Adamantyl-Substituted *N*-Heterocyclic Carbene Ligands in Second-Generation Grubbs-Type Metathesis Catalysts

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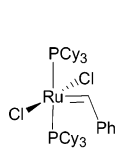
The *N*-heterocyclic carbene (NHC) ligands H_2IAd (H_2IAd = 1,3-di(1-adamantyl)-4,5-dihydroimidazol-2-ylidene) and H_2IAdMes (H_2IAdMes = 1-(1-adamantyl)-3-mesityl-4,5-dihydroimidazol-2-ylidine) were prepared and treated with [$RuCl_2$(=CHPh)(PCy_3)$_2$] (**1**). While H_2IAd failed to react with **1**, H_2IAdMes readily produced [$RuCl_2$(=CHPh)(H_2IAdMes)(PCy_3)] (**7**). Only a single isomer of **7** was formed, this being that with the mesityl ring situated above the benzylidene moiety, as confirmed by an X-ray structure. Complex **7** 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 benzylidene group.

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.[1] The ruthenium-based metathesis catalyst systems, particularly the first- and now the 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.



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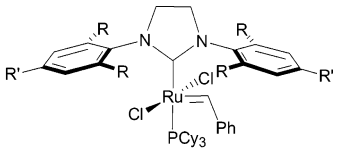
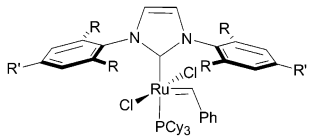


2a R, R' = Me

2b R = *i*-Pr; R' = H



3a R, R' = Me

3b R = *i*-Pr; R' = H

While the most widely used second-generation metathesis catalysts **2a**[2] (containing the H_2IMes ligand, H_2IMes = 1,3-dimesityl-4,5-dihydroimidazol-2-ylidene) and its unsaturated relative **3a**[3] (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 efforts at creating enantioselectivity for ring-closing metathesis,[4] studying the activity of the 2,6-diisopropylphenyl variants **2b**[5] and **3b**,[6,7] and the preparation and reactivity of a range of mixed mesityl/CH_2CH_2X (X = CH=CH_2, $OSiMe_2t$-Bu, $(CF_2)_5CF_3$) NHC analogues of **3a**.[6] 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, our research has shown that the 2,6-diisopropylphenyl-substituted complex **2b** (containing the H_2IPr ligand, H_2IPr = 1,3-bis(2,6-diispropylphenyl)-4,5-dihydroimidazol-2-ylidene) displays considerably superior activity than **2a** for the metathesis of terminal olefins.[5] 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 were superlative for all substrates.[6]

We were intrigued by these results and wished to examine the metathesis activity of catalysts incorporat-

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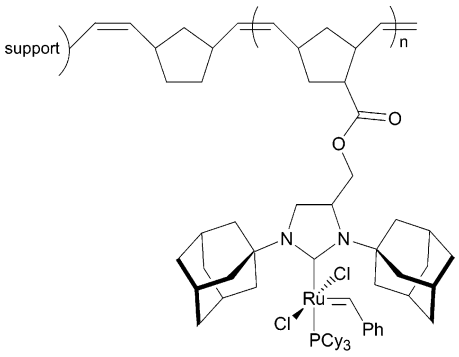
ing other NHC ligands. Of particular interest were the recent accounts of an immobilized, second-generation ruthenium metathesis catalyst with a di(1-adamantyl)-substituted NHC ligand (**5**) reported by Buchmeiser et al.[8] In these articles no efforts toward the characterization of the proposed complex were reported, and homogeneous analogues could not be prepared.[9] 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,[10] so 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 complexes.



