Ruthenium Alkylidene Complexes of Chelating Amine Ligands

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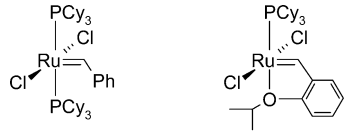
A density functional theory-based computational comparison of various [Ru]−L bonds in $L(PCy_3)Cl_2Ru{=}CH_2$ complexes, where L is a dative ligand, shows that similar bond strengths can be expected for ruthenium−imine and ruthenium−amine bonds. The similarity remains when comparing the corresponding bond strengths in ruthenium olefin metathesis catalysts coordinated by bidentate Schiff-base ligands with those of ruthenium complexes of corresponding chelating amino-benzyloxy ligands. This observation prompted us to synthesize two bidentate amino-benzyloxy ligands and one tridentate amino-bis(benzyloxy) ligand. Ruthenium alkylidene complexes coordinated by the bidentate ligands proved to be unstable and eluded isolation. Reaction of the potassium salt of the tridentate ligand with $(PCy_3)_2Cl_2Ru{=}CHPh$ and $(PCy_3)_2Cl_2Ru(=CH\text{-}o\text{-}O^iPrC_6H_4)$ resulted in two complexes, **10** and **11**, respectively, that represent the first examples of ruthenium alkylidenes (arylidenes) coordinated by an amine. **10** and **11** contain an essentially symmetrically coordinated tridentate ligand and both are also coordinated by a tri-cyclohexylphosphine ligand. The isopropyloxy function of the alkylidene group in **11** is not coordinated to the metal. Complexes **10** and **11** are fairly stable to air, moisture, and protic solvents, but display low thermal stability. Only very low catalytic activity has been obtained in ring-closing metathesis of diethyl diallylmalonate using **10** or **11** dissolved in acid-free solvents. The presence of a Brønsted acid increases the activity dramatically, although at the expense of an increased decomposition rate of the catalyst.

Introduction

The development of highly active transition-metal-based catalysts for olefin metathesis[1−3] has opened a wide range of applications of this class of reaction in organic synthesis, polymer chemistry, and production of fine chemicals.[4] Whereas both contemporary Schrock[1] and Grubbs[2,3,5] catalysts are highly active for olefin metathesis, the latter family of ruthenium alkylidene complexes have also proven relatively air-stable and tolerant toward a plethora of functional groups, reacting more readily with olefins than with acids, alcohols, and water.[3] Because of their ease of use and compatibility with a broad range of substrates and metathesis reactions, the Grubbs catalysts, in particular, have found numerous applications. Much effort has also been spent on improving the activity of the ruthenium catalysts while at the same time maintaining, or even increasing, their stability and robustness toward functional groups. A highly successful variation of Grubbs' original catalyst design (**1**, Chart 1) was introduced by Hoveyda and involves a chelating alkylidene ligand and only one phosphine (**2**, Chart 1).[6] Subsequently, a range of highly active stable monosubstituted variations of **1** and **2** containing a N-heterocyclic carbene (NHC) ligand have been reported.[7]

Chart 1. Original First-Generation Grubbs 1 and Hoveyda 2 Catalysts for Olefin Metathesis



1 **2**

Other variations of the original catalyst design, **1**, involve ligands incorporating pyridine[8] or imine functions.[9−14] Notably, ruthenium complexes coordinated by bidentate Schiff base ligands and a phosphine[9,10] or N-heterocyclic carbene[12−14] as

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(1) Schrock, R. R.; Murdzek, J. S.; Bazan, G. C.; Robbins, J.; Dimare, M.; Oregan, M. *J. Am. Chem. Soc.* **1990**, *112*, 3875. Schrock, R. R.; Hoveyda, A. H. *Angew. Chem., Int. Ed.* **2003**, *42*, 4592.

(2) Nguyen, S. T.; Johnson, L. K.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1992**, *114*, 3974. Schwab, P.; France, M. B.; Ziller, J. W.; Grubbs, R. H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2039.

(3) Trnka, T. M.; Grubbs, R. H. *Acc. Chem. Res.* **2001**, *34*, 18.

(4) *Handbook of Metathesis*; Grubbs, R. H., Ed.; Wiley-VCH: Weinheim, Germany, 2003. Astruc, D. *New J. Chem.* **2005**, *29*, 42.

