Immobilisation of Ru-based metathesis catalysts and related aspects of olefin metathesis
Nieczypor, P.

Citation for published version (APA):

General rights
It is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), other than for strictly personal, individual use, unless the work is under an open content license (like Creative Commons).

Disclaimer/Complaints regulations
If you believe that digital publication of certain material infringes any of your rights or (privacy) interests, please let the Library know, stating your reasons. In case of a legitimate complaint, the Library will make the material inaccessible and/or remove it from the website. Please Ask the Library: http://uba.uva.nl/en/contact, or a letter to: Library of the University of Amsterdam, Secretariat, Singel 425, 1012 WP Amsterdam, The Netherlands. You will be contacted as soon as possible.
Chapter 4

Adamantyl-Substituted

N-Heterocyclic Carbene Ligands in

Second Generation Grubbs-Type Metathesis Catalysts

Keywords: Ru carbenes / Adamantyl / Imidazolium / Metathesis

Abstract: The N-heterocyclic carbene (NHC) ligands \( \text{H}_2\text{Ad} \) (1,3-di(1-adamantyl)-4,5-dihydroimidazol-2-ylidene) and \( \text{H}_2\text{AdMes} \) (1-(1-adamantyl)-3-mesityl-4,5-dihydroimidazol-2-ylidine) were prepared and treated with \([\text{RuCl}_2(=\text{CHPh})(\text{PCy}_3)_2]\) (1). While \( \text{H}_2\text{IAd} \) failed to react with 1, \( \text{H}_2\text{AdMes} \) readily produced \([\text{RuCl}_2(=\text{CHPh})(\text{H}_2\text{AdMes})(\text{PCy}_3)]\) (9). Only a single isomer of 9 was formed, this being that with the mesityl ring situated above the benzyldene moiety, as confirmed by an X-ray structure. Complex 9 was found to be only a very poor olefin metathesis catalyst, likely a consequence of the excessive steric crowding imparted by the 1-adamantyl moiety towards the position trans to the benzyldiene group. Additionally, a crystal structure of a phosphine-free, dinuclear analogue of 9 is also presented.
4.1 Introduction

The utility of olefin metathesis continues to attract interest with more and more chemists adopting this powerful carbon-carbon double-bond breaking/making reaction for various applications. The ruthenium-based metathesis catalyst systems, particularly the first- and second generation Grubbs metathesis catalysts (1 and 2a), are enjoying considerable popularity, a result of their relatively high activity, ease of use and ready commercial availability.

While the most widely used second generation metathesis catalysts 2a (containing the H2IMes ligand, H2IMes = 1,3-dimesityl-4,5-dihydroimidazol-2-ylidene) and its unsaturated relative 3a (containing the IMes ligand, IMes = 1,3-dimesitylimidazol-2-ylidene) both debuted in 1999, only relatively few articles have since appeared on the effects of the modification of the N-heterocyclic carbene (NHC) component of the catalysts. Noteworthy contributions, where the NHC was varied from the seemingly de facto dimesityl systems, include studies on the activity of the 2,6-diisopropylphenyl variants 2b and 3b as well as efforts at creating enantioselectivity for ring closing metathesis, e.g. the second generation Grubbs-type architectures 4a-d and the Hoveyda-type chiral system 4e.

Additionally, the preparation of a range of mainly mixed mesityl/alkyl NHC analogues of 3a, e.g. 4f-m, and their reactivity in ring closing metathesis (RCM), self-metathesis and enyne metathesis (by IR thermography) was explored. Complex 4n was shown to be a useful catalyst for preparation of cyclic polymers of particular physical properties via ring opening metathesis polymerisation (ROMP) of cis-cyclooctene without the need of application of high dilution reaction conditions.
This relative paucity of research is somewhat surprising because at this time no definitive comparative study has been carried out that suggests that the dimesityl-substituted NHC ligands are necessarily the best choice for optimum metathesis activity in all reactions. Indeed, in our research group it was shown that the 2,6-diisopropylphenyl-substituted complex 2b (containing the H$_2$IPr ligand, H$_2$IPr = 1,3-bis-(2,6-diispropylphenyl)-4,5-dihydroimidazol-2-ylidene) displays considerably superior activity than 2a for the metathesis of terminal olefins. Similarly, Fürstner et al. found that the variation of the NHC ligands in 3a can have a significant effect on the activity of the resulting catalysts, and that none of the tested catalysts was superlative for all substrates.

We were intrigued by these results and wished to examine the metathesis activity of catalysts incorporating other NHC ligands. Of particular interest were the recent accounts of an immobilised second generation ruthenium metathesis catalyst with a di(1-adamantyl)-substituted NHC ligand (5) reported by Buchmeiser et al.

In these articles no efforts toward the characterisation of the proposed complex were reported nor the preparation of homogeneous analogues. We found this latter point particularly surprising, since the related unsaturated free NHC, 1,3-di(1-adamantyl)imidazol-2-ylidene (IAd), is both easy to prepare and very stable in solution. It seemed to us that the problem may lie in the ligand displacement reaction with 1, as opposed to the instability of any formed NHCs or their resulting ruthenium complexes.
The replacement of the currently ubiquitous mesityl-substituted NHC ligand with a 1-adamantyl-substituted one offers a number of potential activity enhancements. First, while the mesityl group, being flat, is bulky in only two dimensions, the adamantyl is bulky in three dimensions. This extra bulk may induce more rapid dissociation of the phosphine ligand, an essential step for the initiation of the “precatalyst” to the four-coordinate 14-electron metathesis active species. Furthermore, the greater steric bulk may also provide greater shielding of the metal centre, possibly further hindering unfavourable decomposition reactions that lead to catalytic death. Second, the aliphatic adamantyl group is more electron-donating than the aromatic mesityl, which should make adamantyl-substituted NHCs slightly better σ-donors than the mesityl analogue. The increased σ-donation of an NHC ligand over phosphines is considered the main reason for the higher activity of the second generation catalyst systems relative to their first generation counterparts. With these points in mind, we decided to further explore the prospect of utilising NHC ligands incorporating the 1-adamantyl moiety for use in metathesis.