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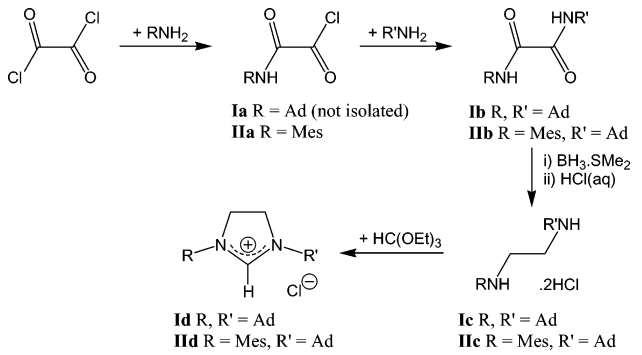
The replacement of the currently ubiquitous mesityl-substituted NHC ligand with a 1-adamantyl-substituted one offers a number of potential activity enhancements. First, while the mesityl group, being flat, is bulky in only two dimensions, the adamantyl is bulky in three dimensions. This extra bulk may 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.[11] Furthermore, the greater steric bulk may also provide greater shielding of the metal center, possibly further hindering unfavorable 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.[12] 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.[11] With these points in mind, we decided to further explore the prospect of utilizing NHC ligands incorporating the 1-adamantyl moiety for use in metathesis.

Results and Discussion

Ligand Precursor Synthesis. 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 (PCy_3),[7a] 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. Second, it has been found that catalyst **3a** is considerably less active (with respect to turnover numbers) than **2a** for the metathesis of simple olefins.[13] 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**,[8] which is based on the saturated H_2IAd (H_2IAd = 1,3-di(1-adamantyl)-4,5-dihydroimidazol-2-ylidene) framework, providing literature precedence.

Scheme 1



Surprisingly, while IAd is very well known and even commercially available, the saturated analogue, H_2IAd, has, to the best of our knowledge, not been previously reported. Naturally, we initially attempted to synthesize the H_2IAd ligand precursor, 1,3-di(1-adamantyl)-4,5-dihydroimidazolinium chloride (**Id**, Scheme 1), following the now standard protocol developed by Arduengo et al.[14] However, all of these attempts were unsuccessful.[15] 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). Following this method, the desired **Id** could be obtained in moderate yield by reaction of oxalyl chloride with 2 equiv of 1-adamantamine, followed by reduction and cyclization. For comparison, we also prepared the mixed mesityl/1-adamantyl NHC precursor 1-(1-adamantyl)-3-mesityl-4,5-dihydroimidazolinium chloride (**IId**) as a source of H_2IAdMes (H_2IAdMes = 1-(1-adamantyl)-3-mesityl-4,5-dihydroimidazol-2-ylidine). Unlike the vast majority of 1,3-substituted 4,5-dihydroimidazol-2-ylidene systems, H_2IAdMes 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 **Id** could be easily

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(12) Calorimetric studies revealed 1,3-dicyclohexylimidazol-2-ylidene (ICy) to be 5.6 kcal mol^{-1} more exothermic than IMes (ref 7).

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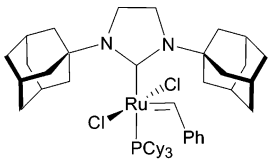
(14) Arduengo, A. J., III; Krafczyk, R.; Schmutzler, R. *Tetrahedron* **1999**, *55*, 14523−14534.

(15) When glyoxal was reacted with 2 equiv of 1-adamantamine, an intractable white precipitate formed that we were unable to characterize due to its poor solubility. This material did not reduce to *N*,*N*′-di(1-adamantyl)ethane-1,2-diamine (**Ic**) on treatment with sodium borohydride.

modified to make **IId**, simply by first reacting 2,4,6-trimethylaniline with a large excess of oxalyl chloride to give the monosubstituted acetyl chloride (**IIa**). Compound **IIa** was then reacted with 1-adamantamine to give **IIb**, which was subsequently reduced and cyclized to give **IId** (Scheme 1).

