 4 M HCl, dioxane, RT, 30 min; d) dansyl-chloride, iPr_2NEt, MeOH, 2 h, RT; e) Ag_2O, CH_2Cl_2, 40 °C, 60 min; f) [(NHC)$RuCl_2$(CHPh)$(py)_2$], 60 °C, toluene, 60 min. R_{FL} = dansylamide.

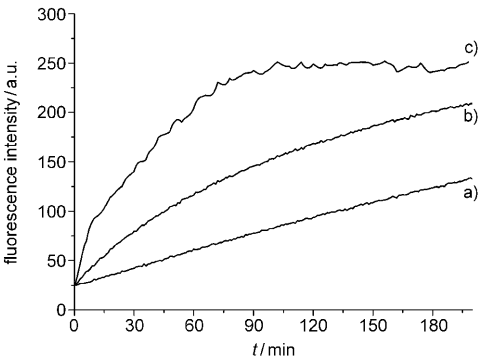
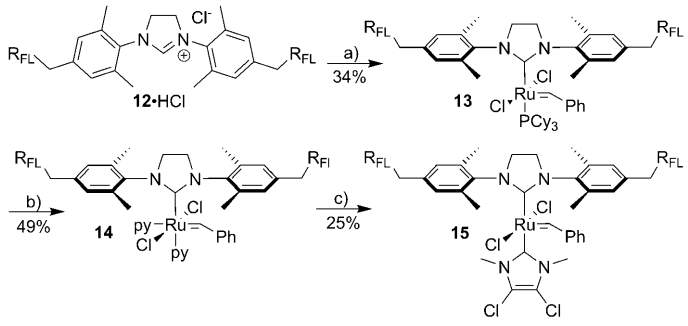


Figure 3. Fluorescence-time curve of **11** (1.2×10^{-6} M): a) in CH_2Cl_2, b) in pyridine, and c) during the ROMP reaction in CH_2Cl_2.



Scheme 4. Synthesis of the dansyl-tagged NHC ligand and [(NHC)-(NHC_{ewg})$RuCl_2$(CHPh)] complex. a) KO*t*Bu, THF, 50 °C, 2 h; b) pyridine, RT, 15 min; c) [AgI(NHC)], toluene, 60 °C. R_{FL} = dansylamide.

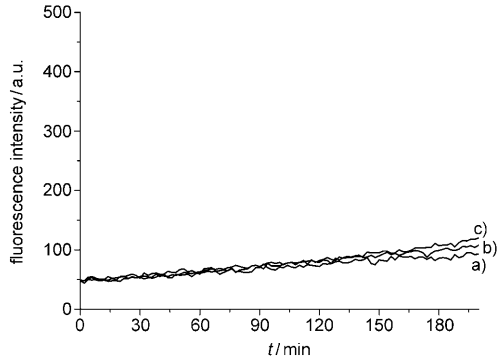


Figure 4. Fluorescence-time curve of **15** (1.2×10^{-6} M): a) in CH_2Cl_2, b) in pyridine, and c) during the ROMP reaction in CH_2Cl_2.

served, showing that the FL-NHC ligand remains bonded to ruthenium (Figure 4, trace b). In complex **11**, with the dansyl-tag attached to the NHC_{ewg} ligand, the fluorescence intensity increases much faster than the background reaction (Figure 4, trace b). This indicates the release of the fluorophore-tagged NHC_{ewg}. We next tested the application of fluorophore tags in RCM. However, the high temperatures (80 °C) needed for such reactions led to a significant fluorescence signal in the blind experiment. This is why we chose the ring-opening metathesis ploymerization (ROMP) reaction of norbornene instead, as it can be carried out at room temperature. Under the specified conditions (0.0025 mol % of **11** or **15**, $T=30$ °C), the polymerization of norbornene is complete within less than 100 min. The monomer/ruthenium ratio of 40.000:1 also provides evidence for the excellent ROMP activities of the $[(NHC)(NHC_{ewg})RuCl_2(CHPh)]$ complexes. In the present experiments, the precatalyst concentration was 1.2×10^{-6} M. During the ROMP reaction utilizing complex **15**, the fluorescence again remains almost constant. This provides firm evidence that the FL-NHC ligand remains ligated to the ruthenium during the olefin metathesis reaction. Quite in contrast, the fluorescence intensity of **11** increases rapidly and reaches saturation at around the time the ROMP reaction is finished. This clearly demonstrates that olefin metathesis with $[(FL\text{-}NHC_{ewg})(NHC)RuCl_2(CHPh)]$ complexes goes along with the dissociation of the NHC_{ewg} ligand, whereas the other NHC ligand remains coordinated to ruthenium.

