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Synthesis of a new bidentate NHC–Ag(I) complex and its unanticipated reaction with the Hoveyda–Grubbs first generation catalyst

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ABSTRACT

A new sterically demanding bidentate imidazolium bromide has been prepared and used as ligand precursor for the synthesis of the corresponding NHC–silver(I) complex. The X-ray analysis of the silver(I) complex revealed a rare Ag_4O_4 core cubane cluster. The silver(I) complex reacts readily with the Grubbs first generation catalyst providing a labile alkylidene complex. When the transmetallation was attempted with Hoveyda–Grubbs first generation catalyst in the presence of THF as solvent, two very stable phosphine free bis-bidentate *N*-heterocyclic carbene complexes, one green and one orange, were formed. Notably, one of these complexes is the first observation of a metal alkylidene group substituted by a NHC ligand, a surprising result since the new complex is formally derived from a nucleophile substitution of a hydride by a NHC ligand on the alkylidene carbon. A proposal for the reaction mechanism is elaborated.

1. Introduction

During the past decades *N*-heterocyclic carbenes (NHCs)[1–4] have emerged as a versatile class of dative ligands in metal coordination chemistry, particularly in the field of homogeneous catalysis. The particular electronic features[5,6] of the these ligands allow formation of stable complexes both with early[7–9] and late transition metals[10–12] both in low and high oxidation states as well with s,[13,14] p,[15] and f[4,16] block elements. Due to their excellent σ-donor ability, which surpasses even that of the most basic phosphines,[5,10] NHCs have been extensively utilized as ligands in homogeneous catalysis. Substitution of phosphine ligands with NHC ligands has in many cases provided both more robust and active catalysts.[1,3,17–19] The ruthenium based olefin metathesis catalysts where a phosphine ligand is substituted with a NHC ligand provide an important modification that in general affords more active and robust catalysts.[19–21] *N*-heterocyclic carbenes possess a good structural flexibility that permits functionalizations to operate as chelate or pincer ligands.[1,8,9,14,22–27] Chelate NHC ligands have afforded particularly efficient and usable catalysts for asymmetric catalysis purposes.[23,24,28]

A current project in our laboratories involves the design, synthesis, and investigation of novel ruthenium alkylidene complexes as catalysts for olefin metathesis. Monodentate ligands were initially investigated[29] and the results directed us subsequently to the design of bidentate and tridentate ligands[30,31] with the ambition to synthesize new asymmetrical ruthenium catalysts. In this context, we wanted to investigate the electronic and steric features of the sterically demanding 4-nitrobenzyloxy substituted *N*-heterocyclic carbenes (**1a**–**1d**), Chart 1.

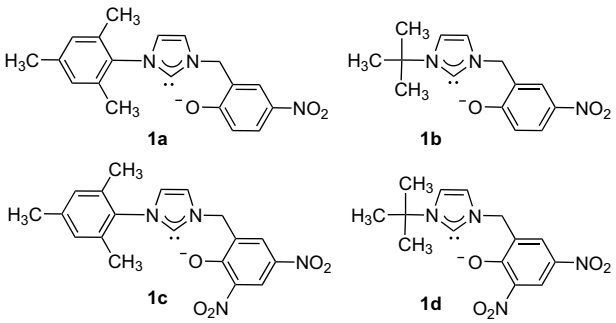

Chart 1.

Structurally similar ligands previously described by Zhang and co-workers[8,14,25,26] and Kawaguchi and co-workers,[9] were used to synthesize a series of Mg(II), Na(I), Li(I), Y(III), Yb(III), Fe(II), Ni(II), Zr(IV), and Ti(IV) complexes.

In a recent short communication[32] we reported the first imidazolium-substituted metal alkylidene together with investigations of the electronic structure by means of quantum chemistry calculations.

Herein, a detailed account of the synthesis and a thoroughly structural analysis of the precursor, a new rare bidentate NHC–Ag(I)-complex is given. The reaction leading to the imidazolium-substituted ruthenium alkylidene is discussed in detail and a reaction

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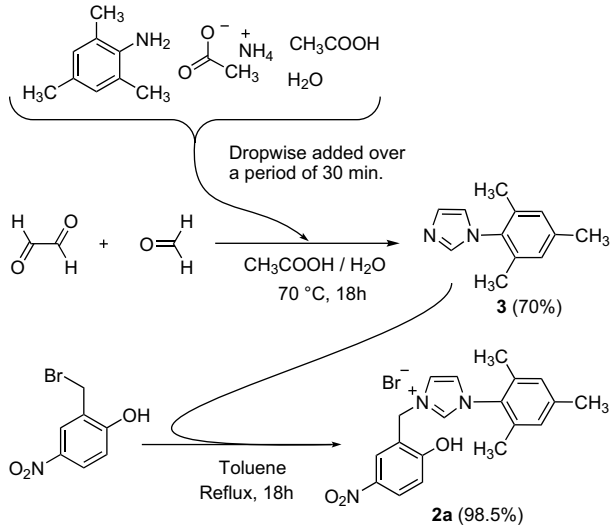
mechanism is proposed. A detailed NMR-based structural analysis of the imidazolium–alkylidene complex is presented along with new olefin metathesis tests performed in ionic solvents.

2. Method and results

2.1. Synthesis of the new imidazolium salt

The synthesis of the novel imidazolium salt 1-(2-hydroxy-5-nitrobenzyl)-3-(2,4,6-trimethylphenyl)-3*H*-imidazol-1-ium bromide **2a** is outlined in Scheme 1. The intermediate product 1-(2,4,6-trimethylphenyl)-1*H*-imidazole **3** was prepared by means of a slightly modified multi component reaction protocol previously disclosed by Arduengo and co-workers:[33] glacial acetic acid, aqueous formaldehyde and glyoxal were mixed and heated at 70 °C, after which a mixture of glacial acetic acid, ammonium acetate in water, and 2,4,6-trimethylphenylamine was added dropwise over a period of 30 min. During a reaction period of 18–20 h at 70 °C, the intermediate product **3** was achieved in good yield (≈70%). 1-(2,4,6-Trimethylphenyl)-1*H*-imidazole **3** and 2-hydroxy-5-nitrobenzyl bromide was then reacted at refluxing temperature in toluene to obtain the target imidazolium salt 1-(2-hydroxy-5-nitrobenzyl)-3-(2,4,6-trimethylphenyl)-3*H*-imidazol-1-ium bromide **2a** that was easily isolated by filtration in an excellent yield (>98%). The X-ray structure of the new imidazolium bromide **2a** and the crystal data of the structural refinement are given in Supplementary data.



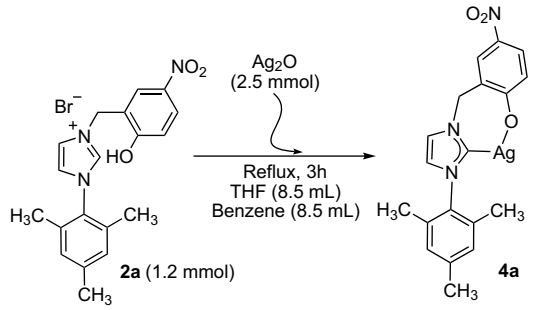
Scheme 1. Synthetic pathway to 1-(2-hydroxy-5-nitrobenzyl)-3-(2,4,6-trimethylphenyl)-3*H*-imidazol-1-ium bromide **2a**.

2.2. The synthetic plan

The synthetic plan to reach the novel ruthenium complexes disclosed herein was initially attempted by reacting deprotonated imidazolium bromide **2a** with the commercially available Grubbs[34] or Hoveyda–Grubbs[35] first generation catalysts. This strategy implies a direct substitution of a phosphine ligand and a chlorine anion with the new bidentate ligand.[36] However, attempts to deprotonate **2a** with potassium *tert*-butoxide resulted only in decomposition of the ligand, a result that was in line with previous reports[12] using analogous conditions for other types of ligands (methylene-linked imidazolium salts). This direct path for the preparation of the Ru-complexes was thus abandoned in favor of a strategy involving a transmetallation step using the corresponding NHC–silver (I) complex of the bidentate ligand **1a**. This approach has also earlier been utilized successfully for the synthesis of NHC–Ru(IV),[24,37] NHC–Pd(II),[18,38] and NHC–Ni(II)[39] complexes.