4.2 Results and Discussion

4.2.1 Synthesis of Ligand Precursors

We resolved to concentrate exclusively on the saturated (4,5-dihydroimidazol-2-ylidene) ligand class for three reasons. First, Nolan et al. have found that IAd is effectively less donating than tricyclohexylphosphine (PCy3), which might be anticipated to complicate the ligand substitution of the starting material 1, although the low lability of NHC ligands relative to phosphines may alleviate this problem. Secondly, it has been found that catalyst 3a is considerably less active (with respect to turnover numbers) than 2a for the metathesis of simple olefins. This observed difference in activity can only be attributed to the saturated (in 2a) versus unsaturated (in 3a) NHC portion of the complexes, since 2a and 3a are otherwise identical. Third, Buchmeiser reported on the di(1-adamantyl)-substituted complex 5, which is based on the saturated H2IAd (H2IAd = 1,3-di(1-adamantyl)-4,5-dihydroimidazol-2-ylidene) framework, providing literature precedence.

Surprisingly, while IAd is very well known and even commercially available, the saturated analogue H2IAd has, to the best of our knowledge, not been previously reported. Naturally, we initially attempted to synthesise the H2IAd ligand precursor, 1,3-di(1-adamantyl)-4,5-dihydroimidazolinium chloride (6d, Scheme 1), following the now standard protocol developed by Arduengo et al. However, all of these attempts were unsuccessful. Therefore, a slightly different strategy was developed that retains the advantages of the Arduengo methodology in that it requires only inexpensive reagents and is practical for large scale synthesis while providing increased generality and flexibility (Scheme 1).
ADAMANTYL-SUBSTITUTED N-HETEROCYCLIC CARBENE LIGANDS
IN SECOND GENERATION GRUBBS-TYPE METATHESIS CATALYSTS

\[
\text{R-}N^+\text{R'} = \text{SCl}_2
\]

6a \( R = \text{Ad} \) (not isolated)
7a \( R = \text{Mes} \)
6b \( R, R' = \text{Ad} \)
7b \( R = \text{Mes}, R' = \text{Ad} \)

de
d
6d \( R, R' = \text{Ad} \)
7d \( R = \text{Mes}, R' = \text{Ad} \)
6c \( R, R' = \text{Ad} \)
7c \( R = \text{Mes}, R' = \text{Ad} \)

**Scheme 1.** Synthetic procedures towards symmetrical, 6d, and unsymmetrical, 7d, saturated NHC ligands.

Following this method, the desired compound 6d could be obtained in moderate yield by reaction of oxalyl chloride with two equivalents of 1-adamantanamine, followed by reduction and cyclisation. For comparison, we also wished to prepare the mixed mesityl/1-adamantyl NHC precursor 1-(1-adamantyl)-3-mesityl-4,5-di-hydroimidazolium chloride (7d) as a source of H2IAdMes (H2IAdMes = 1-(1-adamantyl)-3-mesityl-4,5-dihydroimidazol-2-ylidine). Unlike the vast majority of 1,3-substituted 4,5-di-hydroimidazol-2-ylidene systems, H2IAdMes is unsymmetrical and we were curious to see if any catalyst derived from this ligand would give properties divergent from the symmetrical systems. The synthesis used for 6d could be easily modified to make 7d, simply by first reacting 2,4,6-trimethylaniline with a large excess of oxalyl chloride to give the monosubstituted acetyl chloride 7a. Compound 7a was then reacted with 1-adamantan-amine to give 7b, which was subsequently reduced and cyclised to give 7d (Scheme 1).

4.2.2 Synthesis of Ruthenium Carbene Complexes

With the precursors 6d and 7d in hand, we attempted to prepare their respective complexes \([\text{RuCl}_2(=\text{CPh})(\text{H}_2\text{IAd})(\text{PCy}_3)] \) (8) and \([\text{RuCl}_2(=\text{CPh})(\text{H}_2\text{IAdMes})(\text{PCy}_3)] \) (9) following the now well-established literature routes. Accordingly, 6d was treated with potassium tert-butoxide or potassium tert-pentoxide to give a solution containing free H2IAd. When this solution was subsequently added to catalyst 1, however, no changes were apparent, regardless of the reaction conditions. The reactions, conducted using a range of different temperatures (25-110°C) and various stoichiometries (1-5 equivalents of 6d relative to 1), were monitored by \(^{31}\text{P}\) NMR. In no instance was any reaction involving the phosphine displacement of 1 observed to take place. While we did not attempt to isolate free H2IAd, its presence was implied by proton NMR, which clearly showed the absence of the central hydrogen (at 8.49 ppm) in 6d and the diagnostic \(-1\) ppm upfield shift of the signal from the four methylene hydrogens (at \(-4\) ppm in 6d).
The failure of the reaction of H$_2$IAd with 1 under the usual standard reaction conditions is presumably a consequence of the benzylidene moiety in 1, which is possibly too bulky to permit the presence of a 1-adamantyl group directly overhead. We tentatively suggest that even if a second generation Grubbs catalyst could be formed with the H$_2$IAd ligand, it almost certainly could not retain the square pyramidal geometry found for 1, 2a and 3.

With this knowledge in mind, we predicted that the mixed 1-adamantyl/mesityl ligand system, H$_2$IAdMes, should successfully react with 1 to give exclusively complex 9a. The other isomer, 9b, with the H$_2$IAdMes in the opposite orientation (with the adamantyl group above the benzylidene), would almost certainly be disallowed on steric grounds. When 1 was added to an H$_2$IAdMes solution (rapidly formed \textit{in situ} from 7d and potassium tert-pentoxide), the mixture became muddy green. $^{31}$P NMR showed that complex 1 had been completely consumed and two new peaks at $\sim$16 ppm (complex 9) and 10 ppm (free PCy$_3$) had appeared. Methanolic workup isolated 9 as an air-stable powder. The complex was completely characterised by NMR and a single crystal X-ray structure (\textit{vide infra}).

It is noteworthy that there was only a single $^{31}$P NMR signal and only a single benzylidene peak in the $^1$H NMR. This result strongly suggested either the formation of only a single isomer of 9 (with the NHC ligand in only one orientation) as predicted or, less likely, the free rotation of the NHC ligand on the NMR time scale. A NOESY spectrum of 9 was acquired to clarify this point. The benzylidene carbene showed NOE enhancements to the phosphine cyclohexyl groups, as expected, and to one of the aromatic hydrogens and to one of the methyl groups of the mesityl moiety. No correlations to adamantyl groups were observed, indicating only a single isomer was formed (that with the mesityl above the benzylidene) with no rotation of the NHC taking place.