Conclusion

We have demonstrated the facile synthesis of nine optimized $[(NHC)(NHC_{ewg})RuCl_2(CHPh)]$ complexes **5a–h** in excellent yields. The catalytically most efficient complex **5g** is available in 95 % yield from easily available starting materials. The new complexes show unprecedented activities in RCM reactions leading to a variety of tetrasubstituted olefins. Specifically, complex **5g** generates the respective RCM products in excellent yields at 0.2–0.5 mol % loading. Furthermore, we now have a toolbox of catalytically active complexes at hand, which we are currently testing in various other olefin metathesis reactions. The modification of the leaving group quality of the NHC_{ewg} ligand allows the easy fine-tuning of the catalytic activities for different olefin metathesis reactions—despite the fact that following the initiation reaction, the same catalytically active species as in olefin metathesis reactions for Grubbs 2nd-generation or Grubbs–Hoveyda complexes appears to be formed. Evidence for this was obtained through the use of fluorophore-tagged NHC ligands. This approach represents a new tool for homogeneous catalysis, which can provide valuable mechanistic evidence in the low-concentration regime. In the present case, it was shown that NHC_{ewg} ligands act as efficient leaving groups in olefin metathesis reactions.

Finally, it is important to note that up until now the research into new NHC ligands was focused on creating more and more strongly donating NHC ligands; we have now demonstrated that it is also worth taking a different view, by studying applications for NHC_{ewg} ligands with a weaker donor capacity.

Experimental Section

General: All chemicals were purchased as reagent grade from commercial suppliers and were used without further purification unless otherwise noted. Dansyl chloride was prepared from dansyl acid according to the literature procedure.[32] Solvents were dried by passing over Al_2O_3 and/or by storing over molecular sieves unless otherwise noted. 1,2-Dichlorobenzene and pyridine were degassed by the freeze-pump-thaw cycle technique. Flash column and preparative TLC were performed by using silica gel 60 (0.063–0.20 mesh ASTM). TLC was performed by using silica gel 60 F_{254} (0.2 mm) on alumina plates. NMR spectra were recorded on Bruker DRX500 and Bruker DRX300. The chemical shifts (δ) are given in ppm relative to TMS, coupling constants J are in Hz. MS spectra were recorded on a Finnigan MAT95 spectrometer. GC experiments were run on a Clarus 500 GC with autosampler and FID detector. Column: Varian CP-Sil 8 CB ($l=15$ m, diameter $=0.25$ mm, $dF=1.0$ μm), N_2 (flow: 17 cm s^{-1}; split 1:50); injector-temperature: 200 °C, detector temperature: 270 °C. Temperature program: isotherm 60 °C for 5 min, heating to 300 °C with 25 °C min^{-1}, isotherm for 5 min. The identity of all GC product peaks was established by GCMS on a Finnigan MAT GCMS. The spectroscopic data (^{1}H NMR) of the isolated products are identical to those reported in the literature. Cyclic voltammetry: EG&G 263A-2 potentiostat. Cyclic voltammograms were recorded in dry CH_2Cl_2 under an argon atmosphere at ambient temperature. A three-electrode configuration was employed. The working electrode was a Pt disk (diameter: 1 mm) sealed in soft glass with a Pt wire as counter electrode. The pseudo reference electrode was an Ag wire. Potentials were calibrated internally against the formal potential of octamethylferrocene (−10 mV (CH_2Cl_2) vs. Ag/AgCl). NBu_4PF_6 (0.1 mol L^{-1}) was used as supporting electrolyte. UV/Vis spectra were recorded on a Zeiss Specord S10 spectrometer. Fluorescence spectra were recorded on a J&M FL3095 spectrometer; fluoresceine was used as a reference standard.

General procedure for the synthesis of 1-alkylimidazoles 1: Solid KOH (0.84 mg, 15 mmol, 1.5 equiv) was added to a solution of imidazole (10 mmol, 1 equiv) in DMSO (20 mL). The mixture was stirred at RT for 5 h. Next the appropriate alkyl iodide (11 mmol, 1.1 equiv) was added and the solution was stirred at 50 °C for 2 days. After this time, the reaction mixture was diluted with water (500 mL) and extracted with $CHCl_3$ (2×20 mL). The solvent was removed from the combined organic fractions affording the product.

1-Isopropyl-4,5-dichloroimidazole: Orange-brown oil; yield: 84 %; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=7.42$ (s, 1H), 4.34 (septet, $J=6.6$ Hz, 1H), 1.47 ppm (d, $J=6.6$ Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=132.3$, 125.9, 112.5, 49.0, 22.5 ppm.

1-Ethyl-4,5-dichloroimidazole: Red oil; yield: 94 %; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=7.40$ (s, 1H), 3.97 (q, $J=7.3$ Hz, 2H), 1.44 ppm (t, $J=7.3$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=133.6$, 126.0, 113.0, 41.4, 15.5 ppm.

General procedure for the synthesis of imidazolium salts 2: A mixture of 1-alkylimidazole (2 mmol, 1 equiv) and the respective alkyl iodide (5–7 equiv) was heated at 85 °C for 2 days in a closed vessel. The obtained suspension was filtered and washed with ether affording the desired product.