2.3. Synthesis of the bidentate NHC silver(I) complex

In attempts to prepare a silver(I) complex with our novel bidentate NHC ligand **1a**, variations of reaction medium, reaction time, reaction temperature, concentrations, and the molar ratios of the imidazolium bromide **2a**, and Ag_2O were investigated. Initially, we used a slightly modified procedure previously disclosed by Lin and co-workers[40] and by Hoveyda and co-workers.[28] A protocol providing good yield (≈65%) of the bidentate NHC silver(I) complex **4a** is reported in Scheme 2. The silver(I) complex **4a** was easily isolated and purified, namely filtered through a pad of Celite after which the solvent was removed under reduced pressure. Further purification was conducted by dissolving the isolated solid in methylene chloride followed by precipitation by the addition of *n*-pentane.



Scheme 2. The imidazolium bromide **2a** reacts with silver (I) ions to produce bidentate NHC silver(I) complex **4a**.

Initial structural analyses of the isolated product were conducted using ^{1}H NMR. As expected, the ^{1}H NMR spectrum revealed that the proton signals of both the phenolic group and the C2–H of the imidazole ring were absent.

An aliquot of the prepared silver(I) complex was further purified by re-crystallization in THF. The solid was dissolved at 65–70 °C, followed by slowly cooling to room temperature. A suitable crystal was selected from the crystallized product and investigated on an X-ray diffractometer. The surprising result of that analysis is presented in Figure 1, revealing the very first Ag_4O_4 core cubane

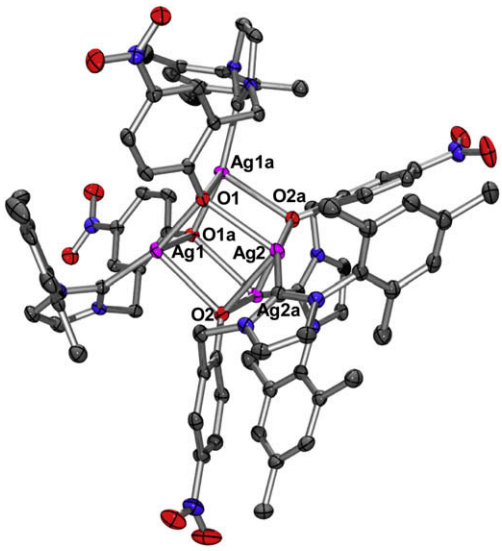


Figure 1. Structure of one of the two enantiomers of the silver-oxygen cubane cluster **4a**, where the ligand 1-(4-nitrobenzyloxy)-3-mesityl-imidazole-2-ylidene is coordinated to Ag(I). The molecule has C2 symmetry, the symmetry related part (a), −x+3/2, y, −z+1/2. Anisotropic displacement parameters are given at the 50% probability level. Hydrogen atoms are omitted for clarity.

cluster that also contains Ag–C bonds. Moreover, this cluster also represents the first cubane cluster that contains a bidentate *N*-heterocyclic carbene ligand. The only previous report demonstrating the use of a monodentate NHC ligand in cubane clusters was recently disclosed.[41]

The tetrameric Ag_4O_4 structure disclosed herein, Figure 1, consists of a dissymmetric silver(I)–oxygen cubane (Ag_4O_4) type cluster. The silver complex **4a** represents a rare oxygen–silver cubane cluster. Even if the core Ag_4O_4 cubane is rather distorted, a C2 symmetry axis passes through the left hand, O1–Ag1a–O1a–Ag1 and the right hand face O2–Ag2a–O2a–Ag2. This implies that the reported structure is chiral and both enantiomers are present in the unit cell that contains eight THF molecules forming a solvent channel along the b-axis. A figure is provided in Supplementary data. The structure is composed of two different and non-planar quadrilateral parts bonded into a sandwich structure through four dative O–Ag bonds (two bonds of length 2.642 (2) Å for Ag1–O2, and the other two of length 2.640(2) Å for Ag2–O1.). Each part forms the face of a quadrangle having two equal covalent Ag–O bonds and two equal dative Ag–O bonds. In the same face, each silver center is bonded to the first ligand by a short dative NHC–Ag bond (2.075(3) Å for Ag1–C8 and 2.069(2) Å for Ag2–C27). It is connected to the second ligand by a covalent Ag–O bond (2.150(2) Å or 2.162(2) Å). Finally, each silver atom is coordinated to the oxygen belonging to the first ligand through a dative Ag–O bond. Half of the cubane cluster contains the same Ag_2O_2 core complex of dimeric bidentate NHC–silver(I) complexes as discovered by Hoveyda and coworkers.[28] However, the complexes found by those authors did not allow further sandwich complexation to give a cubane cluster similar to **4a**. The reason for this is most probably the steric hindrance due to the more bulky bidentate ligands.

It is interesting to note that the covalent and dative bonds for Ag or O belonging to various faces are rather different. However, when comparing the sum of the Ag–O bond lengths in the cubane cluster, it is evident that these are equivalent within the statistical experimental significance. The sum of the three bond distances C8–Ag1–O2–C20 and C1–O1–Ag2–C27 belonging to opposite faces is the same (6.018 Å), see Figure 2, while the two intramolecular space distances from the carbene carbon atom and the arene carbon atom are significantly different, namely C8–C20=4.053(3) Å and C1–C27=4.447(3) Å, differing by 0.394 Å, see Figure 2. The bonding angle NHC–Ag–O where silver is covalently bonded to oxygen are only slightly different, namely 166.2° and 164.5°. Further details regarding the crystal data and results of the structural refinement for this silver(I)-oxygen cubane cluster are provided in Supplementary data.

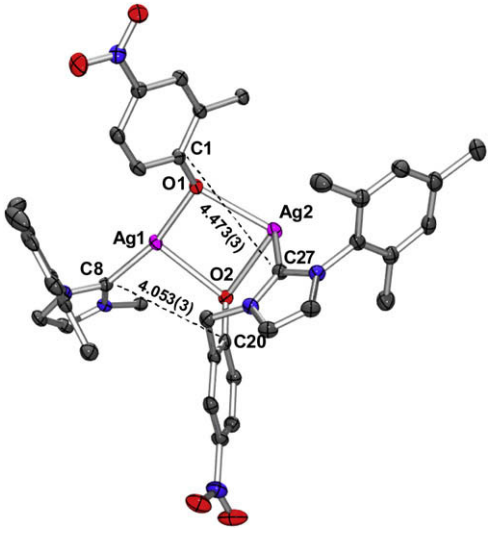


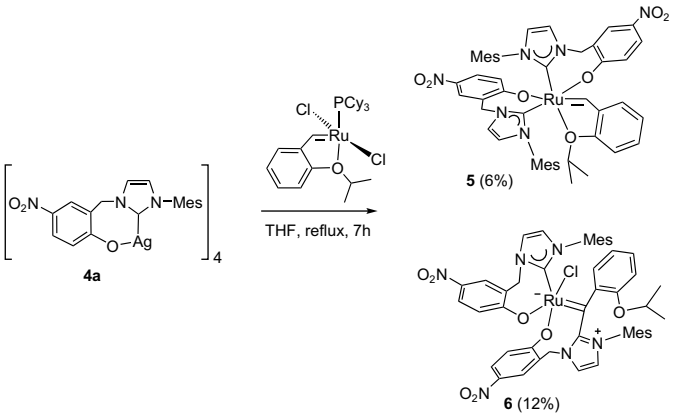
Figure 2. A simplified sketch of complex **4a**. Selected bond and intra molecular distances [Å]: Ag1–O1a 2.162(2), Ag1–O1 2.664(2), Ag2–O2 2.149(2), Ag2–O2a 2.687(2), Ag1–O2 2.642(2), Ag2–O1 2.640(2), Ag1–Ag1a 3.3893(4), Ag2–Ag2a=3.3366(5), Ag1–Ag2a 3.8403(3), Ag1–Ag2 3.7048(3). [Symmetry operator a; −x+3/2, y, −z+1/2].

2.4. Reactivity of silver complex 4a with Grubbs first generation catalyst

The reaction of the silver complex **4a** with the Grubbs first generation catalyst[34] goes to completion in 20 min at a temperature of 65 °C, or in 2 h at room temperature, to provide a rather labile alkylidene Ru complex (red colored) as the major product. The new complex was identified by a sharp singlet 1H peak at δ 19.52 ppm, which is a typical shift value for the ruthenium–alkylidene proton.[17,20,23,35,42] Furthermore, the ^{1}H NMR spectrum of the reaction mixture[43] suggests a mono substituted NHC ruthenium complex, although we were not able to perform a complete characterization of the structure due to the instability of the complex.

