

Synthesis and Structure of N-Heterocyclic Carbene Complexes with Tethered Olefinic Groups: Application of the Ruthenium Catalyst in Olefin Metathesis

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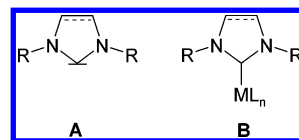
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Silver(I) and rhodium(I) complexes bearing the bisallyl-substituted N-heterocyclic carbene ligand (4*R*,5*S*)-4,5-diallyl-1,3-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene (allyl₂SIMes) have been prepared in a straightforward synthesis. The reaction of (4*R*,5*S*)-4,5-diallyl-1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydro-3*H*-imidazol-1-ium tetrafluoroborate (**1a**) with Ag₂O affords the ionic biscarbene complex [(allyl₂SIMes)₂Ag]⁺BF₄[−] (**2**), while the reaction of (4*R*,5*S*)-4,5-diallyl-1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydro-3*H*-imidazol-1-ium chloride (**1b**) with Ag₂O leads to the monocarbene complex (allyl₂SIMes)AgCl (**3**). Sequential treatment of **1a** with KO*t*Bu and dimeric [RhCl(cod)]₂ (cod = cyclooctadiene) yields the rhodium carbene complex (allyl₂SIMes)RhCl(cod) (**4**). However, the reaction of **1a** with the first-generation Grubbs catalyst (PCy₃)₂Cl₂Ru=C(H)Ph (Cy = cyclohexyl) leads to ring-closing metathesis of the two allylic groups, yielding 1,3-bis(2,4,6-trimethylphenyl)-3a,4,7,7a-tetrahydro-3*H*-benzimidazol-1-ium tetrafluoroborate (**5**). Subsequent reaction of this new imidazolium salt with KO*t*Bu and 1 equiv of (PCy₃)Cl₂Ru=C(H)(C₆H₄O*i*Pr-2) forms [1,3-bis(2,4,6-trimethylphenyl)-3a,4,7,7a-tetrahydro-3*H*-benzimidazolin-2-ylidene]dichloro(2-isopropanolatobenzylidene)ruthenium(II) (**8**). All new complexes have been thoroughly characterized, including X-ray crystallographic analyses of **2**, **3**, and **8**. The most intriguing feature of **8** is the presence of an innocent C=C bond that is part of a highly active olefin metathesis catalyst, which offers many options for further functionalization of the ligand backbone. The catalytic activity of complex **8** has been evaluated for the ring-closing metathesis of *N,N*-diallyl-4-toluene-sulfonamide.

Introduction

During the past decade, the use of N-heterocyclic carbene (NHC) ligands derived from imidazolium ions has emerged as an alternative to phosphine ligands in the design of new organometallic compounds and catalysts.¹ N-Heterocyclic carbenes (type **A**), generated by the abstraction of the proton at C-2 of an imidazolium salt by a suitable base, show unique coordination properties such as particularly strong σ-donor but poor π-acceptor abilities. The interest in those nucleophilic carbene ligands was low until Arduengo et al. discovered in 1991 that the introduction of sterically demanding groups R (adamantyl) in **A** enables the isolation and crystallization of the free imidazol-2-ylidene carbene.²

The bulky groups R provide steric protection from dimerization and carbene degradation pathways.



N-Heterocyclic carbenes bound to metal complex fragments (type **B**) are significantly less reactive than Schrock and Fischer carbenes. They do not undergo metathesis reactions, cyclopropanations, or many of the other reactions attributed to metal carbenes.³ In recent years the potential of N-heterocyclic carbenes as truly useful ligands for catalysis, especially for ruthenium-mediated olefin metathesis, has been shown by Herrmann,⁴ Grubbs,⁵ Nolan,⁶ Hoveyda,⁷ Fürstner,⁸ Blechert,⁹ and others.¹⁰ The key discovery was the replacement of a phosphine with an NHC ligand in the

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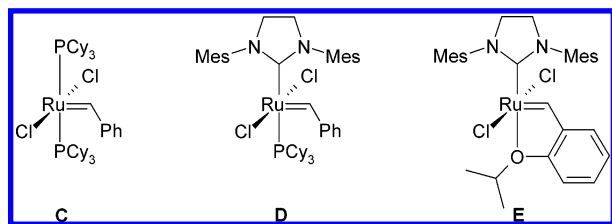
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ruthenium alkylidene complex **C**,¹¹ leading to the ruthenium catalyst **D**^{5a} with improved robustness and activity in metathesis of a wide range of olefins. Other ruthenium-based metathesis catalysts are phosphine-free and take advantage of chelating alkylidene fragments (catalyst **E**) to achieve greater stability, recyclability, and improved performance of the catalyst.^{7a}



In principle, N-heterocyclic carbenes with functional groups bound to the N atoms of the heterocycle are accessible using the synthetic sequence established for type **A** molecules. Herrmann et al. described the introduction of various functionalities such as ether, amino, and phosphino groups tethered to the N atoms of the N-heterocyclic carbene in order to generate potentially chelating NHC ligands,¹² and this area has seen much progress in recent years.¹³ In contrast, relatively few examples of NHC ligands **A** and NHC-bearing metal

complexes **B** with functionalities (Cl, CH₂OH, or others) attached to the backbone of the heterocycle have been reported, since the preparation of those ligands and their complexes often requires lengthy and sophisticated synthetic routes.¹⁴ The 4- and 5-positions of the heterocycle, however, appear to be ideally suited for the introduction of functional groups, since they are quite remote from the catalytically active metal site; any disturbing effect of those substituent groups on the catalytic reaction should therefore be minimized. Proper functionalization of the NHC ligand at its backbone C-4 and C-5 atoms hence is a promising approach with respect to process improvements such as immobilization of the catalyst to a solid support or biphasic liquid catalysis.

In this contribution, we report on the synthesis and properties of novel ruthenium(II), rhodium(I), and silver(I) NHC complexes bearing one or two olefin groups at the backbone of the heterocycle. We investigated the catalytic behavior of the new ruthenium complex in a ring-closing olefin metathesis reaction and compared it to the related known catalyst **E**. For the first time, the X-ray crystallographic investigation of an olefin metathesis catalyst bearing itself an olefinic group could be carried out.

Results and Discussion

Synthesis and Spectroscopic Characterization.