Synthesis of Ruthenium Complexes. With the precursors **Id** and **IId** in hand, we attempted to prepare their respective complexes [$RuCl_2$(=CHPh)(H_2IAd)(PCy_3)] (**6**) and [$RuCl_2$(=CHPh)(H_2IAdMes)(PCy_3)] (**7**) following the now well-established literature routes.[2] Accordingly, **Id** was treated with potassium *tert*-butoxide or potassium *tert*-pentoxide to give a solution containing free H_2IAd. When this solution was subsequently added to catalyst **1**, however, no changes were apparent, regardless of the reaction conditions. The reactions, which were conducted using a range of different temperatures (25−110 °C) and stoichiometries (1−5 equiv of **Id** relative to **1**), were monitored by ^{31}P NMR. In no instance was any reaction observed to take place. While we did not attempt to isolate free H_2IAd, its presence was implied by ^{1}H NMR, which clearly showed the absence of the central hydrogen (at 8.49 ppm) in **Id** and the diagnostic ∼1 ppm upfield shift of the signal from the four methylene hydrogens (at ∼4 ppm in **Id**).



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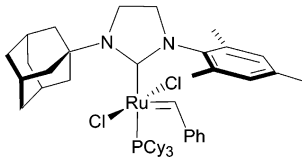

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The failure of the reaction of H_2IAd with **1** under the usual standard reaction conditions is presumably a consequence of the benzylidene moiety in **1**, which is possibly too bulky to permit the presence of a 1-adamantyl group directly overhead. We tentatively suggest that even if a second-generation Grubbs catalyst could be formed with the H_2IAd 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_2IAdMes, should successfully react with **1** to give exclusively complex **7**. The other isomer of **7**, with the H_2IAdMes 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_2IAdMes solution (rapidly formed in situ from **IId** 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 ∼16 ppm (complex **7**) and 10 ppm (free PCy_3) had appeared. Methanolic workup isolated **7** as an air-stable powder. The complex was completely characterized by NMR and a single-crystal X-ray structure (vide infra).

The color and some of the spectroscopic properties of **7** were unanticipated. While the very closely related second-generation Grubbs catalysts **2a** and **2b** are brownish in appearance, complex **7** was green. The ^{31}P NMR peak at 15.7 ppm for **7** 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; however, the corresponding carbene signals for **2b** appear at 222.2 and 296.7 ppm.[5]

Table 1. Crystal Data and Structure Refinement for Complex 7

empirical formula	$C_{47}H_{69}N_2PCl_2Ru$
fw	864.98
cryst habit	block
cryst size	0.45 × 0.40 × 0.40 mm
cryst color	green
diffractometer	Enraf-Nonius CAD-4
wavelength	λ = 0.71069 Mo Kα
temperature	293 K
unit cell dimens	a = 12.497(3) Å
	b = 15.426(3) Å
	c = 23.201(5) Å
volume	4472.9(15) Å^3
Z	4
cryst syst	orthorhombic
space group	$P2_12_12_1$
density (calcd)	1.284 g cm^{-3}
θ range	1.59−26.42°
h min,max	0, 15
k min,max	0, 19
l min,max	0, 29
no. of reflns collected	5128
no, of indep reflns	5093
GOF on F^2	1.092
final R indicies [$I > 2\sigma(I)$]	0.0398
final weighted R (F_o^2)	0.1056

It is noteworthy that there was only a single ^{31}P NMR signal and only a single benzylidene carbene peak in the ^{1}H NMR. This result strongly suggested either the formation of only a single isomer of **7** (with the NHC ligand in a only one orientation) as predicted or, less likely,[16] the free rotation of the NHC ligand on the NMR time scale. A NOESY spectrum of **7** 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.

Crystal Structure of 7. To confirm the connectivity of complex **7** and the orientation of the adamantyl group with respect to the benzylidene group, the single-crystal X-ray structure was determined. The collection and refinement parameters for the crystallographic analysis are presented in Table 1. The structure of **7** is shown in Figure 1, while selected bond lengths and angles are given in Table 2 together with the analogous data for **2a**,[17] for comparison.

The structure confirms the predicted formulation of **7**, essentially resembling the overall geometry of com-

(16) NHC ligands on the second-generation Grubbs metathesis catalysts generally cannot rotate.

(17) Obtained from supplementary crystallographic data CCDC-161995, courtesy of Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK.