1,3-Diisopropyl-4,5-dichloroimidazolium iodide: Grey precipitate; yield: 52 %; ^{1}H NMR (300 MHz, [D$_6$]DMSO): $\delta=9.49$ (s, 1H), 4.68 (septet, $J=6.6$ Hz, 1H), 1.54 ppm (d, $J=6.6$ Hz, 6H); ^{13}C NMR (75 MHz, [D$_6$]DMSO): $\delta=133.0$, 118.1, 53.1, 21.4 ppm.

1-Isopropyl-3-methyl-4,5-dichloroimidazolium iodide: Off-white precipitate; yield: 97 %; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=9.59$ (s, 1H), 4.66 (s, $J=6.6$ Hz, 1H), 3.82 (s, 3H), 1.50 ppm (d, $J=6.6$ Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=135.1$, 119.3, 117.5, 52.6, 35.0, 21.4 ppm.

1-Isopropyl-3-methylimidazolium iodide: Orange precipitate; yield: 75%; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.73 (s, 1H), 7.49 (s, 2H), 4.68 (septet, J = 6.6 Hz, 1H), 3.96 (s, 3H), 1.47 ppm (d, J = 6.6 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 134.8, 123.4, 120.1, 52.9, 36.6, 22.7 ppm.

1-Isopropyl-3-methyl-4-nitroimidazolium iodide: Yellow precipitate; yield: 70%; ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 9.66 (s, 1H), 9.27 (s, 1H), 4.74 (septet, J = 6.6 Hz, 1H), 4.07 (s, 3H), 1.52 ppm (d, J = 6.6 Hz, 6H); ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 138.2, 123.3, 54.4, 37.3, 22.0 ppm, one peak (C–NO_2) is not observed.

1,3-Diethyl-4,5-dichloroimidazolium iodide: Off-white powder; yield: 79%; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.55 (s, 1H), 4.22 (q, J = 7.3 Hz, 4H), 1.44 ppm (t, J = 7.3 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 135.4, 118.3, 44.0, 13.8 ppm.

General procedure for the synthesis of [AgI(NHC)] complexes 4: A Schlenk tube containing Ag_2O (0.4 mmol, 1 equiv) and the appropriate imidazolium salt (0.8 mmol, 2 equiv) was filled with CH_2Cl_2 (3 mL) under an argon atmosphere and stirred at 50 °C until the silver oxide dissolved. Finally the reaction mixture was added dropwise to diethyl ether or pentane to precipitate the complex.

1,3-Diisopropyl-4,5-dichloroimidazolinium-silver(I) iodide: White precipitate; yield: 72%; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.00 (septet, J = 6.6 Hz, 1H), 1.63 ppm (d, J = 6.6 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 182.9, 116.3, 55.3, 22.5 ppm.

1-Isopropyl-3-methyl-4,5-dichloroimidazolinium-silver(I) iodide: Brown solid (69%); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.92 (s, J = 6.8 Hz, 1H), 3.87 (s, 3H), 1.57 ppm (d, J = 6.8 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 181.8, 117.4, 115.4, 53.8, 38.1, 22.4 ppm.

1-Isopropyl-3-methyl-4-nitroimidazolinium-silver(I) iodide: Yellow solid; yield: 80%; ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 8.99 (s, 1H), 4.92 (septet, J = 6.6 Hz, 1H), 4.13 (s, 3H), 1.50 ppm (d, J = 6.6 Hz, 6H); ^{13}C NMR (125 MHz, [D$_6$]DMSO): δ = 187.1, 139.7, 123.1, 55.2, 39.6, 22.9 ppm.

1,3-Diethyl-4,5-dichloroimidazolinium-silver(I) iodide: Off-white solid; yield: 98%; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.29 (q, J = 7.3 Hz, 4H), 1.41 ppm (t, J = 7.3 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 182.7, 115.6, 45.2, 15.4 ppm.

1-Isopropyl-3-methylimidazolinium-silver(I) iodide: Off-white glue; yield: 80%; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.53 (s, 1H), 7.40 (s, 1H), 4.90–4.70 (m, 1H), 3.82 (s, 3H), 1.43 ppm (d, J = 6.6 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 180.3, 122.8, 118.3, 52.9, 38.3, 23.4 ppm.

General procedure for the synthesis of [(NHC)(NHC$_{ewg}$)RuCl$_2$(CHPh)] 5: A dry Schlenk flask containing [(NHC)RuCl_2(CHPh)(py)$_2$] (132 mg, 0.18 mmol) and [AgI(NHC)] (0.13 mmol) was evacuated and backfilled with argon three times. Toluene (5 mL) was added by syringe and the reaction mixture was stirred at 65 °C until the reaction was finished (ca. 10–20 min, TLC). Finally the volatiles were evaporated on a rotavap and the residue purified by column chromatography.