The colour and some of the spectroscopic properties of 9a were unanticipated. While the very closely related second generation Grubbs catalysts 2a and 2b are brownish in appearance, complex 9a was green. The $^{31}$P NMR peak at 15.7 ppm for 9a is remarkably far upfield when compared with the signals for 2a and 2b at 30.5 and 28.1 ppm, respectively. Less significantly, the diagnostic methine resonance of the benzylidene in the $^1$H NMR spectrum was also further upfield than usual, and appeared at 19.05 ppm, compared with 19.59 and 19.77 ppm for 2a and 2b. In the $^{13}$C NMR the two most important signals, the NHC carbene and the benzylidene carbons, resonated at 217.0 and 302.6 ppm, respectively. Surprisingly, the $^{13}$C NMR spectrum for 2a has, to the best of our knowledge, not been reported, though, the corresponding carbene signals for 2b appear at 222.2 and 296.7 ppm.
4.2.3 Crystal Structure of 9a

To confirm the connectivity of complex 9a and the orientation of the adamantyl group with respect to the benzyldiene group, the single crystal X-ray structure was determined. The collection and refinement parameters for the crystallographic analysis are presented in Table 2. The structure of 9a is shown in Figure 1, while selected bond lengths and angles are given in Table 1 together with the analogous data for 2a for comparison.

Figure 1. ORTEP representation of 9a with thermal ellipsoids drawn at the 30% probability level and hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°) are given in Table 1.

The structure confirms the predicted formulation of 9a, essentially resembling the overall geometry of complex 2a. However, a number of subtle, but significant dissimilarities are noteworthy. The most important involves the orientation of the PCy₃ ligand. The Ru-P bond length of 9a is 0.1 Å longer than that of 2a. Furthermore, the P-Ru-C(8) angle is considerably straightened out in 9a and is 7.4° more linear than in 2a. This significant change in angle is shared by both the imidazolin-2-ylidene and the phosphine ligands, which are both tipped more than 3° relative to 2a towards the benzyldiene moiety. Thus, the closest contact of the mesityl and the benzyldiene groups is 2.901 Å in 9a (for C(11)-C(1)) and 3.035 Å in 2a.
In light of the close similarities of 2a and 9a, the main reason for this deformation, which in fact results in more idealised square-pyramidal geometry, must be due to the presence of the adamantyl group. Most of the remaining equivalent geometric parameters of 9a and 2a are very similar with the exception of the Ru-Cl distances, particularly Ru-Cl(1), which is considerably longer in 9a.

In addition to the simple steric requirements demanded by the presence of a bulkier group, there may be an interaction of C(21) of the adamantyl with the metal centre, these being only 2.883 Å distant. The inclusion of C(21) at the back of the pyramid results in an effectively distorted octahedral geometry about the ruthenium atom. Possibly, this close contact could be forced purely by the rigorous steric constraints of the complex.

<table>
<thead>
<tr>
<th>Bond length</th>
<th>9a</th>
<th>2a</th>
<th>Bond angle</th>
<th>9a</th>
<th>2a</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru-C(1)</td>
<td>1.851(5)</td>
<td>1.835(2)</td>
<td>P-Ru-C(8)</td>
<td>171.1(1)</td>
<td>163.73(6)</td>
</tr>
<tr>
<td>Ru-C(8)</td>
<td>2.083(5)</td>
<td>2.085(2)</td>
<td>Cl(1)-Ru-Cl(2)</td>
<td>167.98(5)</td>
<td>167.71(2)</td>
</tr>
<tr>
<td>Ru-P</td>
<td>2.521(1)</td>
<td>2.4245(5)</td>
<td>C(1)-Ru-C(8)</td>
<td>96.9(2)</td>
<td>100.24(8)</td>
</tr>
<tr>
<td>Ru-Cl(1)</td>
<td>2.427(1)</td>
<td>2.3988(5)</td>
<td>P-Ru-C(1)</td>
<td>91.5(2)</td>
<td>95.89(6)</td>
</tr>
<tr>
<td>Ru-Cl(2)</td>
<td>2.398(1)</td>
<td>2.3912(5)</td>
<td>P-Ru-Cl(1)</td>
<td>96.40(4)</td>
<td>91.06(2)</td>
</tr>
<tr>
<td>C(8)-N(1)</td>
<td>1.336(6)</td>
<td>1.348(2)</td>
<td>P-Ru-Cl(2)</td>
<td>89.30(5)</td>
<td>87.75(2)</td>
</tr>
<tr>
<td>C(8)-N(2)</td>
<td>1.346(6)</td>
<td>1.347(2)</td>
<td>Cl(1)-Ru-C(1)</td>
<td>102.7(2)</td>
<td>103.15(7)</td>
</tr>
<tr>
<td>N(1)-C(10)</td>
<td>1.470(8)</td>
<td>1.482(3)</td>
<td>Cl(2)-Ru-C(1)</td>
<td>87.7(2)</td>
<td>89.14(7)</td>
</tr>
<tr>
<td>N(2)-C(9)</td>
<td>1.494(7)</td>
<td>1.476(2)</td>
<td>Cl(1)-Ru-C(8)</td>
<td>84.7(1)</td>
<td>83.26(5)</td>
</tr>
<tr>
<td>N(1)-C(11)</td>
<td>1.446(6)</td>
<td>1.432(2)</td>
<td>Cl(2)-Ru-C(8)</td>
<td>88.1(1)</td>
<td>94.55(5)</td>
</tr>
<tr>
<td>N(2)-C(20)</td>
<td>1.490(6)</td>
<td>1.440(2)</td>
<td>C(1)-Ru...C(21)</td>
<td>165.0(2)</td>
<td>-</td>
</tr>
<tr>
<td>Ru...C(21)</td>
<td>2.883(6)</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*a* Data collected at 293 K. *b* Data collected at 98 K.

To shed further light on this structural feature, variable temperature $^1$H NMR (-100 to +40°C) was carried out. Unfortunately, due to the complexity of the spectra, particularly in the aliphatic region, no concrete conclusions could be drawn, although changes from the NMR spectrum measured at room temperature clearly took place.
In order to gain a better understanding of the steric interactions of the adamantyl group compared with mesityl, a space-filling model generated from the crystal structure data of 9a was rendered (Figure 2). From the image, it is immediately obvious why only a single isomer of 9 had formed. Clearly, the steric encumbrance from the adamantyl group precludes the possibility of the rotated NHC analogue. The model lends further evidence that the diadamantyl complexes 5 and 8 are unrealistic on steric grounds if the square-pyramidal geometry is to be retained.
4.2.4 Crystal Structure of Dinuclear Complex 10

In the process of obtaining crystals of the complex 9a suitable for X-ray, we also attained a crystal structure of a dinuclear, phosphine-free analogue of complex 9a, namely [(IAdMesH$_2$)(=CHPh)ClRu(μ-Cl)$_2$RuCl(=CHPh)(IAdMesH$_2$)] (10). The crystals resulted from prolonged (weeks) crystallisation from dichloromethane solution of the complex 9a. We suppose that the phosphine moiety that is somewhat more labile in 9a than in the regular complex 2a, was scavenged by atmospheric oxygen that diffused into the crystallisation vessel forming the more stable dichloro-bridged diruthenium species 10. Although we did not attempt to prepare 10 systematically and consequently its analytical data are missing, it is still instructive to analyse and compare the structure of 10 with its mononuclear parent complex 9a.