(5) Grubbs, R. H. *Angew. Chem., Int. Ed.* **2006**, *45*, 3760.

(6) Kingsbury, J. S.; Harrity, J. P. A.; Bonitatebus, P. J.; Hoveyda, A. H. *J. Am. Chem. Soc.* **1999**, *121*, 791.

(7) Scholl, M.; Trnka, T. M.; Morgan, J. P.; Grubbs, R. H. *Tetrahedron Lett.* **1999**, *40*, 2247. Scholl, M.; Ding, S.; Lee, C. W.; Grubbs, R. H. *Org. Lett.* **1999**, *1*, 953. Huang, J. K.; Stevens, E. D.; Nolan, S. P.; Petersen, J. L. *J. Am. Chem. Soc.* **1999**, *121*, 2674. Frenzel, U.; Weskamp, T.; Kohl, F. J.; Schattenman, W. C.; Nuyken, O.; Herrmann, W. A. *J. Organomet. Chem.* **1999**, *586*, 263. Ackermann, L.; Fürstner, A.; Weskamp, T.; Kohl, F. J.; Herrmann, W. A. *Tetrahedron Lett.* **1999**, *40*, 4787.

(8) Sanford, M. S.; Love, J. A.; Grubbs, R. H. *Organometallics* **2001**, *20*, 5314. Denk, K.; Fridgen, J.; Herrmann, W. A. *Adv. Synth. Catal.* **2002**, *344*, 666. Wright, J. A.; Danopoulos, A. A.; Motherwell, W. B.; Carroll, R. J.; Ellwood, S. *J. Organomet. Chem.* **2006**, *691*, 5204. Wasilke, J. C.; Wu, G.; Bu, X. H.; Kehr, G.; Erker, G. *Organometallics* **2005**, *24*, 4289. Jordaan, M.; Vosloo, H. C. M. *Adv. Synth. Catal.* **2007**, *349*, 184.

(9) Chang, S.; Jones, L.; Wang, C. M.; Henling, L. M.; Grubbs, R. H. *Organometallics* **1998**, *17*, 3460.

(10) Occhipinti, G.; Jensen, V. R.; Bjørsvik, H. R. *J. Org. Chem.* **2007**, *73*, 3561.

(11) Hejl, A.; Day, M. W.; Grubbs, R. H. *Organometallics* **2006**, *25*, 6149.

(12) Binder, J. B.; Guzei, I. A.; Raines, R. T. *Adv. Synth. Catal.* **2007**, *349*, 395.

(13) Allaert, B.; Dieltiens, N.; Ledoux, N.; Vercaemst, C.; Van der Voort, P.; Stevens, C. V.; Linden, A.; Verpoort, F. *J. Mol. Catal. A: Chem.* **2006**, *260*, 221. Drozdzak, R.; Ledoux, N.; Allaert, B.; Dragutan, I.; Dragutan, V.; Verpoort, F. *Cent. Eur. J. Chem.* **2005**, *3*, 404. De Clercq, B.; Verpoort, F. *Tetrahedron Lett.* **2002**, *43*, 9101. De Clercq, B.; Verpoort, F. *J. Mol. Catal. A: Chem.* **2002**, *180*, 67.

(14) De Clercq, B.; Verpoort, F. *Adv. Synth. Catal.* **2002**, *344*, 639.

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the second dative ligand give thermally stable catalysts exhibiting high activity for ring-closing metathesis (RCM) at elevated reaction temperatures. The bidentate Schiff-base complexes also display improved tolerance toward, and catalytic activities in, polar protic solvents[9,12] and thus widen the range of accessible reactions and reaction conditions in which to apply the transition-metal catalysts for olefin metathesis. The complexes that are coordinated by both a NHC ligand and a Schiff-base ligand display even higher activities in RCM and ring-opening metathesis polymerization (ROMP) than the corresponding phosphine complexes.[13,14] Schiff-base ligands have successfully been applied in a range of ruthenium-based complexes and catalytic reactions in recent years, and some of these developments have been reviewed.[15]