Complex ***5a***: Reaction time: 30 min; chromatography: (cyclohexane/EtOAc 2:1). It is strongly recommended to use a short column and degassed eluent to minimize the decomposition of this complex. The crude product was dissolved in a minimal amount of CH_2Cl_2 and added to pentane (40 mL). The solution was cooled to −20 °C and was next placed in an ultrasonic bath causing precipitation of a green solid. The product was collected by decantation of the mother liquor (60%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 19.21 (s, 1H), 7.70 (brs, 2H), 7.41 (t, J = 7.5 Hz, 1H), 7.08 (t, J = 7.5 Hz, 2H), 7.02 (s, 2H), 7.00–6.00 (brs, 2H), 6.62 (s, 1H), 6.51 (s, 1H), 4.26–3.72 (m, 4H), 3.20 (s, 3H), 3.00–1.40 (brs, 12H), 2.64 (s, 3H), 2.33 (s, 3H), 2.24 ppm (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 299.5 (m), 223.8, 186.1, 151.1, 140.1, 140.0, 138.6, 137.6, 137.4, 137.2, 134.9, 129.7, 129.4, 128.5, 127.7, 122.4, 121.9, 51.7, 51.2, 37.2, 36.6, 21.0, 20.9, 20.1, 18.3 ppm (brs); HRMS (EI): m/z: calcd for $C_{33}H_{40}N_4Cl_2Ru$: 664.1628 $[M]^+$; found: 664.1665.

Complex ***5b***: Reaction time: 30 min; chromatography: (cyclohexane/EtOAc 4:1). Evaporation of the eluent and washing with pentane affords the product as a green precipitate (90%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 19.19 (s, 1H), 7.70 (brs, 2H), 7.45 (t, J = 7.5 Hz, 1H), 7.11 (t, J = 7.5 Hz, 2H), 7.04 (s, 2H), 6.68 (brs, 2H), 4.20–3.80 (m, 4H), 3.17 (s, 3H), 3.00–1.40 (brs, 12H), 2.26 (s, 3H), 2.35 (s, 3H), 2.25 ppm (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 303.2 (m), 222.2, 187.7, 151.0, 140.0, 139.9, 138.8, 137.7, 137.2, 134.6, 129.7, 129.4, 129.1, 127.7, 116.7, 116.5, 51.6, 51.1, 35.0, 34.7, 20.9, 20.0, 18.2 ppm (brs); HRMS (EI): m/z: calcd for $C_{33}H_{36}N_4Cl_4Ru$: 732.0847 $[M]^+$; found: 732.0877.

Complex ***5c***: Two rotamers 1:1.7; reaction time: 15 min; chromatography: (cyclohexane/EtOAc 3:1). Evaporation of the eluent and washing with pentane affords the product as a brown precipitate (75%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 19.19 (s, 1H), 19.15 (s, 1H), 7.90–7.60 (m, 5H), 7.75 (s, 1H), 7.47 (t, J = 7.5 Hz, 2H), 7.12 (t, J = 7.5 Hz, 4H), 7.05 (s, 2H), 7.03 (s, 2H), 6.72 (brs, 4H), 4.20–3.80 (m, 8H), 3.52 (s, 3H), 3.29 (s, 3H), 3.00–1.40 (brs, 12H), 2.93 (s, 3H), 2.69 (s, 3H), 2.64 (brs, 12H), 2.37 (s, 3H), 2.34 (s, 3H), 2.26 (s, 3H), 2.24 ppm (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 304.3 (m), 221.1, 220.9, 197.7, 196.5, 151.0, 150.9, 140.1, 140.0, 139.3, 139.2, 138.9, 137.9, 137.9, 137.1, 137.0, 134.6, 134.4, 130.0, 129.9, 129.5, 129.4, 129.4, 127.9, 127.9, 126.0, 125.4, 51.7, 51.1, 38.5, 38.0, 37.1, 36.9, 20.9, 20.0, 18.2 ppm (brs); HRMS (EI): m/z: calcd for $C_{33}H_{39}N_5Cl_2O_2Ru$: 709.1561 $[M]^+$; found: 709.1516.

Complex ***5d***: Reaction time: 30 min; chromatography: (cyclohexane/EtOAc 4:1). The crude product was dissolved in a minimal amount of CH_2Cl_2 and was added to pentane (40 mL)—crystals started growing in a few minutes. Green crystals were collected by decantation of the mother liquor (116 mg, 89%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 19.14 (s, 1H), 7.65 (brs, 2H), 7.51 (t, J = 7.5 Hz, 1H), 7.15 (t, J = 7.5 Hz, 2H), 7.05 (s, 2H), 6.69 (brs, 2H), 4.15–3.92 (m, 4H), 3.41 (s, 3H), 2.79 (s, 3H), 2.62 (brs, 6H), 2.45–1.80 (brs, 6H), 2.36 (s, 3H), 2.26 ppm (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 307.6 (m), 219.9, 200.5, 150.9, 140.2, 139.2, 138.1, 137.2, 136.8, 134.3, 130.3, 130.0, 129.6, 129.5, 128.2, 115.5, 115.2, 106.8, 106.7, 51.7, 51.1, 37.1, 36.9, 21.0, 20.1, 18.1 ppm; HRMS (EI): m/z: calcd for $C_{35}H_{38}N_6Cl_2Ru$: 714.1566 $[M]^+$; found: 714.1571.