**Figure 2.** Space-filling representation generated using crystallographic coordinates from the structure of complex 9a. The complex is shown viewed perpendicular to the imidazolylidene ring (Im).
As shown in Figure 3, two ruthenium atoms are bridged by two chlorine atoms and the structure consists of two centrosymmetric units. The two benzylidene moieties lie between the mesityl fragment of the NHC ligand attached to the same ruthenium atom and adamantyl group of the NHC ligand attached to the other ruthenium atom. One of the protons of each adamantyl coordinates to the adjacent ruthenium atom opposite to the benzylidene moiety. The contact Ru(1)...C(22) at 2.806 Å is even closer than in the mononuclear complex 9a, which showed a corresponding distance of 2.883(6) Å. This is because the bond between ruthenium and NHC carbene, Ru(1)-C(8), is substantially shorter (by 0.071 Å) than in 9a bringing the adamantyl moiety in closer proximity to the metal centre. Moreover, the carbene bond is slightly shorter (by 0.011 Å) in the dinuclear complex 10 than in 9a.
Interestingly, the phenyl ring of the carbene moiety forms an acute angle of 44.52° with the mesityl ring, contrary to complex 9a where these planes are practically parallel. This phenyl ring accommodates itself between the adamantyl and mesityl fragment in a way that the closest contacts (including hydrogen atoms) are circa 2.8 Å distant. The ‘free’ chlorine atom lies somewhat closer to the ruthenium atom while the two bridging chlorines lie further away with Cl(2a) at a distance of 2.4939(5) Å. The imidazolium ring is practically undistorted with respect to complex 9a. The Cl(1)-Ru(1)-Cl(2) angle is straightened out by -3.5° compared to 9a and 2a while C(8)-Ru(1)-Cl(2a) angle is equal to 164.54°. That is much less than the corresponding P-Ru-C(8) bond in 9a (171.1°), but very close to the value observed in 2a (163.73°). Obviously, a chlorine atom and a phosphorus atom are different entities, but comparing the geometry of the three structures 2a, 9a and 10 it seems that the loss of the phosphine and formation of the dinuclear species 10 is facilitated by release of steric bulk exerted between PCy3 and NHC ligands in complex 9a. The higher initiation constant in metathesis (vide infra) for 9a with respect to 2a corroborates this statement.

4.2.5 Metathesis Activity of Carbene 9a

Perhaps the most remarkable and surprising property of 9a was its extremely poor metathesis activity. By itself, complex 9a completely failed to initiate even the simple self-metathesis of 1-octene, the self-metathesis of methyl oleate and the ring closing metathesis of diethyl diallylmalonate. This lack of activity persisted even at higher temperatures. In fact, 9a failed to produce even trace amounts of any metathesis products of 1-octene at 60 or even 100°C, with isomerisation of the substrate being the only reaction that took place in these cases. The presence or absence of a solvent also had no effect on the activity. However, when
100 equivalents of 1-octene were reacted in the presence of 9a in CH₂Cl₂ and some copper(I) chloride (a phosphine scavenger) was added, 12% conversion (12 turnovers per mol of catalyst) to 7-tetradecene could be achieved. It should be noted that catalysts 2a and 2b are capable of turnover numbers of ~300,000 and over 600,000, respectively, for the metathesis of 1-octene.

Despite these very disappointing results, 9a did display some ring opening metathesis polymerisation (ROMP) activity. Thus, when 2-norbornene (100 equivalents) was reacted with 9a in CH₂Cl₂, polynorbornylene was rapidly formed and isolated in 98% yield. It should be noted, however, that the ROMP of 2-norbornene is quite facile and not a very good test for general metathesis activity.

Finally, the reactivity of 9a toward ethyl vinyl ether (EVE) was tested. EVE typically reacts rapidly (minutes) with Grubbs-type metathesis catalysts to produce the corresponding Fischer-type carbene complex.21 As expected, complex 9a did react with excess EVE (reaction followed by NMR) to produce [RuCl₂(=CHOEt)(H₂1AdMes)(PCy₃)₂] (11). In the ³¹P NMR there was a gradual growth of a peak at 19.8 ppm concomitant with the decline of the peak at 15.7 ppm (from 9a), while in the 'H NMR a new peak at 13.67 ppm was formed and in the same time the benzylidene peak at 19.05 ppm was attenuated. The observed downfield shift in the ³¹P NMR and the upfield shift 'H NMR are highly diagnostic for the formation of a Fischer-type carbene complex.21a The initiation kinetics for this reaction was measured by 'H NMR¹³ at 20°C giving a kₐᵢᵢ value of (9.1 ± 0.2) × 10⁻⁴ s⁻¹. This kₐᵢᵢ value attests that the initiation rate of 9a is in fact faster than that of 2a, which was determined to be 4.6 × 10⁻⁴ s⁻¹ at 35°C,¹³ but remains much slower than the parent complex 1 which displays a kₐᵢᵢ of 1.0 × 10⁻³ s⁻¹ at 10°C.¹³

In light of the typical initiation rate of complex 9a, the reason for the virtual catalytic inactivity for metathesis is not entirely clear. The σ-donating properties of H₂1AdMes and H₂IMes are expected to be only slightly different, and certainly would not be expected to result in such significant differences in activity of their derived complexes. The possible interaction of an adamantyl carbon with the metal centre in 9a observed in the crystal structure is almost certainly unimportant at the reaction temperatures used in the metathesis experiments. Furthermore, the complexes [RuCl₂(=CHPh)(H₂IMes)(Py)₂] and [RuCl₂(=CHPh)(H₂IMes)(3-Br-Py)₂] (Py = pyridine) are both capable metathesis catalysts despite their six-coordinate (octahedral) geometry.²² It therefore seems that the steric hindrance of the position trans to the benzylidene group provided by the adamantyl substituent forms the most convincing explanation for the observed massive decrease in metathesis activity of 9a compared with closely related catalysts. If this steric blocking is the dominant reason for catalytic inactivity of 9a, it may provide some new mechanistic insights.