In comparison, the prospect of developing active olefin metathesis catalysts incorporating amine ligands seems far removed. Despite the fact that amine complexes of ruthenium appear to be relatively common, and some also contain Ru═C double bonds,[16] none of these compounds are alkylidenes (arylidenes) and none have been reported to be active for olefin metathesis. In fact, amines have been known to be detrimental to catalyst activity and stability,[3,17] although there are also reports of successful metathesis reactions in the presence of amines.[18]

A series of experimental[19−22] and computational[22−24] studies have focused on the mechanism of olefin metathesis as catalyzed by ruthenium alkylidene complexes. It is now widely accepted that olefin metathesis mediated by the Grubbs-type ruthenium catalysts follows the general Hérisson-Chauvin mechanism for which the first step is olefin coordination and which passes through a metallacyclobutane intermediate.[25] For the Grubbs-type ruthenium complexes, experimental[20,26] and computational studies[23] have shown that this olefin coordination is preceded by dissociation of a dative ligand, usually a phosphine, from the precursor complex.

Apart from the above-mentioned lack of reported ruthenium alkylidenes coordinated by amines and recorded problems related to the use of this class of ligands in olefin metathesis, there are also reasons to investigate the influence of amines on this reaction more closely. For example, in a recent broad density-functional-theory-based quantitative structure−activity (QSAR) screening of a large number of common dative ligands, L, in active Grubbs-type complexes of the kind $LL'Cl_2Ru{=}CH_2$, it was suggested that the intrinsic catalysis-promoting properties of amine ligands may be comparable to or higher than those of phosphines and imines.[27] These properties were found to be both steric and electronic in nature. Ligand-to-metal σ-donation was found to enhance and metal-to-ligand π back-donation to lower catalytic activity, whereas bulky dative ligands were seen to drive the reaction toward the less sterically congested metallacyclobutane intermediate and thus to contribute to catalytic activity. Amines are good σ donors but are less π acidic than phosphines and imines, and they are also inherently more sterically demanding than imines.

It should be pointed out that the QSAR screening[27] of the dative ligands only pertained to their intrinsic ability to give a low activation barrier for olefin metathesis for a catalyst precursor dissociating a dative ligand, L′, trans to the ligand, L, being screened and did not directly consider other factors such as differences in stability and Ru−L bond enthalpy among the different complexes. In other words, amines as dative ligands possess properties known to promote olefin metathesis activity, but an investigation is needed before concluding upon the potential of using these ligands in ruthenium catalysts for olefin metathesis.

To this end, we have designed novel chelating N-benzyloxy ligands and subjected ruthenium alkylidene complexes thereof to investigation using density functional theory (DFT) calculations to assess their stability toward dissociation of the Ru−amine bond. Subsequently, we have subjected selected ligands and complexes to synthesis and structural characterization. A couple of successfully isolated complexes have also been tested for activity toward RCM.

(15) Drozdzak, R.; Allaert, B.; Ledoux, N.; Dragutan, I.; Dragutan, V.; Verpoort, F. *Coord. Chem. Rev.* **2005**, *249*, 3055. Drozdzak, R.; Allaert, B.; Ledoux, N.; Dragutan, I.; Dragutan, V.; Verpoort, F. *Adv. Synth. Catal.* **2005**, *347*, 1721.

(16) Of the 14700 crystal structures containing ruthenium registered in the Cambridge Structural Database (CSD) of the Cambridge Crystallographic Data Centre (CCDC) (version 5.28, updated January 2007), 958 contain amine- and 1169 contain imine-groups as dative ligands coordinated to ruthenium. Some (21) of the amine complexes also contain Ru═C double bonds. The latter compounds are Fischer-type carbene or metallacumulene complexes.

(17) Fürstner, A.; Ackermann, L.; Beck, K.; Hori, H.; Koch, D.; Langemann, K.; Liebl, M.; Six, C.; Leitner, W. *J. Am. Chem. Soc.* **2001**, *123*, 9000. Fürstner, A. *Angew. Chem. Int. Ed.* **2000**, *39*, 3013. Maughon, B. R.; Grubbs, R. H. *Macromolecules* **1997**, *30*, 3459. Fu, G. C.; Nguyen, S. T.; Grubbs, R. H. *J. Am. Chem. Soc.* **1993**, *115*, 9856.

(18) Toste, F. D.; Chatterjee, A. K.; Grubbs, R. H. *Pure Appl. Chem.* **2002**, *74*, 7. Schwab, P.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1996**, *118*, 100.