As previously described, 4,5-dihydroimidazolium salts of type **1** with two allylic groups attached to the backbone of the heterocycle can be obtained by double allylation of glyoxalbis(2,4,6-trimethylphenyl)imine with allylic Grignard reagents. Ring closure of the initially formed vicinal diamine is then achieved by reaction with HC(OEt)₃ and NH₄X.¹⁵

The study of silver(I) complexes containing N-heterocyclic carbene ligands is becoming increasingly important due to their ease of preparation, their function as carbene transfer reagents, and their structural variety that results from silver–silver interactions leading to dimerization, oligomerization, or polymerization.¹⁶ An elegant method to afford these silver carbene complexes is the in situ deprotonation of imidazolium salts by Ag₂O. As the starting materials as well as the silver carbene complex are air-stable, this reaction can be carried out under aerobic conditions and gives a convenient entry into metal carbene chemistry. The reac-

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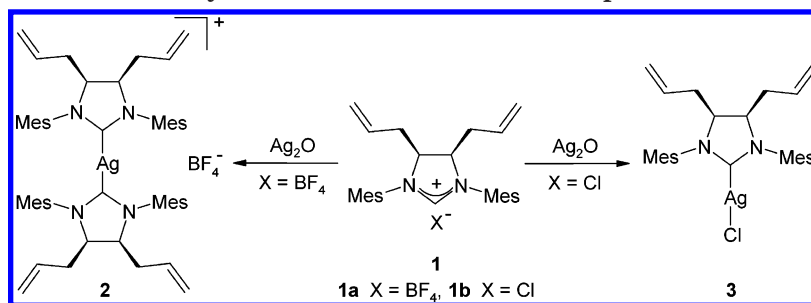
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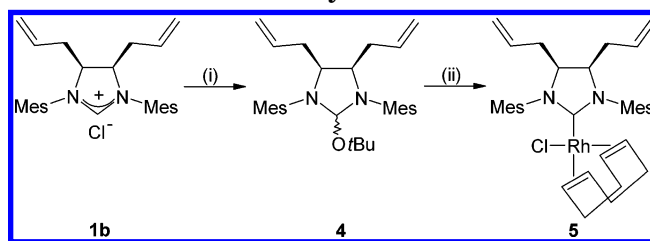
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Scheme 1. Synthesis of Silver Carbene Complexes **2** and **3**

tion of the allyl-substituted imidazolium salts **1a** and **1b** with 0.5 equiv of Ag_2O gave the silver carbene complex **2** or **3**, respectively, in good yields (Scheme 1).

The synthesis of the silver carbene complex **2** could even be carried out in water without hydrolysis of the Ag–C bonds, while the silver chloride complex **3** was prepared in THF. After stirring the reaction mixtures for several hours at room temperature under the exclusion of light, **2** and **3** were isolated as white solids by simple filtration (**2** is insoluble in water) or by filtration and evaporation of the solvent (**3** is soluble in THF). Both compounds are stable as solids for several weeks at room temperature under the exclusion of light. In contrast, solutions of **2** and **3** gradually decompose at 25 °C within several hours with the formation of elemental silver. Both compounds are soluble in polar solvents such as THF or CH_2Cl_2 . Crystals of **2** could be grown from a saturated THF solution at room temperature. Spectroscopic data corroborate the results of the crystallographic analysis (see below) and confirm that two N-heterocyclic carbene ligands are bound to one silver atom, forming a cationic linear silver(I) species with BF_4^- as the noncoordinating counterion. The ^1H and ^{13}C NMR spectra of **2** and **3** in CDCl_3 consist of the expected sharp and well-resolved signals for each of the organic groups. Formation of the carbene adducts **2** and **3** is accompanied by the loss of the proton signal of the NC(H)N group in **1a** (8.21 ppm) and **1b** (10.40 ppm) and a significant shift to higher frequency of the two protons attached to the heterocycle. Carbene formation is also clearly seen in the ^{13}C NMR spectra: the signal of the carbon atom of the NCN group is shifted from 158.2 ppm in **1a** to 206.5 ppm in **2** and from 160.4 ppm in **1b** to 207.1 ppm in **3**. These carbene carbon signals each appear as two doublets with Ag–C coupling constants of 170.4 and 196.3 Hz in **2** and 224.4 and 259.1 Hz in **3**, which is attributed to coupling with ^{107}Ag and ^{109}Ag , respectively. The smaller coupling constants for **2** compared to **3** are consistent with values reported in the literature for ionic $[(\text{NHC})\text{Ag}(\text{NHC})]^+(\text{X}^-)$ (180–210 Hz)^{16a,b,f} and neutral $(\text{NHC})\text{AgX}$ (230–270 Hz).^{16d,e} Interestingly, solutions of the new silver compounds **2** and **3** in $\text{H}_2\text{O}/\text{MeCN}$ (70:30) show similar ESI mass spectra with a prominent peak for the $[(\text{NHC})_2\text{Ag}^+]$ ion and minor peaks for $[(\text{NHC})\text{Ag}(\text{N}\equiv\text{CMe})^+]$, $[(\text{NHC})\text{Ag}(\text{H}_2\text{O})^+]$, and $[(\text{NHC})\text{Ag}^+]$ ions. This might have been expected for the biscarbene complex **2**, but not for the monocarbene complex **3**. Strongly donating solvents apparently promote the dissociation of $(\text{NHC})\text{AgX}$ complexes to $(\text{NHC})_2\text{Ag}^+$ and AgX_2^- , which has been also found for Ag complexes with N-functionalized NHC ligands.^{16c}

Scheme 2. Synthesis of **5a**

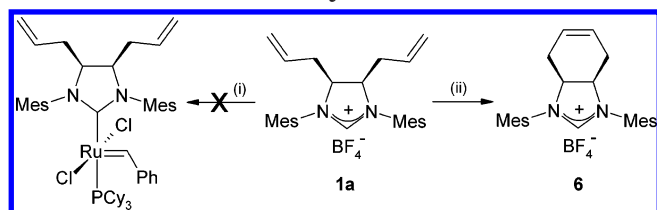
^a (i) KOtBu , THF, 25 °C, 45 min; (ii) $[\text{RhCl}(\text{cod})]_2$, toluene, 80 °C, 1 h.

To further explore the ability of the doubly allyl-substituted carbene ligand derived from **1** to form transition metal complexes, a rhodium(I) complex was prepared according to Herrmann's procedure.¹⁷ The interest in rhodium NHC complexes has grown considerably in recent years, since they have been shown to catalyze various substrate transformations such as hydrosilylation, hydroaminomethylation of olefins, or diastereoselective carbocyclization reactions.¹⁸ Imidazolium salt **1b** was treated with KOtBu in THF at 25 °C in order to generate in situ the doubly allyl-substituted N-heterocyclic carbene adduct **4** (Scheme 2).¹⁵ In accordance with what is usually observed for dihydroimidazolium salts that contain a saturated C–C backbone (and in contrast to imidazolium salts with an unsaturated C=C backbone),^{5d} the parent carbene is not isolated in its free form but forms an adduct with the liberated HOtBu to finally give **4**.