2.5. Reactivity of silver complex 4a with Hoveyda–Grubbs first generation catalyst

The silver(I) cubane cluster **4a** reacts with Hoveyda–Grubbs first generation catalyst[35,44] to provide two discrete phosphine free bis coordinated ruthenium complexes **5** (green colored) and **6** (orange colored) both of which proved to be very stable (Scheme 3). The reaction is conducted at 65 °C for at least 7 h in order to be brought to completeness. If the reaction is conducted with tetrahydrofuran as reaction medium, both complexes **5** and **6** were produced. However, if toluene is used as reaction medium, only complex **5** was obtained, and a mixture of toluene and THF provided both complex **5** and **6**. It was observed that the presence of PCy_3 results in an immediate decomposition of the cubane cluster **4a**. It was thought that this could be used in order to promote the desired reaction forming the complex **5** and **6**, however, PCy_3 suppresses both the reaction pathways to **5** and **6** under the formation of other alkylidene complexes.[45]



Scheme 3. Synthesis of the ruthenium complexes **5** and **6** using silver(I)-oxygen cubane cluster **4a** and Hoveyda-Grubbs first generation catalyst.

2.6. Molecular structures of the Ru-complexes 5 and 6

The Ru-complexes **5** and **6** were purified and isolated using column chromatography on silica gel. Initial characterization was conducted by means of ^{1}H NMR, ^{13}C NMR, mass spectrometry, high-resolution mass measurements, and elemental analysis. The interpretation of the MS and the NMR spectra were in agreement with the structures of the two Ru-complexes both of which coordinate two bidentate NHC ligands. The number of proton and carbon resonances in ^{1}H NMR and ^{13}C NMR spectra reveal an

asymmetrical structure for each of the two complexes. The Ru-complex **5** appeared clearly as a ruthenium alkylidene complex formally derived from the substitution of one tricyclohexylphosphine ligand and two chloride ions by two bidentate NHC ligands. The alkylidene proton resonance (Ru=CH, 15.90 ppm in CD_2Cl_2) appears shifted toward higher fields with respect to that of the Hoveyda catalyst[35] (Ru=CH, 17.44 ppm in $CDCl_3$), while the alkylidene carbon resonance (Ru=C, 297.9 ppm in CD_2Cl_2) is shifted toward lower fields also with respect to the Hoveyda catalyst (Ru=C, 280.6 ppm). Moreover the ^{1}H NMR (5.78 ppm) and ^{13}C NMR (77.8 ppm) chemical shifts of the isopropyloxy group in comparison with those of the Hoveyda–Grubbs first generation catalyst, respectively, (5.28 ppm) and (75.5 ppm), strongly suggest a structure having the isopropoxy group coordinated to the metal. The NMR analysis suggests for complex **5** an octahedral ruthenium alkylidene complex with the metal coordinated by the chelating isopropoxy group and by two different NHC bidentate ligands.

MS spectra reveal that the Ru-complex **6** contains one chlorine more and one hydrogen less than the Ru-complex **5**. ^{1}H NMR spectra reveal that the Ru-complex **6** does not contain any alkylidene proton, while the expected signal for the alkylidene carbon appears at 244 ppm, namely shifted 54 ppm toward high field compared to the resonance observed in the Ru-complex **5**. Moreover the ^{1}H NMR (4.55 ppm) and ^{13}C NMR (70.0 ppm) chemical shifts of the isopropoxy group in comparison with the Ru-complex **5** and the Hoveyda–Grubbs first generation catalyst **8** strongly suggest a structure having the isopropoxy group not coordinated to the metal. Based on routine 1D ^{1}H NMR, 1D ^{13}C NMR and MS analyses, it was difficult to determine if the chlorine was coordinated to the metal or to the alkylidene. Moreover the carbon resonance at 244 ppm could also be compatible with an alkylidyne carbon.[46]

Additional 2D NMR experiments were conducted using the DQF-COSY,[47] HSQC/HETCOR[48] and HMBC[49] techniques in order to unveil more structural information for the Ru-complex **6**.

By means of these techniques, we were able to correlate ^{1}H NMR and ^{13}C NMR resonances together through homonuclear (J_{HH}) and heteronuclear ($^1J_{CH}$ and $^nJ_{CH}$) couplings and thereby assign most of them to the correct ligand atoms. These experiments have enabled us to assign the proton and carbon resonances of complex **6**. From HMBC analysis it is clear that the alkylidene carbon is substituted with one NHC ligand. This is evident from several cross-peaks, in particular two cross peaks ($^4J_{CH}$) between alkylidene carbon (244 ppm) and both hydrogens in the NHC backbone (6.97 and 7.25 ppm) and two cross-peaks between the carbene carbon of the NHC ring (161.7 ppm) and two hydrogens belonging to the arylidene group (6.5 ppm, $^4J_{CH}$) and (6.3 ppm, $^5J_{CH}$), see Figure 3 and Supplementary data.

Taken together, the MS, NMR, and elemental analyses suggest a penta-coordinated Ru-complex with one chlorine, two aryloxy groups, a NHC ligand bonded to the Ru, and finally a NHC ligand bonded to the Ru-alkylidene carbon, see Chart 2. Detailed assignment of all carbon and proton resonances is given in Supplementary data.

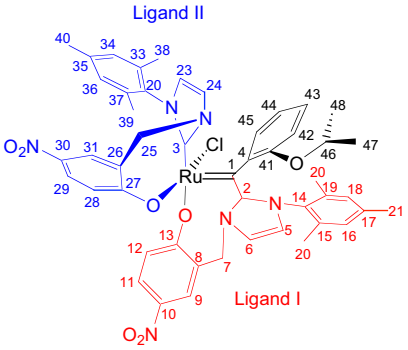


Chart 2.

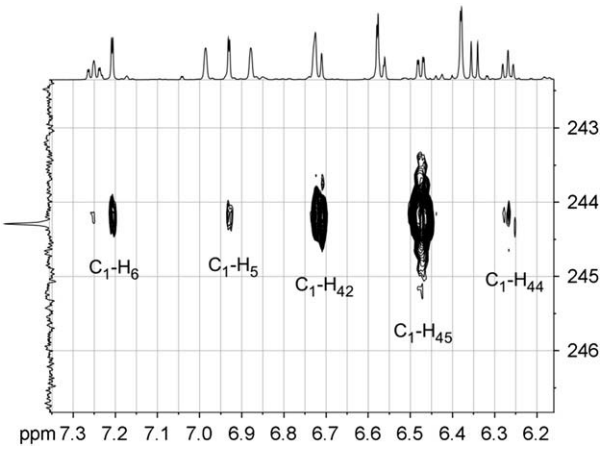


Figure 3. Expanded region of a superposition of two 2D ^{1}H–^{13}C HMBC spectra of Ru-complex **6** in dichloromethane-d_2 at 298 K. The two HMBC experiments are optimized for two different long range couplings ($^nJ_{CH}$=4.0 and 10.0 Hz). The corresponding regions of the 1D 600.13 MHz ^{1}H spectrum and the 1D ^{1}H-decoupled 150.91 MHz ^{13}C spectrum are shown on the top and left edge of the contour plot, respectively. The expanded region shows the most important cross peaks connecting the ^{13}C resonance belonging to C1 (Chart 2) to the ligand I (see Chart 2) ^{1}H resonances.

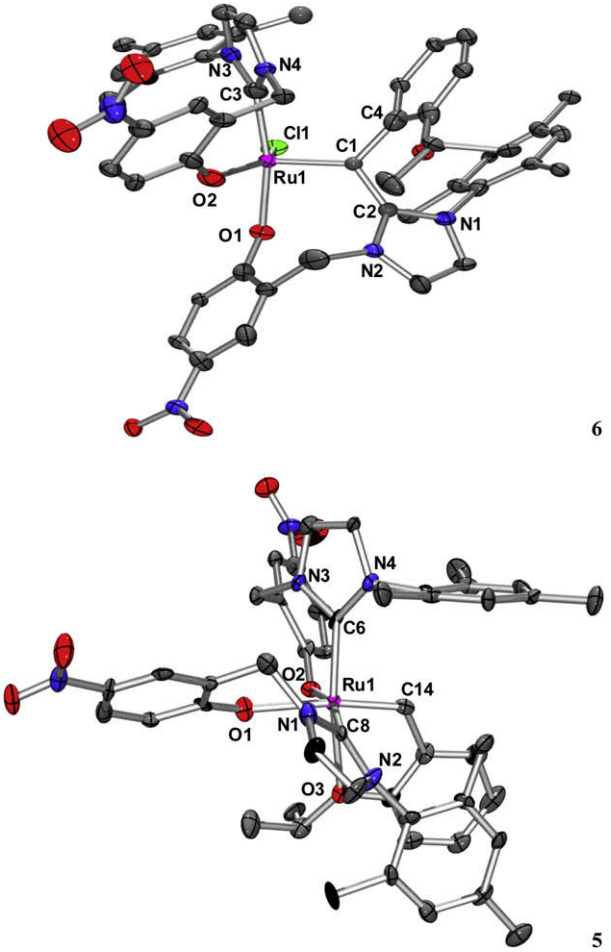


Figure 4. ORTEP diagram of the complexes **5** and **6** with the ellipsoids drawn at 50% probability level. The hydrogens have been removed for clarity. Color coding: C—dark gray, N—blue, O—red, Ru—magenta.