(19) Sanford, M. S.; Ulman, M.; Grubbs, R. H. *J. Am. Chem. Soc.* **2001**, *123*, 749. Sanford, M. S.; Love, J. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **2001**, *123*, 6543.

(20) Dias, E. L.; Nguyen, S. T.; Grubbs, R. H. *J. Am. Chem. Soc.* **1997**, *119*, 3887. Hinderling, C.; Adlhart, C.; Chen, P. *Angew. Chem., Int. Ed.* **1998**, *37*, 2685.

(21) Ulman, M.; Grubbs, R. H. *Organometallics* **1998**, *17*, 2484. Love, J. A.; Sanford, M. S.; Day, M. W.; Grubbs, R. H. *J. Am. Chem. Soc.* **2003**, *125*, 10103. Adlhart, C.; Chen, P. *Helv. Chim. Acta* **2000**, *83*, 2192. Adlhart, C.; Volland, M. A. O.; Hofmann, P.; Chen, P. *Helv. Chim. Acta* **2000**, *83*, 3306. Adlhart, C.; Chen, P. *Helv. Chim. Acta* **2003**, *86*, 941. Basu, K.; Cabral, J. A.; Paquette, L. A. *Tetrahedron Lett.* **2002**, *43*, 5453. Lehman, S. E.; Wagener, K. B. *Macromolecules* **2002**, *35*, 48. Stuer, W.; Wolf, J.; Werner, H. *J. Organomet. Chem.* **2002**, *641*, 203. Hansen, S. M.; Rominger, F.; Metz, M.; Hofmann, P. *Chem.—Eur. J.* **1999**, *5*, 557. Volland, M. A. O.; Hansen, S. M.; Hofmann, P. In *Chemistry at the Beginning of the Third Millennium: Molecular Design, Supramolecules, Nanotechnology and Beyond*; Fabrizzi, L., Poggi, A., Eds.; Springer: Berlin, 2000. Volland, M. A. O.; Adlhart, C.; Kiener, C. A.; Chen, P.; Hofmann, P. *Chem.—Eur. J.* **2001**, *7*, 4621. Hofmann, M.; Puskas, J. E.; Weiss, K. *Eur. Polym. J.* **2002**, *38*, 19. Courchay, F. C.; Sworen, J. C.; Ghiviriga, I.; Abboud, K. A.; Wagener, K. B. *Organometallics* **2006**, *25*, 6074. Anderson, D. R.; Hickstein, D. D.; O'Leary, D. J.; Grubbs, R. H. *J. Am. Chem. Soc.* **2006**, *128*, 8386.

(22) Adlhart, C.; Hinderling, C.; Baumann, H.; Chen, P. *J. Am. Chem. Soc.* **2000**, *122*, 8204. Jordaan, M.; van Helden, P.; van Sittert, C.; Vosloo, H. C. M. *J. Mol. Catal. A: Chem.* **2006**, *254*, 145.

(23) Aagaard, O. M.; Meier, R. J.; Buda, F. *J. Am. Chem. Soc.* **1998**, *120*, 7174. Vyboishchikov, S. E.; Bühl, M.; Thiel, W. *Chem.—Eur. J.* **2002**, *8*, 3962. Fomine, S.; Vargas, S. M.; Tlenkopatchev, M. A. *Organometallics* **2003**, *22*, 93. Bernardi, F.; Bottoni, A.; Miscione, G. P. *Organometallics* **2003**, *22*, 940. Cavallo, L. *J. Am. Chem. Soc.* **2002**, *124*, 8965. Adlhart, C.; Chen, P. *J. Am. Chem. Soc.* **2004**, *126*, 3496.