Upon heating to 80 °C for 1 h in toluene the carbene adduct **4** eliminates HOtBu , and in the presence of dimeric $[\text{RhCl}(\text{cod})]_2$ the doubly allyl-substituted (NHC)- $\text{RhCl}(\text{cod})$ complex **5** is formed. After filtration and purification by column chromatography **5** was obtained as a yellow air-stable solid. It is soluble in polar aprotic solvents such as THF or CH_2Cl_2 , and no decomposition of **5** could be observed over several days in solution (NMR control). In the ^1H and ^{13}C NMR spectra of complex **5** two diastereomers in a ratio of around 4:1 were observed at room temperature in CDCl_3 solution. This is most likely due to hindered rotation around the carbene carbon–rhodium bond, assuming that the NHC plane is perpendicular to the square planar rhodium environment (as observed previously in related complexes),^{18d,19} and the two backbone allyl groups are *cis*-oriented.

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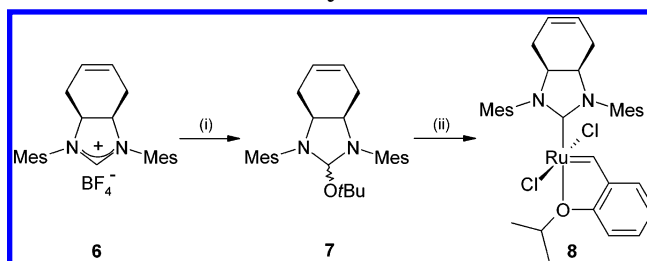
Scheme 3. Synthesis of **6**^a

^a (i) KOtBu, THF, 25 °C, 30 min, 1 equiv (PCy₃)₂Cl₂Ru=C(H)Ph, toluene, 80 °C, 1 h; (ii) 0.1 mol % (PCy₃)₂Cl₂Ru=C(H)Ph, CH₂Cl₂, 25 °C, 17 h.

Hindered rotation around a carbene carbon–rhodium bond was already found in chiral chloro(η^4 -cyclooctadiene)(triazolinylidene)rhodium complexes.^{18a} The ¹³C NMR spectrum of **5** shows the characteristic NCN carbon doublet (¹J_{RhC} = 48.2 Hz) at 214.7 ppm for the major isomer and at 214.3 ppm for the minor isomer, which is similar to the carbene carbon signal of the parent complex (SIMes)RhCl(cod)¹⁷ (212.0 ppm, ¹J_{RhC} = 48.2 Hz). Also for the η^4 -bound cyclooctadiene ligand two sets of doublets (due to rhodium–carbon coupling) could be observed, the olefinic carbon atoms resonating at 67.2 (14.6 Hz) and 97.3 ppm (6.9 Hz) for the major isomer and at 68.4 (14.7 Hz) and 97.0 ppm (7.2 Hz) for the minor isomer. Variable-temperature ¹H NMR spectra in CD₃CN did not reveal any dynamic process up to 70 °C, while spectra in D₈-toluene indicate gradual decomposition upon heating to even higher temperatures.

Fürstner et al. had reported the successful isolation of a ruthenium metathesis catalyst that bears an unsaturated NHC ligand with terminal olefins attached to one of the N atoms of the heterocycle.^{8a,13a} In view of those findings we set out to prepare a ruthenium metathesis catalyst from the olefin-substituted saturated imidazolium salt **1a**. Upon reaction of **1a**/KOtBu with 1 equiv of the first-generation Grubbs catalyst (PCy₃)₂Cl₂Ru=C(H)Ph, however, gas formation (ethene) due to ring-closing metathesis of the two proximate allylic groups of the heterocycle was observed, but no pure and stable product could be isolated (Scheme 3). Under the reaction conditions employed, the present saturated NHC ligand derived from **4** with two allylic groups at the backbone C-4 and C-5 positions apparently is not innocent in the presence of active Ru-benzylidene catalysts. It should be noted that elevated temperatures (80 °C) are required to liberate the carbene from its adduct **4**, as is usually the case for saturated NHC systems. Since the Fürstner ligands were of the unsaturated type, synthesis and isolation of the ruthenium complexes with free terminal olefins tethered to the NHC–N could be carried out at room temperature. Upon heating to 80 °C, those complexes also metathesized their own ligands, yielding metallacyclic species.^{8a}

On the other hand, the present findings now offered a convenient entry into NHC ligands with an annelated cyclohexene moiety, since the imidazolium salt **1a** can be converted into the new imidazolium salt **6** in a straightforward manner by treatment with catalytic amounts of (PCy₃)₂Cl₂Ru=C(H)Ph (0.1 mol %) in CH₂Cl₂ at 25 °C (Scheme 3).¹⁵

Scheme 4. Synthesis of **8**^a

^a (i) KOtBu, THF, 25 °C, 15 min; (ii) (PCy₃)Cl₂Ru=C(H)(C₆H₄OiPr-2), toluene, 80 °C, 1 h.

Imidazolium salt **6** proved to be a valuable NHC precursor for the synthesis of new catalysts that feature an olefinic moiety in the ligand backbone. Similar to the preparation of the carbene adduct **4** from **1b**, imidazolium salt **6** reacts with KOtBu in THF at 25 °C to give the HOtBu adduct **7**.¹⁵ Treatment of in situ prepared **7** with the first generation Hoveyda catalyst (PCy₃)Cl₂Ru=C(H)(C₆H₄OiPr-2) affords the new ruthenium complex **8** (Scheme 4).

After purification of the crude product by column chromatography (silica, CH₂Cl₂), **8** was isolated as an air-stable green solid in 63% yield. Complex **8** is soluble in most common polar and unpolar solvents, and crystals suitable for X-ray crystallographic analysis were grown at room temperature from a chloroform solution that was layered with hexane. The benzylidene ligand in the ruthenium complex **8** gives rise to ¹H and ¹³C NMR absorptions that are very similar to those of the parent complex (SIMes)Cl₂Ru=C(H)(C₆H₄OiPr-2) (**E**):^{7a} the signal of the Ru=CH proton appears at 16.46 ppm in **8** (versus 16.56 ppm in **E**) and the carbon signal of the Ru=C(H) group is observed at 298.3 ppm in **8** (versus 296.8 ppm in **E**). Although the NHC ligands are different in **8** and **E**, the signals for the carbene-C of the respective NHC ligands are alike and appear at 213.2 ppm in **8** versus 211.1 ppm in **E**.

Solid State Structure. The silver complexes **2** and **3** and the ruthenium complex **8** have been investigated by X-ray crystallography in order to corroborate the spectroscopic findings and to provide a solid foundation for interpretation of the catalytic behavior. To the best of our knowledge, this is the first structural information about a ruthenium benzylidene complex incorporating an olefinic group within the same molecule. The molecular structures of **2**, **3**, and **8** are depicted in Figures 1–3, together with selected atom distances and bond angles.