2.7. Single crystal X-ray diffractometer experiments

Several experiments were conducted in order to produce suitable crystals for X-ray diffractometer investigations. Complex **6** was crystallized by slow diffusion at room temperature of *n*-hexane into a concentrated solution of **6** in dichloromethane. Similarly, crystallization of complex **5** was conducted at room temperature by diffusion of *n*-pentane into a concentrated solution of **5** in dichloromethane. Crystals suitable for X-ray diffractometer investigations of both of the complexes **5** and **6** were selected and successfully investigated.

ORTEP diagrams of **5** and **6** are provided in Figure 4. Detailed crystal data and results of the structural refinement are provided in Supplementary data.

2.8. Complex 5

The X-ray diffractometer analysis of complex **5** confirms an octahedral ruthenium alkylidene structures as previously proposed on the basis of MS and NMR analysis. Complex **5** is a rather crowded 18-electron Ru complex having the metal directly connected to three carbon atoms (two NHCs and one alkylidene group) and three oxygen atoms (two covalent and one dative). Interestingly, oxygen-based ligands and carbene ligands are clustered together avoiding location in *trans*-positions to each other. Consequently, carbenes and oxygens are situated in *trans*–positions to each other. The analysis of their bond distances suggests the following order of *trans*-influence: alkylidene >>NHC>4-NO_2-phenoxide>ether. As a consequence of the lower *trans*-influence and the steric congestion present in complex **5**, the three Ru–O bond distances are particularly long, see Table 1. The largest deviation is seen for the covalent Ru1–O1 bond distance that, situated in *trans*-position to the alkylidene group, has a distance (224 pm) typical for a Ru–O dative bond.

Table 1
Selected bond distances and bond angles for complex **5**

Bond distances [pm]		Bond angles [deg.]	
Ru1–C6	200	N1–C8–N2	103
Ru1–C8	207	N3–C6–N4	103
Ru1–C14	184	O1–Ru1–C8	85
Ru1–O1	209	O1–Ru1–C14	172
Ru1–O2	224	O2–Ru1–C6	95
Ru1–O3	238	O2–Ru1–C8	165
C6–N3	139	O3–Ru1–C6	167
C6–N4	136	O3–Ru1–C14	78
C8–N1	136	O2–Ru1–O1	84
C8–N2	138	C6–Ru1–C14	94
C4–C14	147	C8–Ru1–C14	95

2.9. Complex 6

X-ray analysis of complex **6** confirms the extraordinary structure of an imidazolium alkylidene complex. Complex **6** is the first observation of a metal alkylidene group formally substituted by an *N*-heterocyclic carbene[32] and is structurally related to previously described phosphonium-substituted metal alkylidenes[50,51] and metal-substituted ketenes.[52]

The distance between the metal and the alkylidene carbon is 1.855 Å, which is slightly longer than for a double bond, while the distance between the alkylidene carbon and the NHC carbon is 1.479 Å, which is slightly shorter than a C(sp^2)–C(sp^2) single bond, see Table 2. The geometrical features of the NHC ring are in between those of the imidazolium salt **2a** and the corresponding *N*-heterocyclic carbene coordinated to silver or ruthenium, see Chart 3 and Table 3. Previous theoretical investigations conducted by our group[32] reveled that the NHC ring, that is bonded to the alkylidene carbon should be classified as an imidazolium salt.

Table 2
Selected bond distances and bond angles for complex **6**

Bond distances [pm]		Bond angles [deg.]	
Ru1–C1	186	Cl1–Ru1–O2	148
C1–C2	148	Cl1–Ru1–C1	100
C1–C4	150	Cl1–Ru1–C3	93
Ru1–Cl1	232	N1–C2–N2	106
Ru1–O2	201	N3–C3–N4	103
Ru1–O1	211	C2–C1–C4	114
Ru1–C3	201	C3–Ru1–O1	169
C2–N1	136	C3–Ru1–C1	97
C2–N2	134	O1–Ru1–C1	94
C3–N3	137	O1–Ru1–O2	87
C3–N4	136	Ru1–C1–C4	124

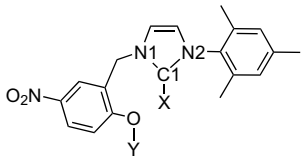


Chart 3. Bidentate ligand framework: X=(H, Ag, Ru, C); Y=(H, Ag, Ru).

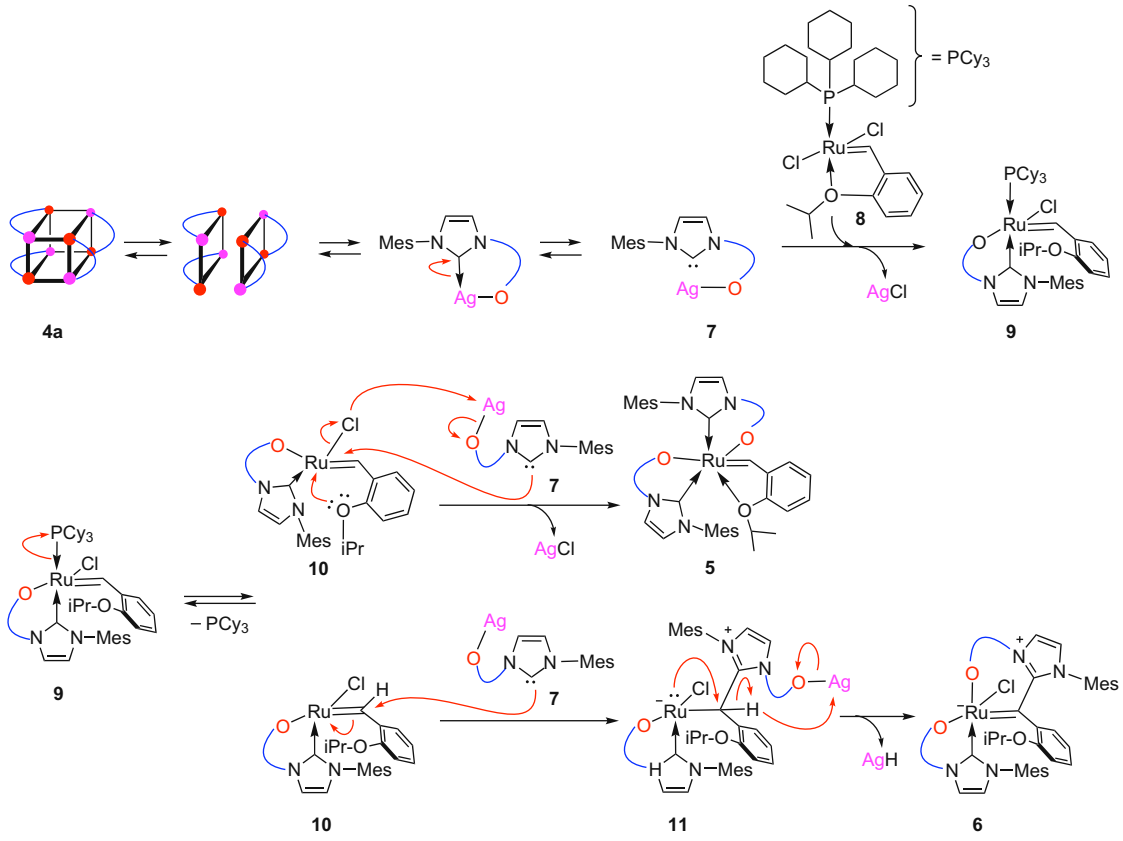
Table 3
Geometrical differences of imidazole ring moiety in the compounds **2a**, **4a**, **5**, and **6**

Structure	N1–C1 [pm]	C1–N2 [pm]	∠ N1–C1–N2 [°]
2a	133	134	108
4a (Bound to Ag1)	135	135	104
4a (Bound to Ag2)	135	136	104
5 (Equatorial)	136	138	103
5 (Axial)	139	136	103
6 (Ligand I)	134	137	106
6 (Ligand II)	136	137	103

2.10. Reaction mechanism

A proposal for a reaction mechanism leading to the Ru complexes **5** and **6** is provided in Scheme 4. The first step involves dissociation of the Ag–O cubane cluster **4a** under the formation of the reactive intermediate, the free NHC-carbene **7**, which in the following operates as the transmetallating species exchanging silver with ruthenium under the production of the intermediate Ru-complex **9** and equimolar quantities of AgCl, or (μ_2-chloro)(tricyclohexylphosphine)silver as a side-product, a product we previously have identified in similar substitution reactions.[30] The intermediate Ru-complex **9** dissociates into the 14-electron complex **10** and the free dative phosphine ligand PCy_3. The 14-electron complex **10** can react in two distinct ways, namely (1) by a nucleophilic attack of a second carbene reactive intermediate **7** on the Ru atom, or (2) by a nucleophilic attack on the alkylidene carbon providing the intermediate complex **11**. Pathway (1) then proceeds in a similar manner as seen in the first transmetallation step, but this time with the 14-electron complex **10** instead of the Hoveyda–Grubbs first generation catalyst **8**. The subsequent step of pathway (2) involves a hydride loss from **9** and the coordination of the aryloxy group to ruthenium providing the novel complex **6**.