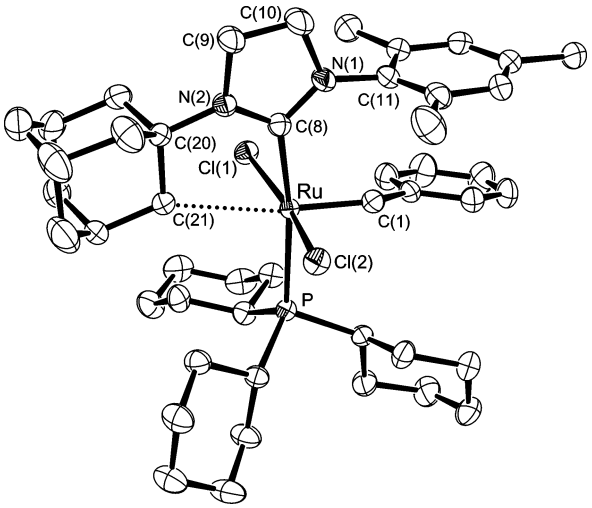

Figure 1. ORTEP representation of complex **7**, with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg) are given in Table 1.

Table 2. Comparison of Analogous Selected Bond Lengths (Å) and Angles (deg) of Complex 7 with 2a

bond length	**7**[a]	**2a**[b]	bond angle	**7**[a]	**2a**[b]
Ru−C(1)	1.851(5)	1.835(2)	P−Ru−C(8)	171.1(1)	163.73(6)
Ru−C(8)	2.083(5)	2.085(2)	Cl(1)−Ru−Cl(2)	167.98(5)	167.71(2)
Ru−P	2.521(1)	2.4245(5)	C(1)−Ru−C(8)	96.9(2)	100.24(8)
Ru−Cl(1)	2.427(1)	2.3988(5)	P−Ru−C(1)	91.5(2)	95.89(6)
Ru−Cl(2)	2.398(1)	2.3912(5)	P−Ru−Cl(1)	96.40(4)	91.06(2)
C(8)−N(1)	1.336(6)	1.348(2)	P−Ru−Cl(2)	89.30(5)	87.75(2)
C(8)−N(2)	1.346(6)	1.347(2)	Cl(1)−Ru−C(1)	102.7(2)	103.15(7)
N(1)−C(10)	1.470(8)	1.482(3)	Cl(2)−Ru−C(1)	87.7(2)	89.14(7)
N(2)−C(9)	1.494(7)	1.476(2)	Cl(1)−Ru−C(8)	84.7(1)	83.26(5)
N(1)−C(11)	1.446(6)	1.432(2)	Cl(2)−Ru−C(8)	88.1(1)	94.55(5)
N(2)−C(20)	1.490(6)	1.440(2)	C(1)−Ru···C(21)	165.0(2)	
Ru···C(21)	2.883(6)				

[a] Data collected at 293 K. [b] Data collected at 98 K.

plex **2a**. However, a number of subtle, but significant dissimilarities are noteworthy. The most important involves the orientation of the PCy_3 ligand. The Ru−P bond length of **7** is 0.1 Å longer than that of **2a**. Furthermore, the P−Ru−C(8) angle is considerably straightened out in **7** 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** toward the benzylidene moiety. Thus, the closest contact of the mesityl and the benzylidene groups is 2.901 Å in **7** (for C(11)−C(1)) and 3.035 Å in **2a**. The main reason for this deformation, which in fact results in more idealized square-pyramidal geometry, is the presence of the adamantyl group. Most of the remaining equivalent geometric parameters of **7** and **2a** are very similar, with the exception of the Ru−Cl distances, particularly Ru−Cl(1), which is considerably longer in **7**.

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 center, 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. 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 room-temperature NMR spectrum clearly took place.

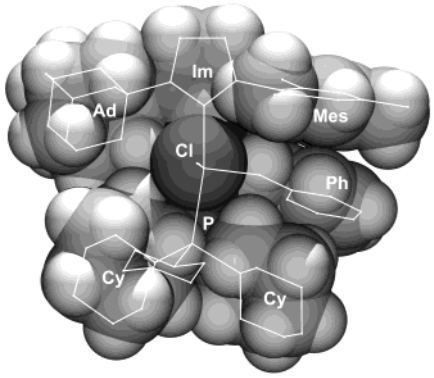

Figure 2. Space-filling representation generated using crystallographic coordinates from the structure of **7**. The complex is shown viewed perpendicular to the imidazolinylidene ring (Im).