In **2** the silver atom is almost linearly coordinated by the two NHC ligands (C–Ag–C 178.4(2)°) with Ag–C distances of 2.082(4) and 2.087(4) Å. The planes of the two NHC ligands defined by the N–C(carbene)–N atoms intersect at 54.7(3)°. The related C₂ symmetric chloro complex **3** features a slightly shorter Ag–C distance of 2.057(7) Å and a linearly coordinated silver atom (Cl–Ag–C 180°). Chlorine, silver, and the carbene carbon atom are located on a crystallographic 2-fold axis. The Ag–Cl distance (2.305(2) Å) lies within the range usually found for (NHC)Ag–Cl complexes (2.3–2.4 Å).^{16c,e,20} While **2** appears to be the first X-ray crystal-

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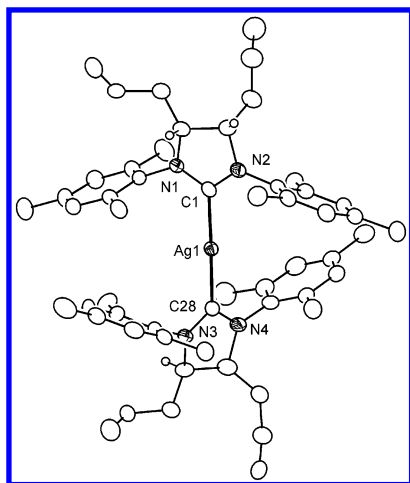


Figure 1. ORTEP plot (30% probability thermal ellipsoids) of the molecular structure of **2**. For the sake of clarity the BF_4^- , all hydrogen atoms except those illustrating the stereochemistry, and the disorder have been omitted. Selected atom distances (Å) and angles (deg): Ag1–C1 2.087(4), Ag1–C28 2.082(4), C1–N1 1.330(5), C1–N2 1.323(5), C28–N3 1.332(5), C28–N4 1.320(5); C1–Ag1–C28 178.4(2), N1–C1–N2 109.0(4), N3–C28–N4 109.8(4).

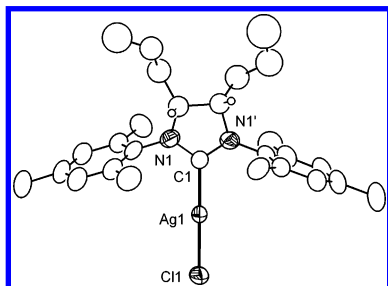


Figure 2. ORTEP plot (30% probability thermal ellipsoids) of the molecular structure of **3**. For the sake of clarity all hydrogen atoms except those illustrating the stereochemistry and the disorder have been omitted. Selected atom distances (Å) and angles (deg): Ag1–C11 2.305(2), Ag1–C1 2.057(7), C1–N1 1.336(6); C1–Ag1–C11 180.0, N1–C1–N1' 109.3(6). Symmetry transformation used to generate equivalent atoms: (') $-x+1, y, -z+1/2$.

lographic structure of a silver(I) biscarbene complex with saturated NHC ligands, the molecular structure of **2** closely resembles that of bis(1,3-dimesitylimidazol-2-ylidene)silver(I) triflate (C–Ag–C 176.3(2)°; $d(\text{Ag–C})$ 2.067(4) and 2.078(4) Å),^{16a} as well as several other silver(I) complexes with two unsaturated NHC ligands.^{16c,f,21} A notable distinction are the values of the N–C–N angles in **2** and **3** (**2**: 109.0(4) and 109.8(4)°; **3**: 109.3(6)°), which are larger than those in related complexes with unsaturated NHC backbone (e.g., 103.6(4)° and 104.8(4)° in bis(1,3-dimesitylimidazol-2-ylidene)silver(I) triflate^{16a} and 104.4(5)° in 1,3-dimesitylimidazol-2-ylidene-silver(I) chloride^{16e}). This can be attributed to the different ring geometries of the NHC ligands derived from either imidazoles or 4,5-dihydroimidazoles. A comparison of the N–C–N angles

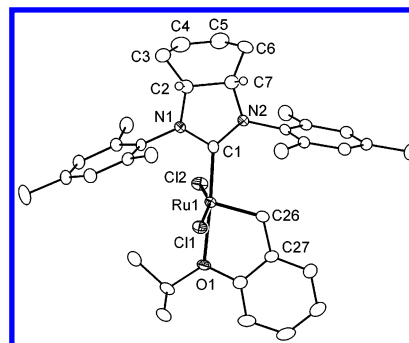


Figure 3. ORTEP plot (30% probability thermal ellipsoids) of the molecular structure of **8**. For the sake of clarity all hydrogen atoms except those illustrating the stereochemistry have been omitted. Selected atom distances (Å) and angles (deg): Ru1–C1 1.967(4), Ru1–C26 1.833(4), Ru1–O1 2.250(3), Ru1–C11 2.345(1), Ru1–C12 2.333(1), C1–N1 1.358(5), C1–N2 1.354(5), C4–C5 1.336(8), C26–C27 1.444(5); C1–Ru1–C26 103.1(2), C1–Ru1–O1 177.0(1), C1–Ru1–C11 94.6(1), C1–Ru1–C12 91.9(1), C26–Ru1–O1 79.6(1), C26–Ru1–C11 97.2(1), C26–Ru1–C12 98.3(1), O1–Ru1–C11 86.34(8), O1–Ru1–C12 86.31(8), C11–Ru1–C12 161.41(4), Ru1–C26–C27 118.2(3), N1–C1–N2 106.0(3).

of **2** or **3** and some silver(I) complexes featuring a single NHC ligand based on 1,3-dimethyl- or 1,3-dibenzyl-substituted (4*R*,5*R*)-4,5-di-*tert*-butylimidazolin-2-ylidene reveals no significant differences ((1,3-(CH_3)₂–NHC)–Ag–I: 108.8(7)°, (1,3-($\text{CH}_2\text{C}_6\text{H}_5$)₂–NHC)Ag–Br: 109.5(15)°).^{16d}

The overall structure of **8** is as anticipated and is analogous to those of the parent complex (SIMes)Cl₂–Ru=C(H)(C₆H₄O*i*Pr-2) (**E**)^{7a} with the ether-O *trans* to the NHC ligand and an almost linear C1–Ru–O1 arrangement (177.0(1)°). The Ru1–C26 distance is in the expected range for ruthenium benzylidene complexes, while the combination of a rather weak O donor and a strong *trans*-influence of the NHC gives rise to a long Ru1–O1 bond of 2.250(3) Å and a Ru1–C1 bond (1.967(4) Å) that is considerably shorter than in the case of second-generation Grubbs catalysts with a phosphine *trans* to the NHC (where $d(\text{Ru–C}_{\text{NHC}})$ is usually found in the range 2.05–2.09 Å).^{5c,f,g,6a,8a,13a} All values for **8** are in good accordance with what has been observed for other complexes of the Hoveyda type characterized crystallographically.^{7a,10c,22}