Three possible modes for the initial coordination of the olefin to the activated 14-electron catalyst have been proposed (Figure 4).⁷ The poor catalytic activity of complex 9a would tentatively suggest that B may be the most important intermediate, since only this possibility requires the position trans to the benzylidene to be unobstructed for the
rearrangement required for the coordination of the olefin. However, complex 9a represents only a single example, and further research and additional complexes are required before a definitive conclusion can be reached.23

Figure 4. Possible geometries for the initial coordination of olefin.

4.3 Conclusions

The H2IAd and H2IAdMes ligand precursors 6d and 7d, respectively, were successfully synthesised. Only H2IAdMes reacted with 1 to give the expected product 9. In light of this result, the apparent inability of H2IAd to displace a PCy3 ligand in 1 suggests that the failure is primarily a consequence of the uncompromising steric bulk of H2IAd ligand. The formation of only a single isomer of 9 (9a), together with a space-filling model generated from its crystallographic coordinates, further support this notion. The crystal structure of phosphine-free, dinuclear analogue 10 shows a similar global spatial arrangement of ligands as found for 9, although some additional peculiar features were also observed.

The activity of complex 9a clearly highlights the relevance of the NHC ligand of the second generation Grubbs-type metathesis catalysts. In the present case, the H2IAdMes ligand imparted the resulting complex 9a with only very limited metathesis activity, considerably lower than the parent complex 1. Indeed, 9a was incapable of initiating the metathesis of 1-octene in the absence of a phosphine scavenger (CuCl) and even then only very low turnover numbers could be obtained. The very low metathesis performance of complex 9a illustrates the importance of the steric bulk of the NHC fragment; clearly this last point needs to be carefully considered in future catalyst designs based on the Grubbs-type motif.

4.4 Experimental Section

General considerations. Unless otherwise stated, all manipulations were carried out under a nitrogen atmosphere on a vacuum line using standard Schlenk techniques. All solvents used were dried and distilled under nitrogen. Complex 1 (Fluka), potassium tert-pentoxide solution (1.7 M in toluene, Fluka), oxalyl chloride (Acros), 1-adamantanamine (Aldrich), 2,4,6-trimethylaniline (Acros), borane-methyl sulfide complex (Aldrich), triethyl orthoformate (Aldrich), ethyl vinyl ether (Aldrich), 2-norbornene (Acros) and 1-octene (Aldrich) were obtained from commercial sources and used as received. NMR spectra were recorded on a Varian Mercury 300 spectrometer, at 300.14, 75.48 and 121.50 MHz for the proton, carbon and phosphorus channels, respectively. Elemental analyses were determined with a Carlo Erba EA1108 CHNS-O elemental analyser at the Department of Organic Chemistry, University of Nijmegen (The Netherlands) and at H. Kolb Mikroanalytisches Laboratorium (Germany).
4.4.1 Ligand Synthesis.

\( N_2N'-\text{Di}(1\text{-adamantyl})\text{oxamide (6b)} \). Oxalyl chloride (1.4 mL, 16.0 mmol) was added slowly to a \( \text{CH}_2\text{Cl}_2 \) (20 mL) solution of 1-adamantanamine (5.0 g, 33.1) and triethylamine (4.6 mL, 33.0 mmol). The resulting mixture was stirred for 1 h, after which time water was added, the organic layer extracted, dried with MgSO\(_4\) and the solvent removed under reduced pressure. Hexanes were added to the residue to stir a white slurry, which was filtered, washed with hexanes and finally dried under vacuum to give 6b as a white powder (3.64 g, 63.6%) of mp. 246°-7°C. IR (KBr): ν 3360 (s, N-H), 1677 (vs, C=O), 1498 (vs, C=O). \(^1\)H NMR (CDCl\(_3\)): δ 7.26 (br s, 2 H, NH), 2.06 (br s, 6 H, -H-Ad), 1.98 (br s, 12 H, H-Ad), 1.65 (br s, 12 H, H-Ad). \(^13\)C NMR (CDCl\(_3\)): δ 159.3 (C(O)), 51.8 (C-1 Ad), 40.9 (C-2 Ad), 36.1 (C-4 Ad), 29.2 (C-3 Ad). FAB-MS: \( m/z \) (rel. intensity, %) 357 ([M+H]\(^+\), 37), 355 ([M-H]\(^-\)), 150 ([AdNH\(_2\)-2H]\(^+\), 15), 135 ([Ad]\(^+\), 100). HRMS (FAB): calcd. for \( \text{C}_{22}\text{H}_{33}\text{N}_2\text{O}_2 \) [M+H]\(^+\) 357.2542, observed 357.2542. Anal. \( \text{C}_{22}\text{H}_{33}\text{N}_2\text{O}_2 \): calcd. C 74.12, H 9.05, N 7.86% ; found C 73.91, H 8.87, N 7.85%.

\( N_2N'-\text{Di}(1\text{-adamantyl})\text{ethane-1,2-diamine dihydrochloride (6c)} \). To a toluene (20 mL) solution of \( N_2N'-\text{di}(1\text{-adamantyl})\text{oxamide 6b (3.5 g, 9.8 mmol)} \) was added borane-methyl sulfide complex (3.75 mL, 39.5 mmol) and the resulting mixture refluxed for 3 h. After cooling to room temperature, hydrochloric acid (1 M) was carefully added with vigorous stirring until the mixture was acidic (litmus paper). Sodium hydroxide solution (10 wt%) was subsequently added until the solution tested basic by litmus paper. The organic layer was extracted and the aqueous layer washed two times with CH\(_2\)Cl\(_2\). The organic extracts were combined, dried with MgSO\(_4\), and most of the solvents evaporated under reduced pressure to leave ~30 mL. Hydrochloric acid (12 M) was then added and the mixture shaken to give a white precipitate. The solid was filtered off, washed with ether and dried under vacuum to give 6c (2.15 g, 55%); mp. 265°C (decomposes without melting). \(^1\)H NMR (d\(_6\)-DMSO): δ 3.45 (br s, 2 H, NH), 2.57 (s, 4H, AdNCH\(_2\)-CH\(_2\)NAd), 2.02 (br s, 6 H, H-Ad), 1.58 (br s, 24 H, H-Ad). \(^13\)C NMR (d\(_6\)-DMSO): δ 51.1 (C-1 Ad), 41.2 (C-2 Ad), 39.5 (NCH\(_2\)CH\(_3\)N, the peak under the solvent resonance), 36.1 (C-4 Ad), 28.9 (CH-3 Ad). \(^13\)C NMR (CDCl\(_3\)): δ 51.2 (C-1 Ad), 42.5 (C-2 Ad), 40.6 (NCH\(_2\)CH\(_2\)N), 36.7 (C-4 Ad), 29.6 (CH-3 Ad). FAB-MS: \( m/z \) (rel. intensity, %) 330 ([M+2H]\(^+\), 86), 329 ([M+H]\(^+\)), 100, 327 ([M-H]\(^-\)), 51, 178 ([M-AdNH]\(^+\)), 24, 164 ([AdNHCH\(_2\)]\(^+\)), 72, 135 ([Ad]\(^+\), 77). HRMS (FAB): calcd. for \( \text{C}_{22}\text{H}_{35}\text{N}_2\text{[M+H]+} \) 329.2957, observed 329.2952.