Complex ***5e***: Reaction time: 30 min; chromatography: (cyclohexane/EtOAc 2:1). Evaporation of the eluent and washing with pentane affords the product as a green precipitate (83%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 19.31 (s, 1H), 7.95 (brs, 2H), 7.43 (t, J = 7.4 Hz, 1H), 7.12 (t, J = 7.4 Hz, 2H), 7.04 (s, 2H), 6.91 (brs, 1H), 6.06 (s, 1H), 4.89–0.67 (m, 3H), 4.29–3.62 (m, 4H), 3.60–2.94 (m, 4H), 2.94–2.82 (m, 9H), 2.65 (s, 3H), 2.18–1.64 (m, 3H), 2.11 (s, 3H), 0.38 ppm (t, J = 7.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 297.9 (m), 222.4, 187.6, 151.3, 139.8, 138.7, 137.8, 137.2, 135.1, 130.4, 129.8, 129.5, 129.3, 129.0, 128.7, 127.9, 116.9, 116.1, 51.6, 51.4, 44.5, 43.6, 21.1, 21.0, 20.1, 18.4 (brs), 16.3, 14.5 ppm; HRMS (EI): m/z: calcd for $C_{35}H_{42}N_4Cl_4Ru$: 760.1207 $[M]^+$; found: 760.1224.

Complex ***5f***: Reaction time: 30 min; chromatography: (cyclohexane/EtOAc 4:1). Evaporation of the eluent and washing with pentane affords the product as an olive precipitate (90%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 19.40 (s, 1H), 8.97 (brs, 1H), 7.43 (t, J = 7.5 Hz, 1H), 7.11 (brs, 2H), 7.06 (s, 1H), 7.04 (s, 1H), 6.96 (s, 1H), 6.80 (brs, 1H), 6.06 (s, 1H), 4.47 (septet, J = 7.0 Hz, 1H), 4.10–3.70 (m, 4H), 3.67 (septet, J = 7.0 Hz, 1H), 2.82 (s, 3H), 2.65 (s, 3H), 2.51 (s, 3H), 2.37 (s, 3H), 2.14 (s, 3H), 1.79 (s, 3H), 1.45 (d, J = 7.0 Hz, 3H), 1.14 (d, J = 7.0 Hz, 3H), 0.95 (d, J = 7.0 Hz, 3H), 0.33 ppm (d, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 299.7 (m), 221.7, 189.1, 151.4, 139.1, 138.4, 137.8, 137.5, 137.4, 137.1, 135.6, 131.6 (brs), 130.2, 129.7, 129.7, 129.0, 128.9, 126.9 (brs), 116.4, 115.6, 56.5, 53.7, 51.7, 51.5, 22.0, 21.7, 21.4, 21.0, 21.0, 19.9, 19.8, 19.1, 18.7, 17.9 ppm; HRMS (EI): m/z: calcd for $C_{37}H_{46}N_4Cl_4Ru$: 788.1546 $[M]^+$; found: 788.1503.

Complex ***5g***: Two rotamers 1:1.3; reaction time: 30 min; chromatography: (cyclohexane/EtOAc 2:1). Evaporation of the eluent and washing with pentane affords the product as a green precipitate (95%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 19.34 (s, 1H), 19.24 (s, 1H), 7.73 (brs, 1H), 7.48–7.40 (m, overlapped triplets, 2H), 7.16–7.08 (m, overlapped triplets, 4H), 7.05 (s, 2H), 7.00 (s, 2H), 4.40 (sep, J = 6.9 Hz, 1H), 4.20–3.75 (m, 8H), 3.70 (sep, J = 7.0 Hz, 1H), 3.21–0.67 (m, 18H), 3.13 (s, 3H), 2.82 (s, 3H), 2.66 (s, 3H), 2.53 (s, 3H), 2.50 (s, 3H), 2.37 (s, 3H), 2.35 (s, 3H), 2.22 (s, 3H), 2.17(s, 3H), 1.78 (s, 3H), 0.97 (d, J = 6.1 Hz, 3H), 0.44 ppm (d, J = 6.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 303.5 (m), 299.7 (m), 222.4, 222.0, 188.7, 188.6, 151.4, 151.3, 140.4, 140.3, 140.1, 139.3, 139.0, 138.4, 137.9, 137.6, 137.4, 137.3, 137.2, 135.5, 135.1, 130.1, 130.0, 129.9, 129.7, 129.6, 129.2, 129.1, 128.0, 118.6, 118.3, 114.8, 114.2, 56.6, 54.2, 51.8,

51.8, 51.7, 51.3, 35.6, 34.8, 22.1, 21.9, 21.2, 20.2, 20.1, 20.0, 19.7, 18.8, 18.4, 18.0 ppm; HRMS (EI): *m/z*: calcd for $C_{35}H_{42}N_4Cl_4Ru$: 760.1207 $[M]^+$; found: 760.1241.