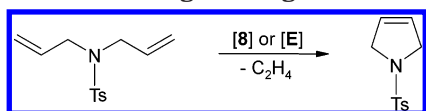
The most intriguing feature of **8** is the presence of an innocent C=C bond that is part of a highly active olefin metathesis catalyst. Very few ruthenium NHC complexes with functional substituents at the backbone C atoms of the NHC ligand have been reported,^{8a} and this appears to be the first such compound of the Hoveyda type and the first with a free olefinic functional group. Second-generation Grubbs catalysts with a long-chain terminal olefin tethered to the NHC–N were shown to undergo internal metathesis to form a metallacycle at elevated temperatures (i.e., at temperatures used for the synthesis of **8**), as already mentioned above.^{8a}

Ring-Closing Olefin Metathesis. Ring-closing metathesis (RCM) has become a very popular method for the formation of unsaturated cyclic compounds from terminal diolefins and is now widely used in organic chemistry.²³ With the described efficient route for the

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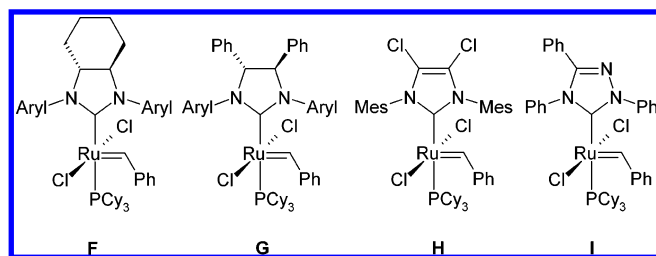
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Scheme 5. Ring-Closing Metathesis

Table 1. RCM of *N,N*-Diallyl-4-toluenesulfonamide by **8** and **E** (reaction time 17 h)

catalyst (mol %)	conversion with 8 (%)	conversion with E (%)
0.05	100.0	100.0
0.02	80.6	97.2
0.005	19.7	52.0
0.002	13.8	33.9

synthesis of the ruthenium complex **8** and in view of the fact that **8** bears itself an olefinic group at the ligand backbone, our focus turned to the evaluation of its catalytic activity in olefin metathesis. So far, only few reports have been given about the synthesis and testing of second-generation ruthenium catalysts bearing substituents at the NHC backbone: Grubbs' complexes **F** and **G**^{5a,h} or Fürstner's complexes **H** and **I**.^{8a}



We could not find any reports about Hoveyda type catalysts with substituents at the NHC backbone, except of Blechert's work concerning type **E** catalysts covalently bound on solid supports via the NHC backbone.²⁴ The olefin-substituted catalyst **8** was probed in ring-closing olefin metathesis in comparison to the parent ruthenium catalyst (SIMes) $\text{Cl}_2\text{Ru}=\text{C}(\text{H})(\text{C}_6\text{H}_4\text{O}i\text{Pr}-2)$ (**E**), using *N,N*-diallyltoluene-4-sulfonamide as a standard RCM substrate (Scheme 5).

When using 0.1 mol % of **8**, the ring-closing metathesis reaction was complete after 165 min in CH_2Cl_2 at 45 °C, indicating high activity. Under identical conditions the benchmark catalyst **E** showed complete conversion after 105 min. We also explored the productivity of **8** in comparison to **E** by decreasing the catalyst amounts from 0.1 to 0.002 mol % (Table 1). Metathesis reactions were again carried out in CH_2Cl_2 at 45 °C over 17 h.

At very low catalyst loadings of less than 0.05 mol %, the benchmark catalyst **E** showed somewhat higher productivities in the RCM reaction of *N,N*-diallyltoluene-4-sulfonamide than the backbone-substituted **8**. However, values for **8** are still in a viable range and are clearly adequate for use of the novel system in RCM applications, bearing in mind that a different catalyst may be optimal for each individual substrate. The subtle influence of the remote olefinic group in **8** that appar-

ently causes a slightly decreased productivity of the new complex in comparison to parent **E** is not clear at present.

Conclusion

Silver and rhodium complexes of a functionalized NHC ligand bearing two allyl groups at the NHC backbone have been prepared via routes previously established for the nonfunctionalized analogues. The X-ray crystal structure of **2** appears to be the first for a biscarbene silver(I) complex with two saturated imidazolin-2-ylidene ligands. In the presence of Grubbs catalyst, however, the backbone allyl groups of imidazolium salt **1** are readily metathesized to give a new imidazolium salt, **6**, with an annelated cyclohexene moiety. The NHC derived from **6** can be smoothly transferred onto ruthenium carbene complexes via the usual phosphine substitution reaction, as has been confirmed by the structural characterization of the new Hoveyda-type ruthenium metathesis catalyst **8**. A particularly attractive feature of **8** is the presence of an internal olefinic group as part of the NHC ligand backbone, which remains innocent with respect to olefin metathesis even at elevated temperatures. It should be noted that unstrained cycloolefins such as cyclohexenes usually do not participate in any ROMP or ROM reactions in the presence of Grubbs or Hoveyda type catalysts.²⁵ This provides many options for further functionalization of the new NHC ligand via, inter alia, dihydroxylation, cyclopropanation, hydroalkoxysilylation, etc. in order to create catalysts that are applicable under various process conditions, for example, in immobilized or biphasic liquid catalysis. The position of this internal olefinic group in **8** appears to be ideally suited for functionalization, since it is quite remote from the catalytically active metal site; any disturbing effect on the catalytic reaction should therefore be minimized. The only slightly lower activity of **8** in RCM of *N,N*-diallyltoluene-4-sulfonamide as compared to the benchmark system **E** underlines its potential to serve as an entry point into advanced metathesis catalysts. Investigations in this regard are in progress.

Experimental Section

General Details. All operations were carried out under an inert atmosphere of argon using standard vacuum and Schlenk techniques or in a glovebox under an atmosphere of argon (Labmaster 130, MBraun, Germany). All solvents were dried and purified by passing through suitable drying columns or by employing standard drying agents.^{26,27} *N,N*-Diallyltoluene-4-sulfonamide was prepared from diallylamine, tosyl chloride, and triethylamine in CH_2Cl_2 . (SIMes) $\text{Cl}_2\text{Ru}=\text{C}(\text{H})(\text{C}_6\text{H}_4\text{O}i\text{Pr}-2)$ was prepared according to the literature procedure.^{7a} Ag_2O (Merck), 1 M KO t Bu/THF (Aldrich), $[\text{RhCl}(\text{cod})]_2$ (Aldrich), and $(\text{PCy}_3)_2\text{Cl}_2\text{Ru}=\text{C}(\text{H})(\text{C}_6\text{H}_4\text{O}i\text{Pr}-2)$ (Aldrich) were used as received. ^1H and ^{13}C NMR spectra were recorded on a Bruker DPX 250 Advance or Bruker AMX 300 at ambient temperature. Data are given in ppm relative to solvent signals for ^1H and ^{13}C NMR spectra. IR spectra were recorded on a Bruker

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Equinox 55 FT-IR instrument as KBr pellets. Bands are characterized as broad (br), strong (s), medium (m), and weak (w). Elemental analyses were measured using a Vario EL. The temperature of the combustion tube was 1150 °C and of the reducing tube 850 °C. He (99.996%) and O₂ (99.995%) were used as supply gases. Melting points were obtained on a Büchi B-540 capillary apparatus. Mass spectra were collected using a Thermo LCQ-DECA (ESI, H₂O/MeCN = 70:30) and Waters VG AutoSpec (EI). HPLC chromatograms were recorded on a Merck Hitachi Elite LaChrom. All silica gel column chromatography was driven with argon and performed with silica gel 60 (0.040–0.063 mm, pH (10% suspension) 6.5–7.5, surface area 480–540 m²/g; pore volume 0.74–0.84 mL/g).