(24) Meier, R. J.; Aagaard, O. M.; Buda, F. *J. Mol. Catal. A: Chem.* **2000**, *160*, 189. Adlhart, C.; Chen, P. *Angew. Chem. Int. Ed.* **2002**, *41*, 4484. Costabile, C.; Cavallo, L. *J. Am. Chem. Soc.* **2004**, *126*, 9592. Vyboishchikov, S. E.; Thiel, W. *Chem.—Eur. J.* **2005**, *11*, 3921. Fomine, S.; Ortega, J. V.; Tlenkopatchev, M. A. *J. Mol. Catal. A: Chem.* **2005**, *236*, 156. Straub, B. F. *Angew. Chem., Int. Ed.* **2005**, *44*, 5974. Lippstreu, J. J.; Straub, B. F. *J. Am. Chem. Soc.* **2005**, *127*, 7444. Tsipis, A. C.; Orpen, A. G.; Harvey, J. N. *Dalton Trans.* **2005**, 2849. Fomine, S.; Tlenkopatchev, M. A. *J. Organomet. Chem.* **2006**, *691*, 5189. van Rensburg, W. J.; Steynberg, P. J.; Kirk, M. M.; Meyer, W. H.; Forman, G. S. *J. Organomet. Chem.* **2006**, *691*, 5312. Correa, A.; Cavallo, L. *J. Am. Chem. Soc.* **2006**, *128*, 13352. Fomine, S.; Ortega, J. V.; Tlenkopatchev, M. A. *J. Organomet. Chem.* **2006**, *691*, 3343.

(25) Hérisson, J.-L.; Chauvin, Y. *Makromol. Chem.* **1970**, *141*, 161.

(26) Tallarico, J. A.; Bonitatebus, P. J.; Snapper, M. L. *J. Am. Chem. Soc.* **1997**, *119*, 7157.

(27) Occhipinti, G.; Bjørsvik, H. R.; Jensen, V. R. *J. Am. Chem. Soc.* **2006**, *128*, 6952.

Table 1. Calculated Ru−Ligand Bond Enthalpies of Selected Monodentate Ru Alkylidene Complexes, $L(PCy_3)Cl_2Ru{=}CH_2$[a]

L	ΔH(Ru−L)	ΔH(Ru−PCy_3)
2,3,4,5-tetrahydropyridine	17.8	27.6
piperidine	19.2	30.5
PCy_3	18.9	18.9

[a] Bond enthalpies at 298 K in kcal/mol.

Results and Discussion

Initial Theoretical Considerations. The strength of the Ru−L bond for amines may indicate to what extent these ligands may form stable and active olefin metathesis catalysts when compared to those for other dative ligands such as phosphines. We have therefore calculated the Ru−L bond dissociation enthalpies for several dative ligands, L (L = 2,3,4,5-tetrahydropyridine, piperidine, and tri-cyclohexyl-phosphine) in $L(PCy_3)Cl_2Ru{=}CH_2$ complexes, see Table 1.

The similar bond dissociation enthalpies calculated for the two cyclic ligands, 2,3,4,5-tetrahydropyridine (ΔH = 17.8 kcal/mol) and piperidine (ΔH = 19.2 kcal/mol), suggest that imines and amines basically should form equally strong bonds to the metal in Grubbs-type ruthenium complexes for olefin metathesis. Moreover, these bond enthalpies are also very similar to those of PCy_3 (Cy = cyclohexyl) in a bis(phosphine)-complex (L = PCy_3, ΔH = 18.9 kcal/mol). In other words, the Ru−amine bond enthalpies are similar to Ru−L bond enthalpies of known ruthenium alkylidene catalysts. In other words, judged from the Ru−L bond enthalpies alone, it should be possible to obtain ruthenium alkylidene complexes bearing amine ligands. Next, the Ru−L bonds of both 2,3,4,5-tetrahydropyridine and piperidine are significantly weaker than their trans-Ru−PCy_3 bonds in the mixed imine/phosphine and amine/phosphine complexes, suggesting that the amine or imine, and not the phosphine, will be the leaving group, as already suggested for the catalysts coordinated by Schiff-base ligands.[14] That the amine function will represent the dissociating ligand implies that the prediction of its intrinsic catalysis-promoting properties[27] is not relevant for these complexes. At the same time, the similarity of our calculated Ru−L bond enthalpies for L = 2,3,4,5-tetrahydropyridine and piperidine suggests that amines also could act efficiently as dissociating ligands in ruthenium complexes for olefin metathesis, analogous to the imine function of the very active catalysts coordinated by Schiff-base ligands. It should be stressed that this conclusion does not suggest that Ru−L bond enthalpies may be directly translated to catalyst activities, as shown by the negative correlation between dissociation enthalpies and catalyst activities when comparing Grubbs first- and second-generation catalysts.[19] That the Ru−amine and Ru−imine bonds are of similar strength, however, suggests that the rate of initiation (the dissociation) can be expected to be comparable for the two classes of complexes. Moreover, dissociation of an imine or amine, respectively, from a 16-electron precursor complex, $L(PCy_3)Cl_2Ru{=}CH_2$, would result in the same 14-electron catalyst complex. The corresponding dissociation in complexes bearing bidentate imine and amine ligands would lead to 14-electron complexes for which differences could, in principle, be limited to the pending imine or amine function. In conclusion, given that ruthenium alkylidene complexes coordinated by amine ligands could be synthesized and prove to be stable under catalytic conditions, our initial comparison of Ru−L bond enthalpies suggests that these amine complexes would display catalytic properties similar to those of the existing catalysts coordinated by Schiff-base ligands.