Complex ***5h***: Two rotamers 1:2.3; reaction time: 15 min; chromatography: (cyclohexane/EtOAc 4:1). Evaporation of the eluent and washing with pentane affords the product as a brown precipitate (88%); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 19.25 (s, 1H), 19.24 (s, 1H), 9.00–6.00 (m, 5H), 7.80 (s, 1H), 7.63 (s, 2H), 7.48–7.43 (m (overlapping triplets), 2H), 7.15–7.09 (m (overlapping triplets), 4H), 7.06 (brs, 4H), 6.99 (brs, 1H), 6.16 (brs, 1H), 4.33 (septet, J = 7.0 Hz, 1H), 4.20–3.80 (m, 8H), 3.51 (septet, J = 7.0 Hz, 1H), 3.50 (s, 3H), 2.85 (s, 3H), 2.81 (brs, 6H), 2.70 (brs, 12H), 2.50 (brs, 6H), 2.38 (s, 3H), 2.37 (s, 3H), 2.25 (s, 3H), 2.18 (s, 3H), 1.78 (brs, 3H), 1.23 (brs, 3H), 0.88 (brs, 3H), 0.33 ppm (brs, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 301.5 (m), 221.3, 220.8, 197.8, 196.2, 151.2, 151.0, 140.8, 140.1, 139.8, 139.4, 139.2, 138.4, 138.0, 137.9, 137.3, 137.1, 135.2, 134.6, 130.5, 130.4, 130.0, 129.8, 129.6, 129.4, 129.0, 127.9, 121.6, 121.0, 54.4, 52.1, 51.7, 51.6, 51.5, 51.2, 37.0, 36.9, 24.8, 21.7, 21.1, 21.0, 20.0, 19.9, 18.8, 18.6, 18.2, 17.8 ppm; HRMS (EI): *m/z*: calcd for $C_{35}H_{43}N_5O_2Cl_2Ru$: 737.1948 $[M]^+$; found: 737.1829.

Synthesis of a NHC$_{ewg}$ fluorophore-tagged [(FL-NHC$_{ewg}$)(NHC)RuCl$_2$(CHPh)] complex

*1-(3-aminopropyl)-4,5-dichloroimidazole (*tert*-butoxycarbonyl (Boc)-protected)* ***6***: 3-Bromopropylamine was protected with a Boc group according to a literature procedure.[33] The corresponding imidazole was synthesized according to a modified literature procedure.[34] 4,5-Dichloroimidazole (0.93 g, 6.8 mmol, 1 equiv) in THF (10 mL) was added to a suspension of NaH (0.27 g, 6.8 mmol, 1 equiv) in dry THF (50 mL) dropwise at 0°C and left warming to ambient temperature. Then, 3-bromopropylamine (Boc-protected, 1.62 g, 6.8 mmol, 1 equiv) in THF (10 mL) was added and stirred at 60°C overnight. NaBr was filtered off and the residue was purified by column chromatography ($CHCl_3$/MeOH/Et_3N 95:4:1). Evaporation of the solvent affords the product as a yellowish viscous oil (1.28 g, 64%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.51 (s, 1H), 4.65 (brs, 1H), 3.98 (t, J = 7.2 Hz, 2H), 3.16 (brs, 2H), 1.96 (quintet, J = 7.2 Hz, 2H), 1.44 ppm (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.1, 126.1, 79.8, 134.4, 43.8, 37.4, 30.8, 28.3 ppm.

Synthesis of imidazolium salt ***7***: Methyl iodide (3 mL) was added to the imidazole (1.3 g, 4.3 mmol, 1 equiv) and the formed solution was stirred at 40°C for 1 day in a closed vessel. Addition of diethyl ether precipitated the off-white product, which was filtered off (1.56 g, 83%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.60 (s, 1H), 5.48 (brs, 1H), 4.39 (t, J = 6.6 Hz, 2H), 4.03 (s, 3H), 3.35–3.15 (m, 2H), 2.24 (quintet, J = 7.2 Hz, 2H), 1.39 ppm (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.2, 137.1, 119.9, 119.0, 79.4, 47.0, 37.0, 35.8, 28.5, 28.3 ppm.

Deprotection of ***7***: HCl (4M) in dioxane (5 mL) was added to a solution of the imidazolium salt **7** (436 mg, 1 mmol) in CH_2Cl_2 (4 mL) and stirring was continued at RT for 15 min. Addition of diethyl ether precipitated the off-white product (**8**, 269 mg, 96%), which was filtered off. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 9.83 (s, 1H), 8.41 (brs, 3H), 4.41 (t, J = 6.6 Hz, 2H), 3.83 (s, 3H), 2.89 (m, 2H), 2.16 ppm (t, J = 6.6 Hz, 2H); ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 136.7, 119.4, 118.0, 45.5, 35.2, 35.0, 26.0 ppm.