\( 1,3\text{-Di}(1\text{-adamantyl})\text{-4,5-dihydroimidazolium chloride (6d)} \). A suspension of \( N_2N'-\text{di}(1\text{-adamantyl})\text{ethane-1,2-diamine dihydrochloride 6c (1.95 g, 4.86 mmol)} \) in triethyl orthoformate (20 mL) containing one drop of formic acid was heated at 130°C for 3 h. No visible changes occurred during this time. The mixture was cooled to 0°C, filtered, the solid washed with diethyl ether and subsequently dried under vacuum to give 6d as a white powder (1.21 g, 67%); mp. >330°C (decomposes without melting). \(^1\)H NMR (CDCl\(_3\)): δ 8.49 (s, 1 H, AdNCH\(_2\)NAd), 4.02 (s, 4 H, AdNCH\(_2\)CH\(_2\)NAd), 2.18 (br s, 6 H, H-Ad), 2.03 (br s, 12 H, H-Ad), 1.67 (br s, 12 H, H-Ad). \(^13\)C NMR (CDCl\(_3\)): δ 151.6 (AdNCH\(_2\)NAd), 56.7 (C-1 Ad), 43.5 (AdNCH\(_2\)CH\(_2\)NAd), 40.3 (C-2 Ad), 35.0 (C-4 Ad), 28.7 (C-3 Ad). FAB-MS: \( m/z \) (rel. intensity, %) 340 ([M+Cl-H]\(^+\)), 43), 339 ([M-Cl]\(^+\)), 100, 135 ([Ad]\(^+\)), 31). HRMS (FAB): calcd. for \( \text{C}_{22}\text{H}_{35}\text{N}_2\text{[M-Cl]+} \) 339.2800, observed 339.2809.

Oxo-(2,4,6-trimethylphenylamino)acetyl chloride (7a). 2,4,6-Trimethylaliline (10 mL, 71.0 mmol) was added dropwise to oxalyl chloride (50 mL, 582.2 mmol) over the course of 1 h at 0°C. The resulting mixture was stirred overnight after which time the excess oxalyl chloride was removed under vacuum. Diethyl ether (80 mL) was added to the yellowish residue and the solids filtered off. The solvent was completely removed under reduced pressure, and pentane was added to the residue. After
vigorously stirring for 30 min, the insoluble material was filtered, washed with pentane and dried under vacuum to give almost pure (by NMR) 7a as a slightly off-white powder (4.8 g, 30%). The compound was used without further purification; mp. 100-2°C. IR (KBr): v 3208 (br s, N-H), 1783 (vs, C=O), 1698 (vs, C=O). 1H NMR (CDCl3): δ 7.98 (br s, 1 H, NH), 6.93 (s, 2 H, C6H2Me3), 2.29 (s, 3 H, p-CH3), 2.19 (s, 6 H, o-CH3). 13C NMR (CDCl3): δ 168.9 (O(O)Cl), 152.7 (O(O)NH), 138.5 (i-C6H2Me3), 134.8 (o-C6H2Me3), 129.4 (m-C6H2Me3), 129.1 (p-C6H2Me3), 21.1 (p-CH3), 18.4 (o-CH3).

N-(1-Adamantyl)-N'-(2,4,6-trimethylphenyl)oxamide (7b). A CH2Cl2 solution (20 mL) of 1-adamantanamine (2.70 g, 17.9 mmol) and triethylamine (2.5 mL, 17.9 mmol) was added dropwise to a CH2Cl2 (100 mL) solution of oxo-(2,4,6-trimethylphenylamino)-acetyl chloride 7a (4.0 g, 17.7 mmol) at 0°C, and the resulting mixture was stirred at room temperature for 2 h. Water (100 mL) was added, the organic layer was extracted, dried with MgSO4 and the solvent removed under reduced pressure. The residue was collected and washed with diethyl ether to give 7b as a white powder (4.53 g, 75%); mp. 288-90°C. IR (KBr): v 3309 (w, N-H), 3263 (s, N-H), 1662 (vs, C=O), 1450 (vs, C=O).

Borane-methyl sulfide complex (2.85 mL, 30.1 mmol) was added to a toluene (50 mL) solution of N-(1-adamantyl)-N'-(2,4,6-trimethylphenyl)oxamide 7b (2.50 g, 7.34 mmol) and the resulting mixture was reﬂuxed for 3 h. After cooling to room temperature, hydrochloric acid (1 M) was added until the stirred solution tested acidic towards litmus paper. Aqueous sodium hydroxide solution (10 wt%) was subsequently added until the solution tested basic by litmus paper. The white slurry was then transferred to a separating funnel, the organic layer extracted and the aqueous layer extracted two more times with CH2Cl2. The organic extracts were combined and concentrated to ~50 mL under reduced pressure. Hydrochloric acid (12 M) was added with stirring to precipitate the product which was collected by filtration, washed with diethyl ether and dried under vacuum to give 7c (1.65 g, 58%) as a white powder; mp. 286-8°C (melts with decomposition). 1H NMR (d6-MSO): δ 8.90 (br s, 2 H, NH), 6.98 (s, 2 H, C6H2Me3), 3.69 (br s, 2 H, CH2NMeHs), 3.42 (br s, 2 H, AdNHCH2), 2.47 (s, 6 H, o-CH3), 2.22 (s, 3 H, p-CH3), 2.13 (br s, 3 H, H-Ad), 1.94 (s, 6 H, H-Ad), 1.63 (pseudo q, JHH ~ 11.5 Hz, 6 H, H-Ad). 13C NMR (d6-MSO): δ 138.0 (i-C6H2Me3), 133.4 (p-C6H2Me3), 131.5 (m-C6H2Me3), 130.2 (o-C6H2Me3), 56.6 (C-1 Ad), 50.0 (MesNCH2), 46.0 (AdNCH2), 37.5 (C-2 Ad), 35.1 (C-4 Ad), 28.4 (CH-3 Ad), 20.2 (p-CH3), 18.1 (o-CH3). FAB-MS: m/z (rel. intensity, %) 314 ([M+H]+, 73), 313 ([M+H]+, 100), 312 ([M]+, 49), 195 ([M-Mes+2H]+, 7), 178 ([M-Ad+H]+, 24), 164 ([AdNHCH2]+, 72), 162 ([M-AdNH]+, 19), 149 ([AdNH-H]+, 53), 148 ([MesNHCH3]+, 50), 135 ([Ad]+, 77), 134 ([MesNH]+, 25), 83 (22), 81 (18), 79 (24), 77 (13). HRMS (FAB): calcd. for C21H23N2 [M+H]+ 313.2644, observed 313.2644.