As mentioned above, the presence of tetrahydrofuran alone or in mixture with other solvents appears indispensable in order to obtain the Ru complex **6** (following pathway 2). An explanation for this might be that the presence of a coordinating solvent such as



Scheme 4. Proposed reaction mechanism of reaction leading to Ru complexes **5** and **6**.

tetrahydrofuran may obstruct a nucleophilic attack of the NHC **7** on the Ru metal, and thus render a nucleophilic attack on the alkylidene carbon more probable.

The discovery that NHC can attack the alkylidene carbon constitutes another 'non-innocent' behavior of NHCs[53] and may have important implications in olefin metathesis. For example this can suggest new routes to deactivation or decomposition of olefin metathesis catalysts coordinated by NHCs and may also explain the low yields sometimes observed in the synthesis of ruthenium alkylidene complexes coordinated by NHC ligands.[20] Finally imidazolium alkylidenes could find applications in novel olefin metathesis catalysts, as found for the phosphonium alkylidenes.[51]

2.11. Catalytic activity in RCM reactions

The complexes **5** and **6** were investigated as olefin metathesis catalyst (1 mol %) in ring closing metathesis using the standard reagent diethyl diallylmalonate (DEDAM) as the substrate. The trials were conducted using either toluene or the ionic solvent 1-ethyl-3-methylimidazolium hexafluorophosphate as reaction medium. The reactions were conducted over a period of 16 h at slightly elevated temperatures (80 °C and 65 °C, respectively). The reaction products were analyzed by means of ^{1}H NMR and revealed that complex **5** is inactive as catalyst, while complex **6** shows a very low activity (providing 0.4% of RCM product) when using 1-ethyl-3-methylimidazolium hexafluorophosphate as reaction medium. The inactivity of the Ru-complex **5** may appear somewhat unexpected since Hermann and co-workes[54] previously have reported catalytic activity for bis-NHC-Ru-alkylidenes. We believe that the absent catalytic activity of complex **5** is mainly due to the chelating effect of the two bi-dentate NHC ligands, which contribute to a substantially lowering of the entropic effect associated to the dissociation of the NHC donor. Moreover, Schrock's empirical rule states that the active species of any olefin metathesis catalyst should be four-coordinated, thus in order to fullfil this requirement the complex **5**, that is a hexacoordinated Ru-alkylidene need to dissociate concurrently two donating groups in order to become an active catalyst.

3. Conclusion

The present investigation has demonstrated the synthesis of a novel NHC–Ag(I) complex **4a**, and its atypical reaction with Hoveyda–Grubbs first generation catalyst **8**. The reaction of **4a** with **8** can follow two distinct mechanistic pathways to provide the complexes **5** and **6**, respectively. The reaction leading to complex **6** represents an unprecedented reaction pathway.

Finally complex **6** shows a very low but detectable olefin metathesis activity, while complex **5** shows no such activity.

4. Experimental section

4.1. General

*4.1.1. 1-(2,4,6-Trimethylphenyl)-1H-imidazole (**3**)*

Glacial acetic acid (10 mL), aqueous formaldehyde (3 mL), and aqueous glyoxal (4.6 mL) were transferred to a round bottom flask (50 mL) and heated at 70 °C. A solution of glacial acetic acid (10 mL), ammonium acetate in water (3.08 g in 2 mL), and mesitylamine (5.6 mL) was then added dropwise over a period of 30 min. The solution was continuously stirred and heated at 70 °C for 18 h. The reaction mixture was then cooled to room temperature, and the reaction mixture was added dropwise to a stirred solution of $NaHCO_3$ (29.4 g) in water (300 mL) when the target product precipitated. The precipitate was isolated on a filter frit, washed with water (3×20 mL), and air dried to obtain a brown–yellow solid (5.18 g). The crude product was re-crystallized by using

ethyl acetate, to obtain target product 1-(2,4,6-trimethylphenyl)-1*H*-imidazole in a yield of 69.7%.

Mp=112–114 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ=7.43 (m, 1H), 7.23 (m, 1H), 6.97 (m, 2H), 6.89 (m, 1H), 2.34 (s, 3H), 1.99 (s, 6H); ^{13}C NMR[55] ($CDCl_3$, 400 MHz): δ=138.9, 137.6, 135.6, 133.5, 129.7, 129.1, 120.2, 21.1, 17.4; IR ν [cm^{-1}]: 3114, 3094, 2970, 2954, 2921, 2860, 1642, 1594, 1499, 1465, 1446, 1379, 1314, 1284, 1237, 1112, 1097, 1068, 1035, 1017, 971, 937, 907, 871, 816, 783, 737, 671.

4.1.2. 3-(2-Hydroxy-5-nitrobenzyl)-1-(2,4,6-trimethylphenyl) imidazolium bromide (**2a**)

1-(2,4,6-Trimethylphenyl)-1*H*-imidazole (0.61 g, 3.3 mmol) and 2-hydroxy-5-nitrobenzyl bromide (0.76 g, 3.3 mmol) was dissolved in toluene (8 mL) and refluxed for 18 h. During the course of the reaction, a pale yellow solid precipitated in the reaction mixture. After the reaction mixture was cooled to room temperature, the solid was isolated on a filter placed in a Büchner funnel, washed with methyl-*tert*-butyl ether (3×10 mL) and dried under vacuum to obtain a yield of 98.5% (1.35 g). The imidazolium salt was successively crystallized by slow diffusion of diethyl ether into a concentrated solution of **2a** in ethanol.

Mp=276–278 °C (dec); ^{1}H NMR ((CD_3)$_2$SO, 400 MHz): δ=11.83 (br, 1H), 9.59 (s, 1H), 8.39 (s, 1H), 8.21 (d, *J*=8.6 Hz, 1H), 8.06 (s, 1H), 7.93 (s, 1H), 7.20–7.07 (m, 3H), 5.56 (s, 2H), 2.32 (s, 3H), 2.01 (s, 6H); ^{13}C NMR ((CD_3)$_2$SO, 400 MHz): δ=162.4, 140.3, 139.4, 138.2, 134.3, 131.2, 129.2, 127.1, 126.9, 124.1, 123.3, 121.4, 115.9, 48.3, 20.6, 16.9; IR ν [cm^{-1}]: 3161, 3067, 2943, 1617, 1593, 1567, 1549, 1524, 1495, 1437, 1388, 1340, 1281, 1197, 1154, 1133, 1118, 1092, 1068, 935, 925, 897, 856, 843, 831, 820, 790, 770, 753, 747, 732, 700, 664; MS (ESI): *m*/*z*: 338 [417−Br]$^+$. Anal. Calcd for $C_{19}H_{20}N_3O_3Br$: C, 54.56; H, 4.82; N, 10.05; Found: C, 54.84; H, 4.76; N, 9.88.

4.1.3. Synthesis of the silver complex (**4a**)

3-(2-Hydroxy-5-nitrobenzyl)-1-(2,4,6-trimethylphenyl) imidazolium bromide (500 mg, 1.195×10^{-3} mol) and silver (I) oxide (569.4 mg, 2.457×10^{-3} mol) were added to a round bottom flask equipped with a cooler. Then, dried THF and benzene (8.5 mL+8.5 mL), and molecular sieves 4 Å (1.115 g) were added. The reaction mixture was stirred at reflux for 3 h, cooled to room temperature and diluted with CH_2Cl_2 (80 mL). The mixture was then filtered through a pad of Celite (2/5 cm, w/l), that was then washed with CH_2Cl_2 (3×20 mL). The solvent was removed under reduced pressure to provide a yellow solid, the silver complex in a yield of ≈65% (342.5 mg).