Introduction of the dansyl fluorophore ***9***: The double salt **8** (233 mg, 0.83 mmol, 1 equiv) was dissolved in *N*,*N*′-diisopropylethylamine (0.4 mL, 2.49 mmol, 3 equiv) and a suspension of dansylchloride (5 mL, 224 mg, 0.83 mmol, 1 equiv) in MeOH (5 mL) was added. After the mixture had been stirred for 2 h at RT, the solvent was removed on a rotavap and water (100 mL) was added to the residue and then extracted with CH_2Cl_2 (2×10 mL). The organic phase was washed with water and dried over $MgSO_4$. Precipitation with ether gave a light-yellow solid (210 mg). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 10.06 (s, 1H), 8.45 (d, J = 8.5 Hz, 1H), 8.34 (d, J = 8.5 Hz, 1H), 8.11 (d, J = 7.0 Hz, 1H), 7.53 (t, J = 6.0 Hz, 1H; N*H*), 7.39 (t, J = 8.0 Hz, 2H), 7.08 (d, J = 8.0 Hz, 1H), 4.37 (t, J = 6.6 Hz, 2H), 3.83 (s, 3H), 3.02 (m, 2H), 2.83 (s, 6H), 2.12 ppm (t, J = 6.6 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 151.6, 141.6, 138.2, 130.0, 129.6, 128.8, 128.6, 125.5, 123.1, 121.5, 119.6, 119.5, 115.3, 47.1, 45.4, 39.8, 35.5, 27.8 ppm. The crude product contains ca. 30% of an unidentified impurity with the dansyl moiety (which also forms under different reaction conditions); attempts to separate the product by column chromatography failed and mainly led to decomposition. It was decided to use impure product for the synthesis of the corresponding silver complex **10**. This complex was prepared according to a standard procedure and used without purification for the synthesis of the corresponding ruthenium complex, which explains the low product yield.

*[(FL-NHC$_{ewg}$)(NHC)RuCl$_2$(CHPh)] (**11**, two rotamers 1:3.3)*: A dry Schlenk flask containing [(NHC)RuCl$_2$(CHPh)(py)$_2$] (60 mg, 0.08 mmol) and [Ag(FL-NHC)] (**10**) was evacuated and backfilled with argon three times. Toluene (4 mL) was added by a syringe and the reaction mixture was stirred at 65°C for 1 h. Then, the solvent was evaporated with a rotavap and the residue purified by chromatography (silica, cyclohexane/EtOAc 2:1) under an argon atmosphere (the solution of the complex is sensitive to air). Evaporation of the solvent gave the pure product as a green solid (43 mg, 49%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 19.32 (s, 1H), 19.13 (s, 1H), 8.54 (d, J = 8.5 Hz, 1H), 8.49 (d, J = 8.5 Hz, 1H), 8.33 (d, J = 8.5 Hz, 1H), 8.23 (d, J = 8.5 Hz, 1H), 8.13 (d, J = 8.5 Hz, 1H), 8.08 (d, J = 8.5 Hz, 1H), 7.93 (brs, 2H), 7.60–6.40 (m, 22H), 5.39 (t, J = 5.5 Hz, 1H), 5.30 (t, J = 5.5 Hz, 1H), 4.15–3.80 (m, 8H), 3.20–1.10 ppm (m, 66H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 300.2, 300.1, 221.5, 220.4, 188.6, 186.9, 151.7, 151.6, 151.1, 150.8, 140.0, 139.5, 138.9, 138.5, 138.0, 137.9, 137.3, 136.9, 136.8, 135.1, 134.9, 134.8, 130.2, 129.9, 129.8, 129.8, 129.7, 129.5, 129.5, 129.4, 129.0, 128.6, 128.6, 128.3, 128.1, 128.0, 127.7, 127.5, 126.4, 122.9, 119.6, 119.5, 117.5, 115.8, 115.2, 51.7, 51.2, 51.1, 48.2, 45.4, 45.3, 40.6, 39.2, 35.0, 34.1, 31.2, 30.0, 29.6, 29.2, 27.0, 26.9, 25.7, 20.9, 20.8, 19.9, 19.8, 18.1 ppm; MS (ESI): *m/z*: calcd for $C_{47}H_{54}Cl_3N_6O_2SRu$: 975.2 $[M^+ - Cl]$; found: 975.3.