1-(1-Adamantyl)-3-mesityl-4,5-dihydroimidazolinium chloride (7d). A suspension of N-(1-adamantyl)-N'-(2,4,6-trimethylphenyl)ethane-1,2-diamine dihydrochloride 7c (1.50 g, 3.89 mmol) in triethyl orthofomate (15 mL) containing one drop of formic acid was heated at 130°C for 3 h. No visible changes occurred during this time. The mixture was cooled to 0°C, filtered, the solid washed
with diethyl ether and subsequently dried under vacuum to give 7d as a white powder (1.09 g, 78%). Analytically pure sample was obtained by redissolving in CH₂Cl₂, filtration and precipitation with hexanes; mp. 318-20°C (melts with decomposition). ¹H NMR (CDCl₃): δ 9.11 (s, 1 H, AdNCH(NMes), 6.84 (s, 2 H, C₆H₂Mes), 4.34 (dd, J_H,H ~ 10.8, 9.3 Hz, AA’BB’ spin system, 2 H, AdNCH₂CH₂NMes), 4.18 (dd, J_H,H ~ 10.8, 9.3 Hz, AA’BB’ spin system, 2 H, AdNCH₂CH₂NMes), 2.25 (s, 6 H, o-CH₃), 2.21 (s, 3 H, p-CH₃), 2.18 (br s, 3 H, H-Ad), 2.07 (s, 6 H, H-Ad), 1.67 (s, 6 H, H-Ad). ¹³C NMR (CDCl₃): δ 156.6 (AdNCH(NMes), 139.4 (i-C₆H₄Me), 134.9 (o-C₆H₄Me), 130.8 (p-C₆H₄Me), 129.4 (m-C₆H₂Mes), 57.5 (C-1 Ad), 50.6 (CH₂NMes), 45.0 (AdNCH₂), 40.6 (C-2 Ad), 35.1 (C-4 Ad), 28.8 (CH-3 Ad), 20.7 (p-CH₃), 17.8 (o-CH₃). FAB-MS: m/z (rel. intensity, %) 323 ([M-Cl]+, 43), 135 ([Ad]+, 13). HRMS (FAB): calcd. for C₂₂H₃₃N₂ [M-Cl]+ 323.2487, observed 323.2466. Anal. C₂₂H₃₃ClN₂: calcd. C 73.61, H 8.70, N 7.80%; found C 73.51, H 8.91, N 7.76%.

4.4.2 Synthesis of Ru Carbene Complexes

[RuCl₂(=CHPh)(H₂AdMes)(PCy₃)] (9a). Potassium tert-pentoxide solution (∼1.7 M in toluene, 0.30 mL, 0.510 mmol) was added to a suspension of 1-(1-adamantyl)-3-mesityl-4,5-dihydroimidazolium chloride 7d (0.185 g, 0.515 mmol) in toluene (0.30 mL, 0.510 mmol) was added to a suspension of 1-(1-adamantyl)-3-mesityl-4,5-dihydroimidazolium chloride 7d (0.185 g, 0.515 mmol) in toluene (6 mL). After stirring the almost clear solution for 5 min, complex 1 (0.250 g, 0.304 mmol) was added all at once as a solid. The resulting solution was heated at 60°C for 2 h, during which time the solution became muddy green. After cooling to room temperature, all of the solvent was removed under vacuum and methanol (20 mL) was added. The mixture was then vigorously stirred for 1 h. The product was filtered off, washed with methanol (2 × 10 mL) and dried under vacuum to give 9a as a green powder (0.152 g, 58%). ¹H NMR (CDCl₃): δ 19.05 (s, 1 H, Ru=CHPh), 9.19 (br s, 1 H, o-C₆H₄), 7.45 (t, J_H,H = 7.2 Hz, 1 H, p-C₆H₄), 7.23 (m, 2 H, m-C₆H₄), 6.89 (br s, 1 H, o-C₆H₄), 6.78 (s, 1 H, C₆H₂Mes), 5.84 (s, 1 H, C₆H₂Mes), 3.96 (pseudo q, J_app = -10 Hz, 2 H, H-Ad), 1.98 (s, 3 H, H-Ad), 1.94-1.48 (m, 31 H, H-PCy/H-Ad), 1.28-1.11 (m, 5 H, H-PCy₃), 0.94 (br s, 6 H H-PCy₃). ¹³C NMR (CDCl₃): δ 302.6 (pseudo t, J_C,C = 11.6 Hz, Ru=CHPh), 217.0 (d, J_C,C = 80.5 Hz, AdNCH₂NMes), 152.1 (i-C₆H₄), 138.5, 138.3, 138.0 and 137.8 (C₆H₄Mes), 132.7 (br, C₆H₄), 129.8 (C₆H₄Mes), 129.4 (p-C₆H₄), 128.6, 127.6 (both br, C₆H₄), 58.9 (C-1 Ad), 51.0 (AdNCH₂CH₂NMes), 45.0 (AdNCH₂CH₂NMes), 41.3 (C-2 Ad), 36.7 (C-4 Ad), 34.9 (d, J_C,C = 13.2 Hz, ipso-PCy₃), 30.7 (C-3 Ad), 29.1 (d, J_C,C = 15.8 Hz, m-PCy₃), 28.3 (d, J_C,C = 21.3 Hz, J_C,C = 7.7 Hz, o-PCy₃), 26.9 (p-PCy₃), 21.2 (p-CH₃), 19.2, 18.7 (both o-CH₃). ³¹P NMR (CDCl₃): δ 15.7 (s). FAB-MS: m/z (rel. intensity, %) 864 ([M]+, 7), 829 ([M-Cl]+, 10), 793 ([M-2Cl]+, 4), 513 ([M-2Cl-PCy₃]+, 22), 421 ([Ru(H₂AdMes)]+), 34), 370 ([CHPh+PCy₃]+, 100), 323 ([H₂AdMes-H]+, 93), 289 (58), 280 ([PCy₃]+, 92), 208 (33), 197 ([PCy₂]+, 20), 135 ([Ad]+, 53). HRMS (FAB): calcd. for C₂₇H₅₀Cl₃N₃P[Ru (M]+ 864.3619, observed 864.3610. Anal. C₄₇H₇₀Cl₃N₃P₂Ru: calcd. C 65.26, H 8.04, N 3.24%; found C 65.12, H 7.95, N 3.17%.