Mp 178–180 °C (dec); ^{1}H NMR ($CDCl_3$, 600 MHz): δ=8.14 (s, 1H), 7.76 (d, *J*=7.9 Hz, 1H), 7.36 (s, 1H), 7.00 (s, 2H), 6.96 (s, 1H), 5.80 (d, *J*=7.9 Hz, 1H), 5.23 (s, 2H), 2.39 (s, 3H), 1.93 (s, 6H). ^{13}C NMR ($CDCl_3$, 500 MHz)[56]: δ=174.6, 139.7, 136.4, 135.2, 134.6, 129.3, 127.5, 127.0, 124.4, 122.0, 121.7, 121.3, 50.7, 21.3, 18.0; IR ν [cm^{-1}]: IR ν: 3127, 2920, 1589, 1566, 1469, 1437, 1408, 1278, 1253, 1237, 1188, 1165, 1151, 1085, 1031, 927, 854, 835, 820, 790, 768, 735, 706, 679, 652; Anal. Calcd for $C_{76}H_{72}O_{12}N_{12}Ag_4$: C, 51.37; H, 4.08; N, 9.46. Found: C, 50.49; H, 3.81; N, 8.92.

4.1.4. Complex **5**

70 mg (1.17×10^{-4} mol) of Hoveyda first generation catalyst and 58 mg (1.31×10^{-4} mol) of silver complex **4a** were added to a 25 mL Schlenk flask. The flask was evacuated and back filled with argon. Then 2.5 mL of dry toluene and 2.5 mL of dry THF were added to the Schlenk flask under argon. The mixture was stirred at 55 °C for 2.5 h, a further 46 mg of silver complex (1.03×10^{-4} mol) then added and the reaction was continued at the same temperature for another 2.5 h, after which the mixture was cooled to room temperature and the solvent removed under reduced pressure. The residue, a dark-brown solid was passed through a silica gel column using diethyl ether/hexanes (9:1) as eluent. The green fraction (complex **5**) as well the orange fraction (complex **6**) were collected and concentrated and afforded 43 mg (40.2%) and 3.2 mg (2.8%), respectively.

Mp 190–192 °C (dec); ^{1}H NMR (CD_2Cl_2, 500 MHz): δ=15.90 (s, 1H), 8.21 (d, *J*=3.0 Hz, 1H), 8.03 (dd, *J*=9.2, 3.0 Hz, 1H), 7.97 (d, *J*=3.0 Hz, 1H), 7.71 (dd, *J*=9.3, 3.0 Hz, 1H), 7.42–7.37 (m, 1H), 7.31 (d, *J*=13.6 Hz, 1H), 7.28 (d, *J*=2.1 Hz, 1H), 7.21 (d, *J*=1.9 Hz, 1H), 7.02 (s, 1H), 6.81–6.91 (m, 4H), 6.67 (d, *J*=9.2 Hz, 1H), 6.60 (d, *J*=2.1 Hz, 1H), 6.37 (d, *J*=1.9 Hz, 1H), 6.21 (s, 1H), 6.08 (s, 1H), 6.04 (d, *J*=9.3 Hz, 1H), 6.01 (d, *J*=13.8 Hz, 1H), 5.78 (septet, *J*=6.7 Hz, 1H), 4.50 (d, *J*=13.8 Hz, 1H), 4.40 (d, *J*=13.6 Hz, 1H), 2.36 (s, 3H), 1.80 (s, 3H), 1.79 (s, 3H), 1.64 (d, *J*=6.7 Hz, 3H), 1.56 (d, *J*=6.7 Hz, 3H), 1.48 (s, 3H), 1.04 (s, 6H); ^{13}C NMR (CD_2Cl_2, 125.8 MHz): δ=297.9 (d, *J*=9.8), 179.0, 177.7, 176.4, 173.1, 154.5, 146.0, 140.0, 138.6, 136.9, 136.3, 135.3, 135.2, 134.2, 133.6, 133.5, 130.1, 129.0, 128.9, 128.5, 127.7, 126.7, 126.5, 126.4, 125.9, 125.4, 125.2, 124.4, 123.6, 123.4, 121.9, 121.8, 120.4, 117.9, 77.8, 52.3, 51.2, 22.7, 21.9, 21.1, 20.9, 18.3, 17.5, 16.75, 16.66; IR (film)3182, 3131, 2963, 2922, 2857, 1935, 1767, 1591, 1563, 1476, 1441, 1404, 1376, 1348, 1272, 1183, 1170, 1149, 1124, 1110, 1085, 1034, 1018, 965, 932, 836, 752, 710, 702, 686, 660 cm^{-1}. MS (EI) *m*/*z*: 922. HRMS (ESIpos) *m*/*z* 923.270932 (M+H)+; calcd for $C_{48}H_{49}N_6O_7Ru$: 923.272688.

4.1.5. Complex **6**

Hoveyda first generation catalyst (135 mg, 2.25×10^{-4} mol) and silver complex **4a** (200 mg, 4.45×10^{-4} mol) were transferred to a 25 mL Schlenk flask. The flask was evacuated and back filled with argon. Then 6 mL of dry THF were added to the Schlenk flask under argon. The mixture was stirred at reflux for 7 h, the mixture cooled to room temperature and the solvent removed under reduced pressure. The residue, a dark-brown solid was passed through a silica gel column using diethyl ether/hexanes (7:3) as eluent. The green fraction (complex **5**) as well as the orange fraction (complex **6**) were collected and concentrated and afforded, respectively, 13.2 mg (6.3%) and 25.5 mg (11.9%).

Mp 193–195 °C (dec); ^{1}H NMR (CD_2Cl_2, 500 MHz): δ=8.05–8.00 (m, 2H), 7.83 (d, *J*=2.9 Hz, 1H), 7.79 (dd, *J*=9.1, 2.9 Hz, 1H), 7.25 (ddd, *J*=8.5, 7.3, 1.8 Hz, 1H), 7.20 (d, *J*=2.0 Hz, 1H), 6.99 (br s, 1H), 6.93 (d, *J*=2.0 Hz, 1H), 6.88 (br s, 1H), 6.75–6.69 (m, 2H), 6.55–6.59 (m, 2H), 6.47 (dd, *J*=7.6, 1.8 Hz, 1H), 6.38 (d, *J*=2.0 Hz, 1H), 6.34 (d, *J*=9.1 Hz, 1H), 6.27 (td, *J*=7.3, 0.8 Hz, 1H) 6.11 (d, *J*=14.1 Hz, 1H), 5.56 (d, *J*=14.1 Hz, 1H), 4.55 (septet, *J*=6.0 Hz, 1H), 4.48 (d, *J*=14.1 Hz, 1H), 3.80 (d, *J*=14.1 Hz, 1H), 2.35 (s, 3H), 2.16 (s, 6H), 1.85 (s, 3H), 1.59 (s, 3H), 1.47 (s, 3H), 1.37 (d, *J*=6.0 Hz, 3H), 1.22 (d, *J*=6.0 Hz, 3H); ^{13}C NMR (CD_2Cl_2, 125.8 MHz): δ=244.3, 179.9, 172.8, 171.5, 161.6, 149.1, 145.6, 140.2, 138.7, 138.3, 138.2, 137.7, 135.0, 134.5, 134.3, 133.9, 130.7, 130.5, 129.7, 129.2, 129.1, 128.9, 127.9, 127.0, 126.2, 126.1, 125.6, 125.0, 124.9, 123.1, 123.0, 121.8, 121.7, 120.8, 120.6, 120.5, 111.3, 70.0, 52.2, 49.4, 22.8, 22.1, 21.1, 20.9, 19.0, 18.6, 18.3, 16.8; IR (film)3165, 3126, 3098, 3064, 2963, 2923, 2845, 1593, 1564, 1472, 1439, 1404, 1382, 1278, 1258, 1172, 1153, 1121, 1087, 1016, 957, 932, 903, 867, 837, 792, 751, 732, 710, 697, 666 cm^{-1}. MS (EI) *m*/*z*: 956. HRMS (ESIpos) *m*/*z* 957.231375 (M+H)+; calcd for $C_{48}H_{48}ClN_6O_7Ru$: 957.232952.

4.1.6. NMR Spectroscopy

Sample preparation: A sample of the Ru-complex **6** (≈5 mg) was transferred to a NMR tube (o.d. 5 mm, Wilmad, model 528-PP-7) and dissolved in dichloromethane-d_2.