Bis[(4*R*,5*S*)-4,5-diallyl-1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydro-3*H*-imidazolin-2-ylidene]silver(I) tetrafluoroborate (2). To a suspension of silver(I) oxide (15.4 mg, 0.11 mmol) in 20 mL water was added the imidazolium salt **1a** (100 mg, 0.21 mmol), and the reaction mixture was stirred for 2 days at room temperature. The precipitate was isolated and resolved in THF. After filtration the solvent was removed under vacuum and the resulting colorless solid was dried under vacuum. Yield: 91 mg, 0.09 mmol, 85%. Mp: 186 °C. ¹H NMR (250 MHz, CDCl₃): δ 1.85 (s, 12 H, o-C₆H₂(CH₃)₂), 1.92 (s, 12 H, o-C₆H₂(CH₃)₂), 2.10–2.21 (m, 4 H, CH₂C=C), 2.38 (s, 12 H, p-C₆H₂CH₃), 2.41–2.52 (m, 4 H, CH₂C=C), 4.36 (m, 4 H, NCHCH₂), 4.84 (dd, ³J = 10.2 Hz, ²J = 1.3 Hz, 4 H, C=C(H)H), 4.90 (dd, ³J = 17.2 Hz, ²J = 1.3 Hz, 4 H, C=C(H)-H), 5.35 (ddt, ³J = 16.8 Hz, ³J = 10.4 Hz, ³J = 6.4 Hz, 4 H, CH=CH₂), 6.81 (s, 4 H, C₆H₂Me₃), 6.85 (s, 4 H, C₆H₂Me₃). ¹³C NMR (75.5 MHz, CDCl₃): δ 17.7, 18.5 (o-C₆H₂(CH₃)₂), 21.1 (p-C₆H₂CH₃), 32.1 (CH₂C=C), 65.2 (NCHCH₂), 117.6 (CH=CH₂), 129.5, 129.7 (Aryl C_{3,5}), 133.2 (CH=CH₂), 134.3 (Aryl C₄), 135.5, 135.8 (Aryl C_{2,6}), 138.5 (Aryl C₁), 206.5 (AgC, ¹J_{107Ag} = 170.4 Hz, ¹J_{109Ag} = 196.3 Hz). IR (KBr, cm⁻¹): 3078 (w), 2978 (w), 2920 (m), 2861 (w), 1634 (m), 1609 (w), 1483 (s), 1377 (w), 1309 (w), 1274 (m), 1231 (w), 1054 (vs), 911 (w), 856 (w), 573 (w), 520 (w). MS (ESI, *m/z* (%)): 881 (100) [M⁺ - BF₄], 799 (22) [M⁺ - BF₄ - 2 C₃H₅], 534 (39) [M⁺ - BF₄ - C₂₇H₃₄N₂ + MeCN], 511 (70) [M⁺ - BF₄ - C₂₇H₃₄N₂ + H₂O], 495 (18) [M⁺ - BF₄ - C₂₇H₃₄N₂]. Anal. Calcd for C₅₄H₆₈N₄AgBF₄ (mol wt 967.85): C, 67.0; H, 7.1; N, 5.8. Found: C, 67.3; H, 7.4; N, 5.8.

[(4*R*,5*S*)-4,5-Diallyl-1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydro-3*H*-imidazolin-2-ylidene]silver(I) chloride (3). To a suspension of silver oxide (8.3 mg, 0.04 mmol) in 5 mL of THF was added the imidazolium salt **1b** (30 mg, 0.07 mmol), and the reaction mixture was stirred for 16 h at room temperature. After filtration the product was precipitated by adding pentane. The resulting colorless solid was filtered, washed with pentane, and dried under vacuum. Yield: 35 mg, 0.07 mmol, 94%. Mp: 226 °C. ¹H NMR (250 MHz, CDCl₃): δ 2.26 (s, 6 H, o-C₆H₂CH₃), 2.29 (s, 6 H, o-C₆H₂CH₃), 2.34 (m, 2 H, CH₂C=C), 2.36 (s, 6 H, p-C₆H₂CH₃), 2.54–2.64 (m, 2 H, CH₂C=C), 4.44 (m, 2 H, NCHCH₂), 4.94 (dd, ³J = 10.2 Hz, ²J = 1.3 Hz, 2 H, C=C(H)H), 4.98 (dd, ³J = 17.1 Hz, ²J = 1.5 Hz, 2 H, C=C(H)H), 5.46 (ddt, ³J = 17.1 Hz, ³J = 10.3 Hz, ³J = 6.7 Hz, 2 H, CH=CH₂), 6.91, 6.93 (s, 4 H, C₆H₂Me₃). ¹³C NMR (75.5 MHz, CDCl₃): δ 18.2, 19.3 (o-C₆H₂(CH₃)₂), 21.0 (p-C₆H₂CH₃), 32.0 (CH₂C=C), 65.4, 65.5 (NCHCH₂), 117.7 (CH=CH₂), 130.0, 130.1 (Aryl C_{3,5}), 133.5 (CH=CH₂), 134.5 (Aryl C₄), 135.2, 136.1 (Aryl C_{2,6}), 138.7 (Aryl C₁), 207.1 (AgC, ¹J_{107Ag} = 224.4 Hz, ¹J_{109Ag} = 259.1 Hz). IR (KBr, cm⁻¹): 3073 (w), 2977 (w), 2918 (m), 2854 (w), 1639 (m), 1610 (m), 1482 (vs), 1464 (vs), 1377 (m), 1311 (w), 1288 (m), 1277 (m), 995 (m), 913 (m), 852 (m), 793 (w), 633 (w), 572 (w), 513 (w). MS (ESI, *m/z* (%)): 881 (100) [2 M⁺ - Ag - 2 Cl], 799 (20) [2 M⁺ - Ag - 2 Cl - 2 C₃H₅], 534 (30) [M⁺ - Cl + MeCN], 511 (87) [M⁺ - Cl + H₂O], 494 (19) [M⁺ - Cl]. Anal. Calcd for C₂₇H₃₄N₂AgCl (mol wt 529.88): C, 61.2; H, 6.5; N, 5.3. Found: C, 60.6; H, 6.6; N, 5.1.