*Synthesis of NHC fluorophore-tagged [(FL-NHC)RuCl$_2$(CHPh)(PCy$_3$)] (**13**)*: A heat-gun dried Schlenk flask containing Grubbs I generation complex (300 mg, 0.36 mmol) and the dansyl-tagged NHC salt[30a] **12** (500 mg, 0.50 mmol) was evacuated and back-filled with argon three times. THF (6 mL) was added by syringe and the mixture was heated to 45°C. Next, potassium *tert*-amylate solution (0.8 mL, 1.7M in toluene) was added to the suspension and stirred at the same temperature for 2 h. The solvent was removed in vacuo and the residue purified by column chromatography (cyclohexane/EtOAc 1:1) to give **13** as a red-brown film (180 mg, 34%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 19.10, 8.56 (m, 2H), 8.47 (t, J = 6.5 Hz, 2H), 8.18 (m, 2H), 7.56–7.49 (m, 4H), 7.28–7.18 (m, 3H), 7.09–6.90 (m, 5H), 6.90 (m, 1H), 6.35 (brs, 2H), 4.04–3.75 (m, 4H), 3.38 (s, 2H), 3.19 (m, 8H), 2.95 (s, 2H), 2.89 (s, 6H), 2.88 (s, 6H), 2.65–2.03 (m, 23H), 1.50–0.70 ppm (m 30H); ^{13}C NMR (125 MHz, $CDCl_3$): very broad resonances from rotamers.

*Synthesis of fluorophore-tagged [(FL-NHC)(NHC$_{ewg}$)RuCl$_2$(CHPh)] (**15**)*: Pyridine (0.5 mL) was added to [(FL-NHC)RuCl$_2$(CHPh)(PCy$_3$)] (**13**) (170 mg) in a Schlenk tube. The solution turned from green to brown rapidly within a few minutes. Cold pentane was added after 5 min to precipitate a green solid. The supernatant was decanted and [(FL-NHC)RuCl$_2$(CHPh)(py)$_2$] (**14**) dried in vacuo (80 mg, 49%). This complex was used directly for the reaction with 1,3-dimethylimidazolinium-AgI according to the general procedure. Purification by column chromatography (cyclohexane/EtOAc 1:1) gave a green solid [(FL-NHC)-(NHC)RuCl$_2$(CHPh)]. Yield: (20 mg, 25%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 19.09 (s, 1H), 8.56 (m, 2H), 8.47(m, 2H), 8.19 (m, 2H), 7.59 (m, 2H), 7.56–7.52 (m, 4H), 7.39 (m, 1H), 7.18 (t, J = 6.5 Hz, 2H), 7.05 (s, 2H), 7.01 (t, J = 6.5 Hz, 2H), 6.72 (brs, 2H), 4.03 (m, 2H), 3.89 (m, 2H), 3.41 (s, 2H), 3.33 (s, 2H), 3.23 (brs, 8H), 3.08 (s, 3H), 2.88 (m, 12H), 2.70–2.40 (m, 17H), 2.20 ppm (brs, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 303.5, 222.1, 187.4, 151.7, 151.0, 140.2, 138.7, 138.5, 137.4, 137.3, 136.4, 132.7, 132.6, 130.6, 130.6, 130.5, 130.1, 129.7, 129.7, 129.3, 128.0, 128.0, 127.9, 123.2, 119.9, 119.8, 116.8, 116.5, 115.2, 115.2, 62.3, 62.2, 52.6, 52.6, 51.7, 51.1, 45.7, 45.4, 35.1, 34.9, 20.1 ppm; MS (ESI): *m/z*: calcd for $C_{65}H_{77}Cl_3N_{10}O_4S_2Ru$: 1334.4 $[M^+ - Cl]$; found: 1333.7.

NHC–pyridine substitution experiments: The appropriate complex **5** ($2.5\cdot10^{-6}$ mol) was weighed into an NMR tube under argon. The tube was filled with dried and degassed [D$_5$]pyridine (99.5% deuteration) under an atmosphere of argon. The exchange of NHC ligands against pyridine at 313 K was observed by NMR spectroscopy (Bruker ARX 300 MHz) through the changes in the benzylidene proton. To keep track of the con-

version of the [(NHC)(NHC_{ewg})$RuCl_2$(CHPh)] reaction of pyridine resulting in [(NHC)$RuCl_2$(CHPh)$(py)_2$] the combined integral of the benzylidene resonances and the signal of [D_4H_1]pyridine were compared at the beginning and the end of the substitution reaction. For **5b**: 80, **5c**: 50, **5d**: 60, **5e**: 95, **5f**: 75, and **5g**: 90% of the signal intensity are observed at the end of the reaction.

Fluorescence experiments: A cuvette under an argon atmosphere was loaded with $1.5\cdot10^{-7}$ (for the blind experiment and pyridine exchange) or $3.75\cdot10^{-9}$ mol (norbornene polymerization) of complex **11** or **15** (from a stock solution in CH_2Cl_2) and diluted with a solvent (3 mL, CH_2Cl_2 or pyridine). The cuvette was placed in the holder, which allows the solution to be stirred and thermostatted (30 °C). The dansyl-tagged complex was added to a norbornene solution in CH_2Cl_2 (10 mg, 30 μL from CH_2Cl_2 stock solution). Fluorescence intensities were recorded at 518 nm by using excitation at 350 nm.

X-ray crystal structure determination: See the Supporting Information. CCDC-735549 (**5d**) 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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