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 **7** was rendered (Figure 2). From the image, it is immediately obvious why only a single isomer of **7** 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 complex **6** may be unrealistic on steric grounds.

Metathesis Activity of 7. Perhaps the most remarkable and surprising property of **7** was its extremely poor metathesis activity. By itself, complex **7** 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, **7** failed to produce even trace amounts of any metathesis products of 1-octene at 60 or even 100 °C, with isomerization being the only reaction that took place in these cases. The presence or absence of a solvent also had no effect on the inactivity. However, when 100 equiv of 1-octene was reacted in the presence of **7** in CH_2Cl_2, and some copper(I) chloride was added, 12% conversion (12 turnovers per mol of catalyst) to 7-tetradecene could be achieved. To compare, catalysts **2a** and **2b** are capable of turnover numbers of ∼300 000 and over 600 000, respectively, for the metathesis of 1-octene.[5]

Despite these very disappointing results, **7** did display some ring-opening metathesis polymerization (ROMP) activity. Thus, when 2-norbornene (100 equiv) was reacted with **7** in CH_2Cl_2, 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 **7** toward ethyl vinyl ether (EVE) was tested. EVE typically reacts rapidly (minutes) with Grubbs-type metathesis catalysts to produce

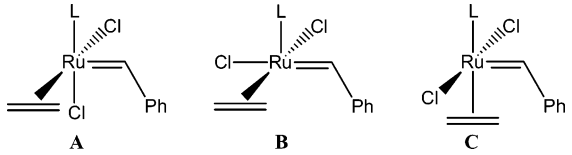

Figure 3. Possible geometries for the initial coordination of olefin.

the corresponding Fischer-type carbene complex.[18] As expected, complex **7** did react with excess EVE (monitored by NMR) to produce [$RuCl_2$(=CHOEt)(H_2IAdMes)(PCy_3)$_2$] (**8**). In the ^{31}P 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 **7**), while in the ^{1}H NMR a new peak at 13.67 ppm was formed while the benzylidene peak at 19.05 ppm was attenuated. The observed downfield shift in the ^{31}P NMR and the upfield shift ^{1}H NMR are highly diagnostic for the formation of a Fischer-type carbene complex.[18a] The initiation kinetics for this reaction was measured by ^{1}H NMR[11] at 20 °C, giving a k_{Init} value of $(9.1 \pm 0.2) \times 10^{-4}$ s^{-1}. This k_{Init} value attests that the initiation rate of **7** is in fact faster than that of **2a**, which was determined to be 4.6×10^{-4} s^{-1} at 35 °C,[11] but remains much slower than the parent complex **1**, which displays a k_{Init} of 1.0×10^{-3} s^{-1} at 10 °C.[11]

In light of the typical initiation rate of complex **7**, the reason for the virtual catalytic inactivity for metathesis is not entirely clear. The σ-donating properties of H_2-IAdMes and H_2IMes 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 center in **7** observed in the crystal structure is almost certainly unimportant at the reaction temperatures used in the metathesis experiments. Furthermore, the complexes [$RuCl_2$(=CHPh)(H_2IMes)(Pyr)$_2$] (**8**) and [$RuCl_2$(=CHPh)(H_2IMes)(3-Br−Pyr)$_2$] (**9**) (Pyr = pyridine) are both capable metathesis catalysts, despite the six-coordinate (octahedral) geometry.[19] 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 **7** compared with closely related catalysts. If this steric blocking is the dominant reason for **7**'s catalytic inactivity, 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 3).[4] The poor catalytic activity of complex **7** 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 **7** represents only a single example, and further research and additional complexes are required before a definitive conclusion can be reached.