Reaction of 9a with vinyl ether ether. Vinyl vinyl ether (6 µl, 0.063 mmol) was added to a CDCl₃ (0.4 mL) solution of 9a (0.010 g, 0.012 mmol) and the resulting mixture was stirred for 30 min; during this time, the solution slowly became yellow. NMR indicated complete conversion to [RuCl₂(=CHOET)(H₂AdMes)(PCy₃)] (11). The product was not isolated. ¹H NMR (CDCl₃): δ 13.67 (s, 1 H, Ru=CHOET), 6.94 (s, 2 H, C₆H₂Mes), 3.89 (m, AA’BB’ system, 2 H, MesNCH₂CH₂NAd), 3.63 (m, AA’BB’ system, 2 H, MesNCH₂CH₂NAd), 3.37 (q, J_H,H = 6.9 Hz, 2 H, OCH₂CH₃), 2.39 (s, 6 H, o-
CH$_3$), 2.26 (s, 3 H, p-CH$_3$), 2.33 (br s, 6 H, H-Ad), 2.03-1.54 (m, 33 H, H-PCy$_3$/H-Ad), 1.24 (t, J$_{HH}$ = 6.9 Hz, 3 H, OCH$_2$CH$_3$), 1.31-1.10 (m, 9 H, H-PCy$_3$). $^{31}$P NMR (CD$_2$Cl$_2$): δ 19.8 (s).

4.4.3 Metathesis Reactions

Complex 9a (5.5 mg, 6.36 µmol) was added to a toluene (1 mL) solution of 1-octene (1 mL, 6.37 mmol) and the resulting mixture was stirred at room temperature, 60°C or 100°C for 24 hours. At room temperature, no colour change was observed for the reaction while those at higher temperatures slowly became yellow. A sample was taken, and analysed by GC/FID. No 7-tetradecene had formed in any of the reactions with only a small amount of isomerisation products (primarily 2-octene) detected. The reaction was repeated in CH$_2$Cl$_2$ (1 mL) using 100 equivalents of 1-octene (90 µL, 0.573 mmol) relative to 9a (5.0 mg, 5.78 µmol) and addition of the phosphine scavenger CuCl (2 mg, 20.2 µmol). After 2 h, a limited amount of metathesis had taken place, and GC/FID analysis of the crude reaction mixture revealed 12% conversion to 7-tetradecene. No additional metathesis took place on longer reaction times. Similarly, complex 9 (5.0 mg, 5.78 µmol) was added to a CH$_2$Cl$_2$ (1 mL) solution of 2-norbornene (55.0 mg, 0.584 mmol) and the resulting mixture stirred at room temperature for 1 hour. After filtering through a short plug of silica, methanol (20 mL) was added, resulting in a tacky precipitate. The solid was dried under vacuum to give poly(norbornene) (54 mg, 98%), ~90% trans by proton NMR.

4.4.4 Crystal Structures of 9a and 10$^{24}$

Green blocks of 9a suitable for X-ray diffraction were grown by the slow evaporation of a CH$_2$Cl$_2$/MeOH solution under nitrogen. Intensity data were corrected for Lorentz effects, polarisation effects and for linear absorption by a Ψ-scan method. The structure of 9a was solved using the direct methods option of SHELXS-97$^{25}$ and subsequently refined using SHELXL-97$^{26}$ All non-hydrogen atoms were assigned anisotropic temperature factors and all hydrogen atom positions were determined by calculation. For the methyl groups of the mesityl substituent, where the location of the hydrogen atoms was uncertain, the AFI X 137 card was used to allow the hydrogen atoms to rotate to the maximum area of residual density while fixing their geometry. The ORTEP drawing$^{27}$ is shown in Figure 1.

Green crystals of 10 were obtained after prolonged storage of a dichloromethane solution of 9a in a tube. A single crystal was mounted in air on a glass fibre. Intensity data were collected at a temperature of -65°C (208 K). A Nonius KappaCCD single-crystal diffractometer was used, Mo-Kα radiation, Ψ and Ω scan mode. Unit cell dimensions were determined from the angular setting of 59798 reflections. Intensity data were corrected for Lorentz and polarisation effects. The structure was solved by the program DIRDIF$^{28}$ and was refined with standard methods (refinement against F$^2$ of all reflections with SHELXL-97$^{26}$ with anisotropic parameters for the non-hydrogen atoms). All hydrogen atoms were taken from a difference Fourier map and were freely refined. Figure 3 shows an ORTEP drawing at 50% probability.

4.5 Acknowledgements and References

We wish to thank Jan Fraanje (Amsterdam University) for the collection of the X-ray data set of 9a and René de Gelder (Nijmegen University) for the structure 10.


11 M. R. Buchmeiser, personal communication.


14 Calorimetric studies revealed 1,3-dicyclohexylimidazol-2-ylidene (ICY) to be 5.6 kcal mol⁻¹ more exothermic than IMes (ref. 6).


17 When glyoxal was reacted with two equivalents of 1-adamantanamine, an intractable white precipitate formed that we were unable to characterise due to its poor solubility. This material did not reduce to N,N-di(1-adamantyl)ethane-1,2-diamine (6c) on treatment with sodium borohydride or borane.


19 NHC ligands on the second generation Grubbs metathesis catalysts generally can not rotate.

20 Structure parameters obtained from supplementary crystallographic data CCDC-161995, courtesy of Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK.


23 A second example of a ruthenium carbene displaying an agostic interaction in the position trans to the carbene moiety has just been presented: J. Patel, W. R. Jackson, A. K. Serelis, *Inorg. Chim. Acta* **2004**, 357, 2374. A somewhat longer Ru...C distance of 2.952(2) Å was determined by X-ray structure in ruthenium bis(pyrazolyl)borate benzylidene 12. The complex was active in RCM only.
at elevated temperature and CuCl activation, but this behaviour is characteristic of the class of tris(pyrazolyl)borate ligands (M. S. Sanford, L. M. Henling, R. H. Grubbs, *Organometallics* 1998, 17, 5384) and so does not lend additional evidence for the hypothesis presented in the current text.

![Diagram](image)

24 The Crystallographic Information File (CIF) for complex 9a has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC-223175.