High-resolution one-dimensional and two-dimensional ^{1}H (600.13 MHz) and ^{13}C (150.91 MHz) NMR spectra were acquired on a Bruker Biospin AVANCE AV600 spectrometer equipped with a narrow bore UltraShield™ Plus magnet. A 5 mm inverse triple resonance (^{1}H, ^{13}C, ^{15}N) CryoProbe with a *z*-gradient coil and cryogenic preamplifier cooling for both the ^{1}H and ^{13}C channels was used. 1D ^{1}H NMR: The spectral width was 7184 Hz, the pulse width

3.2 μs (45 degree flip angle), the recycling delay 2 s, 64 complex points were acquired and 16 transients were averaged. 1D ^{13}C NMR: The spectral width was typically 39,370 Hz, the pulse width 7.4 μs (45 degree flip angle), the recycling delay 2 s, 128 k complex points were acquired and 256 transients were averaged. Broadband ^{1}H composite pulse decoupling was used during the acquisition. Standard 2D gradient-selected (*gs*) DQF-COSY,[57] ^{1}H–^{13}C *gs*-HSQC,[58] ^{1}H–^{13}C *gs*-HMBC[59] and ^{13}C–^{1}H HETCOR[60] experiments were performed. All 2D experiments were performed in the pure-absorption mode except for HMBC and HETCOR for which magnitude mode spectra were recorded. The HSQC and HETCOR experiments were optimized for a 145 Hz one-bond coupling ($^{1}J_{CH}$). Two HMBC spectra were recorded, one was optimized for a 10 Hz long-range coupling ($^{n}J_{CH}$), the other for a 4 Hz coupling. The sample temperature was kept at 298.0 K for all the experiments.

The NMR data were processed and displayed using both Bruker's TopSpin software suite version 1.3 and the general processing program iNMR.[61] The residual ^{1}H signal of the deuterated solvent and ^{13}C solvent signal were used as secondary chemical shift references for ^{1}H (5.32 ppm) and ^{13}C (53.8 ppm), respectively, and the chemical shifts are thus referenced to internal solvent resonances and reported in *parts per million* relative to TMS.

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Supplementary data

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References and notes

1. Herrmann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1291.
2. Arduengo, A. J. *Acc. Chem. Res.* **1999**, *32*, 913.
3. Bourissou, D.; Guerret, O.; Gabbai, F. P.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39.
4. Arnold, P. L.; Liddle, S. T. *Chem. Commun.* **2006**, 3959.
5. Dorta, R.; Stevens, E. D.; Scott, N. M.; Costabile, C.; Cavallo, L.; Hoff, C. D.; Nolan, S. P. *J. Am. Chem. Soc.* **2005**, *127*, 2485.
6. Jacobsen, H.; Correa, A.; Costabile, C.; Cavallo, L. *J. Organomet. Chem.* **2006**, *691*, 4350; Cavallo, L.; Correa, A.; Costabile, C.; Jacobsen, H. *J. Organomet. Chem.* **2005**, *690*, 5407.
7. Herrmann, W. A.; Lobmaier, G. M.; Elison, M. *J. Organomet. Chem.* **1996**, *520*, 231; Liu, C. Y.; Chen, D. Y.; Lee, G. H.; Peng, S. M.; Liu, S. T. *Organometallics* **1996**, *15*, 1055.
8. Zhang, D.; Aihara, H.; Watanabe, T.; Matsuo, T.; Kawaguchi, H. *J. Organomet. Chem.* **2007**, *692*, 234.
9. Aihara, H.; Matsuo, T.; Kawaguchi, H. *Chem. Commun.* **2003**, 2204.
10. Scott, N. M.; Nolan, S. P. *Eur. J. Inorg. Chem.* **2005**, 1815.
11. Cavell, K. J.; McGuinness, D. S. *Coord. Chem. Rev.* **2004**, *248*, 671; Chianese, A. R.; Li, X. W.; Janzen, M. C.; Faller, J. W.; Crabtree, R. H. *Organometallics* **2003**, *22*, 1663.
12. Garrison, J. C.; Youngs, W. J. *Chem. Rev.* **2005**, *105*, 3978.
13. Arnold, P. L.; Rodden, M.; Davis, K. M.; Scarisbrick, A. C.; Blake, A. J.; Wilson, C. *Chem. Commun.* **2004**, 1612; Arnold, P. L.; Rodden, M.; Wilson, C. *Chem. Commun.* **2005**, 1743; Mungur, S. A.; Liddle, S. T.; Wilson, C.; Sarsfield, M. J.; Arnold, P. L. *Chem. Commun.* **2004**, 2738.
14. Zhang, D.; Kawaguchi, H. *Organometallics* **2006**, *25*, 5506.
15. Arduengo, A. J.; Krafczyk, R.; Marshall, W. J.; Schmutzler, R. *J. Am. Chem. Soc.* **1997**, *119*, 3381; Arduengo, A. J.; Tamm, M.; Calabrese, J. C. *J. Am. Chem. Soc.* **1994**, *116*, 3625; Arduengo, A. J.; Dias, H. V. R.; Calabrese, J. C.; Davidson, F. *Inorg. Chem.* **1993**, *32*, 1541; Green, S. P.; Jones, C.; Lippert, K. A.; Mills, D. P.; Stasch, A. *Inorg. Chem.* **2006**, *45*, 7242; Boesveld, W. M.; Gehrhus, B.; Hitchcock, P. B.; Lappert, M. F.; Schleyer, P. V. R. *Chem. Commun.* **1999**, 755; Schafer, A.; Weidenbruch, M.; Saak, W.; Pohl, S. *J. Chem. Soc., Chem. Commun.* **1995**, 1157.
16. Arduengo, A. J.; Tamm, M.; McLain, S. J.; Calabrese, J. C.; Davidson, F.; Marshall, W. J. *J. Am. Chem. Soc.* **1994**, *116*, 7927; Herrmann, W. A.; Munck, F. C.; Artus, G. R. J.; Runte, O.; Anwander, R. *Organometallics* **1997**, *16*, 682; Part 1: Oldham, S. M.; Oldham, W. J.; Scott, B. L.; Schake, A. R.; Costa, D. A.; Smith, W. H. *Abstr. Am. Chem. Soc.* **2001**, *221*, U667; Oldham, W. J.; Oldham, S. M.; Scott, B. L.; Abney, K. D.; Smith, W. H.; Costa, D. A. *Chem. Commun.* **2001**, 1348.
17. Herrmann, W. A.; Kocher, C. *Angew. Chem., Int. Ed.* **1997**, *36*, 2163; Stauffer, S. R.; Lee, S. W.; Stambuli, J. P.; Hauck, S. I.; Hartwig, J. F. *Org. Lett.* **2000**, *2*, 1423; Schoeller, W. W.; Schroeder, D.; Rozhenko, A. B. *J. Organomet. Chem.* **2005**, *690*, 6079; Scholl, M.; Ding, S.; Lee, C. W.; Grubbs, R. H. *Org. Lett.* **1999**, *1*, 953; Bohm, V. P. W.; Gstottmayr, C. W. K.; Weskamp, T.; Herrmann, W. A. *Angew. Chem., Int. Ed.* **2001**, *40*, 3387; Bohm, V. P. W.; Weskamp, T.; Gstottmayr, C. W. K.; Herrmann, W. A. *Angew. Chem., Int. Ed.* **2000**, *39*, 1602; Baratta, W.; Herrmann, W. A.; Rigo, P.; Schwarz, J. *J. Organomet. Chem.* **2000**, *594*, 489; Cetinkaya, B.; Ozdemir, I.; Bruneau, C.; Dixneuf, P. H. *J. Mol. Catal. A: Chem.* **1997**, *118*, L1.
18. McGuinness, D. S.; Cavell, K. J. *Organometallics* **2000**, *19*, 741.
19. Trnka, T. M.; Grubbs, R. H. *Acc. Chem. Res.* **2001**, *34*, 18; Scholl, M.; Trnka, T. M.; Morgan, J. P.; Grubbs, R. H. *Tetrahedron Lett.* **1999**, *40*, 2247.
20. Fürstner, A.; Ackermann, L.; Gabor, B.; Goddard, R.; Lehmann, C. W.; Mynott, R.; Stelzer, F.; Thiel, O. R. *Chem.—Eur. J.* **2001**, *7*, 3236.
21. Grubbs, R. H. *Tetrahedron* **2004**, *60*, 7117; Fürstner, A. *Angew. Chem., Int. Ed.* **2000**, *39*, 3013; Garber, S. B.; Kingsbury, J. S.; Gray, B. L.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2000**, *122*, 8168.
22. Part 1: Miecznikowski, J. R.; Crabtree, R. H. *Abstr. Am. Chem. Soc.* **2004**, *228*, U898; Gillingham, D. G.; Hoveyda, A. H. *Abstr. Am. Chem. Soc.* **2006**, *231*; Hoveyda, A. H.; Schrock, R. R. *Chem.—Eur. J.* **2001**, *7*, 945; Clavier, H.; Coutable, L.; Guillemin, J. C.; Mauduit, M. *Tetrahedron: Asymmetry* **2005**, *16*, 921; Sp. Iss. SI: Clavier, H.; Coutable, L.; Toupet, L.; Guillemin, J. C.; Mauduit, M. *J. Organomet. Chem.* **2005**, *690*, 5237.
23. Peris, E.; Crabtree, R. H. *Coord. Chem. Rev.* **2004**, *248*, 2239; Perry, M. C.; Burgess, K. *Tetrahedron: Asymmetry* **2003**, *14*, 951; Lee, Y.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2006**, *128*, 15604; Van Veldhuizen, J. J.; Gillingham, D. G.; Garber, S. B.; Kataoka, O.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2003**, *125*, 12502.
24. Van Veldhuizen, J. J.; Garber, S. B.; Kingsbury, J. S.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2002**, *124*, 4954.
25. Wang, Z. G.; Sun, H. M.; Yao, H. S.; Shen, Q.; Zhang, Y. *Organometallics* **2006**, *25*, 4436; Chen, M. Z.; Sun, H. M.; Li, W. F.; Wang, Z. G.; Shen, Q.; Zhang, Y. *J. Organomet. Chem.* **2006**, *691*, 2489.
26. Wang, Z. G.; Sun, H. M.; Yao, H. S.; Yao, Y. M.; Shen, Q.; Zhang, Y. *J. Organomet. Chem.* **2006**, *691*, 3383.
27. Danopoulos, A. A.; Tulloch, A. A. D.; Winston, S.; Eastham, G.; Hursthouse, M. B. *Dalton Trans.* **2003**, 1009; Danopoulos, A. A.; Winston, S.; Motherwell, W. B. *Chem. Commun.* **2002**, 1376; Pugh, D.; Danopoulos, A. A. *Coord. Chem. Rev.* **2007**, *251*, 610; Tulloch, A. A. D.; Danopoulos, A. A.; Winston, S.; Kleinhenz, S.; Eastham, G. *J. Chem. Soc., Dalton Trans.* **2000**, 4499; Tulloch, A. A. D.; Winston, S.; Danopoulos, A. A.; Eastham, G.; Hursthouse, M. B. *Dalton Trans.* **2003**, 699.
28. Van Veldhuizen, J. J.; Campbell, J. E.; Giudici, R. E.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2005**, *127*, 6877.
29. Occhipinti, G.; Bjørsvik, H.-R.; Jensen, V. R. *J. Am. Chem. Soc.* **2006**, *128*, 6952.
30. Occhipinti, G.; Jensen, V. R.; Bjørsvik, H.-R. *J. Org. Chem.* **2007**, *72*, 3561.
31. Occhipinti, G.; Bjørsvik, H.-R.; Törnroos, K. W.; Jensen, V. R. *Organometallics* **2007**, *26*, 5803.
32. Occhipinti, G.; Bjørsvik, H.-R.; Törnroos, K. W.; Fürstner, A.; Jensen, V. R. *Organometallics* **2007**, *26*, 4383.
33. Arduengo, A.J. III; Gentry, F.P. Jr.; Taverkere, P.K.; Simmons, H.E., (E.I. Du Pont de Nemours & Co., USA). US Patent 6,177,575, 2001.
34. Schwab, P.; France, M. B.; Ziller, J. W.; Grubbs, R. H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2039.
35. Kingsbury, J. S.; Harrity, J. P. A.; Bonitatebus, P. J.; Hoveyda, A. H. *J. Am. Chem. Soc.* **1999**, *121*, 791.
36. Chang, S.; Jones, L.; Wang, C. M.; Henling, L. M.; Grubbs, R. H. *Organometallics* **1998**, *17*, 3460.
37. There is still a dispute as to whether the formal oxidation state of ruthenium is +2 or +4. Based on DFT calculations, our conclusion is that the correct formal oxidation state of Ru is +4 in such complexes, see reference 29 above.
38. Nielsen, D. J.; Cavell, K. J.; Skelton, B. W.; White, A. H. *Inorg. Chim. Acta* **2002**, *327*, 116; Wang, X.; Liu, S.; Weng, L. H.; Jin, G. X. *Organometallics* **2006**, *25*, 3565.
39. Wang, X.; Liu, S.; Jin, G. X. *Organometallics* **2004**, *23*, 6002.
40. Wang, H. M. J.; Lin, I. J. B. *Organometallics* **1998**, *17*, 972.
41. Deng, L.; Holm, R. H. *J. Am. Chem. Soc.* **2008**, *130*, 9878.
42. Schwab, P.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1996**, *118*, 100–110; Ritter, T.; Day, M. W.; Grubbs, R. H. *J. Am. Chem. Soc.* **2006**, *128*, 11768.
43. ^{1}H NMR of the reaction mixture is enclosed in the supporting information.
44. Nguyen, S. T.; Johnson, L. K.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1992**, *114*, 3974.
45. Initial ^{1}H NMR studies reveled signals in the expected range of chemical shift for an alkylidene. A complete structure elucidation was not conducted for those substances.
46. Values reported in literature are between 211 and 446 ppm, see for example: Hong, S. H.; Day, M. W.; Grubbs, R. H. *J. Am. Chem. Soc.* **2004**, *126*, 7414.
47. DQF-COSY: Double quantum filtrated correlation spectroscopy. See for example Berger, S.; Braun, S. *200 and More NMR Experiments: A Practical Course*; Wiley: New York, NY, 2004.
48. HSQC/HETCOR: Heteronuclear single quantum coherence/Heteronuclear correlation. See for example Berger, S.; Braun, S. *200 and More NMR Experiments: A Practical Course*; Wiley: New York, NY, 2004.
49. HMBC: Heteronuclear multiple bond correlations. See for example Berger, S.; Braun, S. *200 and More NMR Experiments: A Practical Course*; Wiley: New York, NY, 2004.