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Summary

The H_2IAd and H_2IAdMes ligand precursors **Id** and **IId**, respectively, were successfully synthesized. Only H_2IAdMes reacted with **1** to give the expected product **7**. In light of this result, the apparent inability of H_2-IAd to displace a PCy_3 ligand in **1** suggests that the failure is primarily a consequence of H_2IAd's uncompromising steric bulk. The formation of only a single isomer of **7**, together with a space-filling model generated from its crystallographic coordinates, further supports this notion.

The activity of complex **7** clearly highlights the relevance of the NHC ligand of the second-generation Grubbs-type metathesis catalysts. In the present case, the H_2IAdMes ligand imparted the resulting complex **7** with only very limited metathesis activity, considerably lower than the parent complex **1**. Indeed, **7** 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 **7** 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.

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 of the complexes 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 analyzer at the Department of Organic Chemistry, University of Nijmegen (The Netherlands) and H. Kolbe Mikroanalytiches Laboratorium (Germany).

[$RuCl_2$(=CHPh)(IAdMesH_2)(PCy_3)] (7). 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-dihydroimidazolinium chloride (**IId**) (0.185, 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 **7** as a green powder (0.152 g, 58%). ^{31}P NMR (CD_2Cl_2): δ 15.7. ^{1}H NMR (CD_2Cl_2): δ 19.05 (s, 1 H, Ru=C*H*Ph), 9.19 (br s, 1 H, *o*-C_6H_5), 7.45 (t, $J_{H,H}$ = 7.20 Hz, 1 H, *p*-C_6H_5), 7.23 (m, 2 H, *m*-C_6H_5), 6.89 (br s, 1 H, *o*-C_6H_5), 6.78 (s, 1 H, $C_6H_2Me_3$), 5.84 (s, 1 H, $C_6H_2Me_3$), 3.96 (pseudo q, J_{app} = ∼10 Hz, 2 H, AdNCH_2CH_2NMes), 3.89 (pseudo q, J_{app} = 10.2 Hz, 1 H, AdNCH_2CH_2NMes), 3.70 (pseudo q, J_{app} = 9.0 Hz, 1 H, AdNC*H*HCH_2NMes), 3.57 (pseudo q, J_{app} = 9.9 Hz, 1 H, AdNCH*H*CH_2NMes), 2.74 (s, 6 H, *o*-CH_3), 2.47 (s, 3 H, *p*-CH_3), 2.38 (br s, 3 H, *H*-Ad), 1.98 (s, 3 H, *H*-Ad), 1.94−1.48 (m, 31 H, *H*-PCy_3/*H*-Ad), 1.28−1.11 (m, 5 H, *H*-PCy_3), 0.94 (br s, 6 H

H-PCy_3). ^{13}C NMR (CD_2Cl_2): δ 302.6 (pseudo t, $J_{P,C} = 11.6$ Hz, Ru=*C*HPh), 217.0 (d, $J_{P,C} = 80.5$ Hz, AdN*C*NMes), 152.1 (*i*-C_6H_5), 138.5, 138.3, 138.0, 137.8 ($C_6H_2Me_3$), 132.7 (br, C_6H_5), 129.8 ($C_6H_2Me_3$), 129.4 (*p*-C_6H_5), 128.6, 127.6 (both br, C_6H_5), 58.9 (*C*-1 Ad), 51.0 (AdNCH_2CH_2NMes), 45.0 (AdN*C*H_2CH_2-NMes), 41.3 (*C*-2 Ad), 36.7 (*C*-4 Ad), 34.9 (d, $J_{P,C} = 13.2$ Hz, *i*-PCy_3), 30.7 (*C*-3 Ad), 29.1 (d, $J_{P,C} = 15.8$ Hz, *m*-PCy_3), 28.3 (dd, $J_{P,C} = 21.3$ Hz, $J_{P,C} = 7.7$ Hz, *o*-PCy_3), 26.9 (*p*-PCy_3), 21.2 (*p*-*C*H_3), 19.2, 18.7 (*o*-*C*H_3). Anal. Calcd for $C_{47}H_{69}Cl_2N_2PRu$: C 65.26, H 8.04, N 3.24. Found: C 65.12, H 7.95, N 3.17. FAB-MS: *m*/*z* (rel intensity, %) 864 ($[M]^+$, 7), 829 ($[M - Cl]^+$, 10), 793 ($[M - 2Cl]^+$, 4), 513 ($[M - 2Cl - PCy_3]^+$, 22), 421 ($[Ru(H_2IAdMes)]^+$, 34), 370 ($[CHPh + PCy_3]^+$, 100), 323 ($[H_2IAdMes - H]^+$, 93), 289 (58), 280 ($[PCy_3]^+$, 92), 208 (33), 197 ($[PCy_2]^+$, 20), 135 ($[Ad]^+$, 53). HRMS (FAB): calcd for $C_{47}H_{69}Cl_2N_2P^{102}Ru$ $[M]^+$ 864.3619, observed 864.3610.