Chloro(η⁴-1,5-cyclooctadiene)-[(4*R*,5*S*)-4,5-diallyl-1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydro-3*H*-imidazolin-2-ylidene]rhodium(I) (5). A flask was charged with the imidazolium salt **1b** (205 mg, 0.48 mmol) and 5 mL of THF. KOtBu solution (1 M) in THF (0.5 mL, 0.48 mmol) was added, and the reaction solution was stirred for 45 min at room temperature. Dimeric [RhCl(cod)]₂ (100 mg, 0.20 mmol) in 3 mL of toluene was added and stirred at 80 °C for 1 h. After filtration all volatiles were removed under vacuum. The resulting solid was purified by column chromatography (silica, CH₂Cl₂/MeOH = 20:1). After removal of the solvent under vacuum the solid was washed with hexane. The resulting yellow solid was dried under vacuum. Yield: 77 mg, 0.13 mmol, 31%. Mp: 154 °C. ¹H NMR (250 MHz, CD₃CN): δ 1.39–1.89 (m, 8 H, cod-CH₂, isomer 1 + 2), 2.29, 2.34, 2.40, 2.56, 2.68 (s, 18 H, C₆H₂(CH₃)₃, isomer 1 + 2), 2.59 (m, 2 H, CH₂C=C, isomer 1 + 2), 3.07–3.13 (m, 2 H, cod-CH=CH, isomer 1), 3.37–3.43 (m, 2 H, cod-CH=CH, isomer 2), 4.17–4.29 (m, 2 H, NCHCHN, isomer 1 + 2), 4.42–4.54 (m, 2 H, cod-CH=CH, isomer 1 + 2), 4.94–5.04 (m, 4 H, CH=CH₂, isomer 1 + 2), 5.44–5.73 (m, 2 H, CH=CH₂, isomer 1 + 2), 6.94, 6.96, 6.98, 7.04 (s, 4 H, Aryl C₆H₂Me₃, isomer 1 + 2) (the second signal of CH₂C=C is covered by the signal of C₆H₂(CH₃)₃). ¹³C NMR (75.5 MHz, CDCl₃): δ major isomer, 19.2, 21.0, 21.9 (C₆H₂(CH₃)₃), 28.0, 31.9, 32.6 (cod-CH₂, CH₂C=C), 66.1 (NCHCHN), 67.2 (d, ¹J_{RhC} = 14.6 Hz, cod-CH=CH), 97.3 (d, ¹J_{RhC} = 6.9 Hz, cod-CH=CH), 117.1 (CH=CH₂), 128.7, 130.3 (Aryl C_{3,5}), 134.6 (CH=CH₂), 135.1, 135.7, 137.7, 139.4 (Aryl C_{1,2,4,6}), 214.7 (d, ¹J_{RhC} = 48.2 Hz, NCN); δ minor isomer, 20.0, 20.3, 21.6 (C₆H₂(CH₃)₃), 28.1, 31.7, 32.7 (cod-CH₂, CH₂C=C), 65.4 (NCHCHN), 68.4 (d, ¹J_{RhC} = 14.7 Hz, cod-CH=CH), 97.0 (d, ¹J_{RhC} = 7.2 Hz, cod-CH=CH), 117.1 (CH=CH₂), 128.4, 130.2 (Aryl C_{3,5}), 134.4 (CH=CH₂), 136.5, 138.5 (Aryl C_{1,2,4,6}), 214.3 (d, ¹J_{RhC} = 48.2 Hz, NCN). IR (KBr, cm⁻¹): 2920 (s), 2872 (w), 2826 (w), 1640 (m), 1609 (m), 1478 (s), 1448 (w), 1428 (w), 1402 (vs), 1378 (w), 1262 (vs), 1244 (w), 1151 (w), 1101 (w), 1014 (m), 933 (w), 955 (w), 911 (m), 850 (m), 815 (w), 801 (w), 730 (m), 653 (w), 574 (w). MS (EI, *m/z* (%)): 632 (40) [M⁺], 597 (12) [M⁺ - Cl], 488 (55) [M⁺ - Cl - cod], 387 (100) [M⁺ - Cl - cod - Rh]. Anal. Calcd for C₃₅H₄₆ClN₂Rh (mol wt 633.11): C, 66.4; H, 7.3; N, 4.4. Found: C, 66.7; H, 7.6; N, 4.4.

(1,3-Bis(2,4,6-trimethylphenyl)-3a,4,7,7a-tetrahydro-3*H*-benzimidazolin-2-ylidene)dichloro(2-isopropanolato-benzylidene)ruthenium(II) (8). A flask was charged with the imidazolium salt **6** (89 mg, 0.2 mmol) and 5 mL of THF. KOtBu solution (1 M) in THF (200 μL, 0.2 mmol) was added, and the reaction solution was stirred for 15 min at room temperature. The resulting suspension was added to a solution of (PCy₃)Cl₂Ru=C(H)C₆H₄O*i*Pr-2 (100 mg, 0.17 mmol) in 3 mL of toluene. After stirring for 1 h at 80 °C all volatiles were removed in a vacuum. To the resulting residue was added 4 mL of CHCl₃, and the mixture was stirred for an additional 16 h at room temperature. After removal of the volatiles under vacuum the residue was purified by column chromatography (silica, CH₂Cl₂). The green fraction was isolated, and the solvent was removed under vacuum. The resulting green solid was dried under vacuum. Yield: 71 mg, 0.11 mmol, 63%. Mp: 105 °C dec. ¹H NMR (250 MHz, CDCl₃): δ 1.25 (d, ³J = 6.1 Hz, 6 H, OCH(CH₃)₂), 2.06–2.17 (m, 2 H, NCHCH₂), 2.31–2.41 (m, 2 H, NCHCH₂), 2.40 (s, 12 H, o-C₆H₂(CH₃)₂), 2.48 (s, 6 H, p-C₆H₂CH₃), 4.74 (s, 2 H, NCHCHN), 4.86 (septet, ³J = 6.2 Hz, 1 H, OCH(CH₃)₂), 6.00 (m, 2 H, CH=CH), 6.77 (d, 1 H, ³J = 8.3 Hz, C₆H₄), 6.80–6.87 (m, 1 H, C₆H₄), 6.90 (dd, 1 H, ³J = 7.5 Hz, ⁴J = 1.9 Hz, C₆H₄), 7.07 (s, 4 H, C₆H₂Me₃), 7.42–7.52 (m, 1 H, C₆H₄), 16.46 (s, 1 H, Ru=CH). ¹³C NMR (75.5 MHz, CDCl₃): δ 21.0, 21.2 (OCH(CH₃)₂), C₆H₂(CH₃)₃, 25.6 (NCHCH₂), 62.2 (NCHCHN), 74.8 (OCH(CH₃)₂), 112.9, 122.2, 122.7, 127.4, 129.5, 129.6, 129.9 (C₆H₄ C_{2,3,4}, CH=CH, C₆H₂-Me₃ C_{3,5}), 138.6, 140.0, 145.6, 152.1 (C₆H₄ C_{1,6}, C₆H₂Me₃ C_{1,2,4,6}), 213.2 (NCN), 298.3 (Ru=CH). IR (KBr, cm⁻¹): 2972 (m), 2919 (s), 2854 (w), 1607 (w), 1589 (s), 1575 (s), 1476 (vs), 1452 (vs),