50. Kreissl, F. R.; Friedrich, P. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 543.
51. Romero, P. E.; Piers, W. E.; McDonald, R. *Angew. Chem., Int. Ed.* **2004**, *43*, 6161; Dubberley, S. R.; Romero, P. E.; Piers, W. E.; McDonald, R.; Parvez, M. *Inorg. Chim. Acta* **2006**, *359*, 2658.
52. Fischer, E. O.; Schubert, U. *J. Organomet. Chem.* **1975**, *100*, 59; Fischer, E. O.; Meineke, E. W.; Kreissl, F. R. *Chem. Ber. Recl.* **1977**, *110*, 1140; Kreissl, F. R.; Frank, A.; Schubert, U.; Lindner, T. L.; Huttner, G. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 632.
53. Becker, E.; Sting, V.; Dazinger, G.; Mereiter, K.; Kirchner, K. *Organometallics* **2007**, *26*, 1531; Danopoulos, A. A.; Tsoureas, N.; Green, J. C.; Hursthouse, M. B. *Chem. Commun.* **2003**, 756; Galan, B. R.; Gembicky, M.; Dominiak, P. M.; Keister, J. B.; Diver, S. T. *J. Am. Chem. Soc.* **2005**, *127*, 15702; Crudden, C. M.; Allen, D. P. *Coord. Chem. Rev.* **2004**, *248*, 2247; McGuinness, D. S.; Cavell, K. J. *Organometallics* **2000**, *19*, 4918.
54. Weskamp, T.; Schattenmann, W. C.; Spiegler, M.; Herrmann, W. A. *Angew. Chem., Int. Ed.* **1998**, *37*, 2490.
55. Altman, R. A.; Koval, E. D.; Buchwald, S. L. *J. Org. Chem.* **2007**, *72*, 6190.
56. Carbene peaks (after around 20.000 scans) are invisible. One reason for this could be the low solubility of this complex in $CDCl_3$ or other suitable NMR solvents.
57. Ancian, B.; Bourgeois, I.; Dauphin, J.-F.; Shaw, A. A. *J. Magn. Reson.* **1997**, *125*, 348.
58. Kay, L. E.; Keifer, P.; Saarinen, T. *J. Am. Chem. Soc.* **1992**, *114*, 10663.
59. Wilker, W.; Leibfritz, D.; Kerssebaum, R.; Bermel, W. *Magn. Reson. Chem.* **1993**, *31*, 287.
60. Bax, A.; Morris, G. A. *J. Magn. Reson.* **1981**, *42*, 501.
61. Nucleomatica; http://www.inmr.net/index.html.