Reaction of 7 with Ethyl Vinyl Ether. Ethyl vinyl ether (6 μL, 0.063 mmol) was added to a CD_2Cl_2 (0.4 mL) solution of **7** (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 [$RuCl_2$(=CHOEt)(H_2-IAdMes)(PCy_3)] (**8**). The product was not isolated. ^{31}P NMR (CD_2Cl_2): δ 19.8. ^1H NMR (CD_2Cl_2): δ 13.67 (s, 1 H, Ru=C*H*OEt), 6.94 (s, 2 H, $C_6H_2Me_3$), 3.89 (m, AA′BB′ system, 2 H, MesNCH_2CH_2NAd), 3.63 (m, AA′BB′ system, 2 H, MesNCH_2CH_2-NAd), 3.37 (q, $J_{H,H} = 6.9$ Hz, 2 H, OCH_2CH_3), 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, $J_{H,H} = 6.9$ Hz, 3 H, OCH_2CH_3), 1.31−1.10 (m, 9 H, *H*-PCy_3).

Metathesis Reactions. Complex **7** (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 mixtures were stirred at room temperature, 60 °C, or 100 °C for 24 h. At room temperature, no color change was observed for the reaction, while those at higher temperatures slowly became yellow. Samples were taken and analyzed by GC/FID. No 7-tetradecene had formed in any of the reactions, with only a small amount of isomerization products (primarily 2-octene) detected. The reaction was repeated in CH_2Cl_2 (1 mL) using only 100 equiv of 1-octene (90 μL, 0.573 mmol) relative to **7** (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. Similar procedures were used for the self-metathesis of methyl oleate and ring-closing metathesis of diethyl diallylmalonate.

Similarly, complex **7** (5.0 mg, 5.78 μmol) was added to a CH_2Cl_2 (1 mL) solution of 2-norbornene (55.0 mg, 0.584 mmol) and the resulting mixture stirred at room temperature for 1 h. After filtering through a short plug of silica, methanol (20 mL) was added, resulting in a tacky precipitate. The polymer was dried under vacuum to give polynorbornylene (54 mg 98%), ~90% *trans*.

Crystal Structure of 7.[20] Green blocks of **7** suitable for X-ray diffraction were grown by the slow evaporation of a CH_2Cl_2/MeOH solution under nitrogen. Intensity data were corrected for Lorentz effects, polarization effects, and linear absorption by a Ψ-scan method. The structure of **7** was solved using the direct methods option of SHELXS-97[21] and subsequently refined using SHELXL-97.[22] 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 AFIX 137 card was used to allow the hydrogen atoms to rotate to the maximum area of residual density, while fixing their geometry.

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Supporting Information Available: The complete synthesis of the H_2IAd and H_2IAdMes ligand precursors (**Id** and **IId**), a figure showing the complete atom-labeling scheme for complex **7**, tables of crystal and intensity collection data, positional and displacement parameters, and complete bond distances and bond angles. This material is available free of charge via the Internet at http://pubs.acs.org.

OM034062K

(20) The Crystallographic Information File (CIF) for complex **7** has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC-223175. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK.; fax: (internat.) + 44-1223/336-033; e-mail: deposit@ccdc.cam.ac.uk].

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