Table 2. Crystal Data and Refinement Details for **2**, **3**, and **8**

	2	3	8
empirical formula	C ₅₄ H ₆₈ AgN ₄ ⁺ , BF ₄ [−]	C ₂₇ H ₃₄ AgClN ₂	C ₃₅ H ₄₂ Cl ₂ N ₂ ORu
fw	967.80	529.88	678.70
cryst size [mm]	0.48 × 0.41 × 0.36	0.27 × 0.23 × 0.21	0.27 × 0.18 × 0.15
cryst syst	orthorhombic	monoclinic	triclinic
space group	<i>Pccn</i> (No. 56)	<i>C2/c</i> (No. 15)	<i>P</i> $\bar{1}$ (No. 2)
<i>a</i> [Å], α [deg]	18.3537(6), 90	8.4002(11), 90	9.1068(7), 89.870(6)
<i>b</i> [Å], β [deg]	23.3319(8), 90	16.1489(13), 100.859(9)	11.6390(9), 79.381(6)
<i>c</i> [Å], γ [deg]	23.5876(12), 90	19.953(2), 90	15.9346(12), 74.296(6)
<i>V</i> [Å ³]	10100.8(7)	2658.3(5)	1596.1(2)
ρ_{calcd} [g cm ^{−3}]	1.273	1.324	1.412
<i>Z</i>	8	4	2
<i>F</i> (000)	4064	1096	704
μ [mm ^{−1}]	0.453	0.874	0.689
<i>T</i> _{max} / <i>T</i> _{min}	0.8838/0.7611	0.8812/0.7472	0.9266/0.7515
<i>hkl</i> range	±21, −24 to +27, −27 to +25	±9, ±18, −23 to +22	−9 to +10, ±13, ±18
θ range [deg]	1.41–24.82	2.08–24.78	1.82–24.81
no. of measd reflns	39 184	13 084	16 290
no. of unique reflns [<i>R</i> _{int}]	8677 [0.0406]	2279 [0.0509]	5470 [0.0369]
no. of obsd reflns <i>I</i> > 2 σ (<i>I</i>)	5727	1902	4627
no. of refined params	679	141	378
goodness-of-fit	1.004	1.034	1.034
<i>R</i> ₁ , <i>wR</i> ₂ (<i>I</i> > 2 σ (<i>I</i>))	0.0476, 0.1347	0.0497, 0.1348	0.0412, 0.1055
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0743, 0.1468	0.0606, 0.1419	0.0526, 0.1103
resid el dens [e Å ^{−3}]	1.043/−0.577	0.788/−0.710	2.060 (near Ru)/−0.389

1418 (s), 1384 (vs), 1312 (w), 1261 (vs), 1236 (vs), 1198 (w), 1155 (m), 1139 (m), 1113 (vs), 1098 (w), 1034 (m), 938 (s), 877 (w), 851 (m), 841 (m), 798 (m), 746 (s), 679 (m), 663 (w), 577 (m). MS (EI, *m/z* (%)): 678 (53) [M⁺], 600 (10) [M⁺ − C₃H₇Cl], 563 (23) [M⁺ − C₃H₇Cl − Cl], 494 (45) [(C₂₅H₃₀N₂)RuCl⁺], 458 (50) [(C₂₅H₃₀N₂)Ru⁺], 359 (45) [C₂₅H₃₀N₂⁺], 41 (100) [C₃H₅⁺]. Anal. Calcd for C₃₅H₄₂Cl₂N₂ORu (mol wt 678.70 g/mol): C, 61.9; H, 6.2; N, 4.1. Found: C, 61.8; H, 6.2; N, 4.1.

General Procedure for Ring-Closing Metathesis Reaction (RCM). *N,N*-Diallyl-4-toluenesulfonamide was purified by Kugelrohr distillation (4.2 × 10^{−1} mbar, 300 °C) shortly before use in the RCM reaction. The RCM reaction was performed under argon in a Carousel Reaction Station (Discovery Technologies). A 0.05 M solution of *N,N*-diallyl-4-toluenesulfonamide in CH₂Cl₂ was stirred under reflux for 30 min. A solution of the Ru catalyst **8** or (SIMes)Cl₂Ru=C(H)-(C₆H₄O*i*Pr-2) in toluene was then added to the substrate solution, and the reaction mixture was stirred at 45 °C for 17 h. Product formation was monitored by HPLC.

X-ray Crystal Structure of **2, **3**, and **8**.** X-ray data were collected on a STOE IPDS II diffractometer (graphite monochromated Mo K α radiation, λ = 0.71073 Å) by use of ω scans at −140 °C for **2** and **8** (Table 2). After crystal decomposition was observed at −140 °C, X-ray data for **3** were collected at −50 °C (Table 2). The structures were solved by direct methods and refined on *F*² using all reflections with SHELX-97.²⁸ Most

of the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions and assigned to an isotropic displacement parameter of 0.08 Å². The BF₄[−] anion in **2** is positioned on two distinct 2-fold axes with half-occupancy and is disordered in one case. DFIX (*d*_{B−F} = 1.365 Å) and SADI restraints were applied to model the disorder. The atoms were refined isotropically. Parts of the carbene ligands in **2** are disordered about two positions (occupancy factors C5−C6: 0.756(17)/0.244(17); C29>C36: 0.683(6)/0.317(6)). DFIX (*d*_{C=C} = 1.30 Å), SADI (N3−C29, N4−C30), and SAME (C29>C36) restraints were applied to model the disorder. The carbon atoms were refined anisotropically by use of DELU and SIMU restraints. Parts of the carbene ligand (C2>C9) in **3** are disordered about a 2-fold axis. DFIX (*d*_{C=C} = 1.30 Å, *d*_{C−C} = 1.50 (−C−C=) and 1.53 Å (−C−C−)) and DANG (*d*_{C=(C)−C} = 2.5 Å) restraints were applied to model the disorder. The atoms were refined isotropically. Face-indexed absorption corrections were performed numerically with the program X-RED.²⁹

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Supporting Information Available: X-ray data of **2**, **3**, and **8** as a CIF file. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(29) X-RED; STOE & CIE GmbH: Darmstadt, Germany, 2002.

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