Chart 2. Bidentate and Tridentate Ru Alkylidene Complexes Investigated in This Work

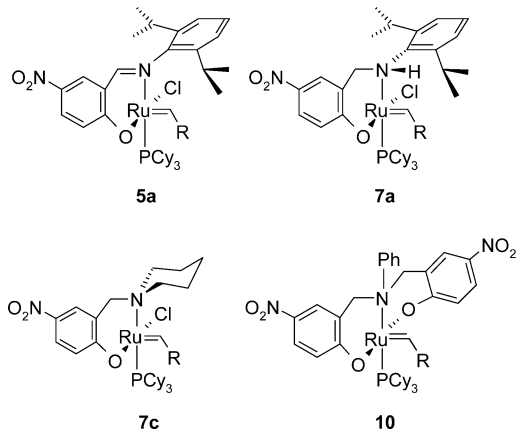


Table 2. Calculated Bond Dissociation Enthalpies of Selected Bidentate and Tridentate Ru Alkylidene Complexes[a]

complex[b]	ΔH (Ru−N)	ΔH (Ru−PCy_3)
5a	21.5	31.9
7a	8.6	23.9
7c	17.8	27.6
10	16.0	31.1

[a] Bond enthalpies at 298 K in kcal/mol. [b] See Chart 2 for the structures of the complexes. A methylidene group, that is, R = H in Chart 2, has been used in the calculations.

Essentially following the catalyst design used in the latter class of catalysts, we have designed two novel bidentate amino-benzyloxy ligands and their ruthenium complexes; see structures **7a** and **7c** in Chart 2. To further assess the expected stabilities and initial dissociation behaviors of these complexes, we have calculated the Ru−L bond enthalpies and compared them with those of a closely related Schiff-base complex; see structure **5a** in Chart 2 and in Table 2. We have also designed a corresponding tridentate amino-bis(benzyloxy) ligand and the corresponding ruthenium complex **10**. Calculation of the Ru−amine bond enthalpies of the chelating ligands involved dissociated states generated mainly by rotation around C−C single bonds of the ligand backbone (**7a** and **7c**) or mainly by increasing a number of angles along the ligand backbone (**10**), as seen in the optimized geometries in Figure 1.

Whereas the difference in Ru−N bond strength between 2,3,4,5-tetrahydropyridine and piperidine was found to be 1.4 kcal/mol, the Ru−N bond enthalpy for **5a** is 3.7 kcal/mol higher than that of the 2,3,4,5-tetrahydropyridine complex and much higher (by 12.9 kcal/mol) than that of **7a**, showing that, as expected, a sterically encumbering substituent may have a much more detrimental effect on a metal−amine bond than on the corresponding metal−imine bond. For **7c**, we see that a basic but much less sterically encumbering amine contributes to a significantly higher bond enthalpy (17.8 kcal/mol), not much lower than that of **5a**. It is interesting to note that the Ru−imine bond enthalpy of **5a** is larger than that of the Ru−PCy_3 bond in the bis(phosphine)-complex (L = PCy_3, Table 1), suggesting that the Schiff-base-coordinated catalyst would need more activation than the Grubbs "first-generation" catalyst for the initial ligand-dissociation to take place. Indeed, elevated reaction temperatures are needed to obtain high catalytic activity for catalysts such as **5a**, that is, coordinated by a phosphine and a bidentate Schiff-base ligand.[3,9]

Also the complex coordinated with a tridentate amine ligand (**10**) has a metal−amine bond that is only a few kilocalories

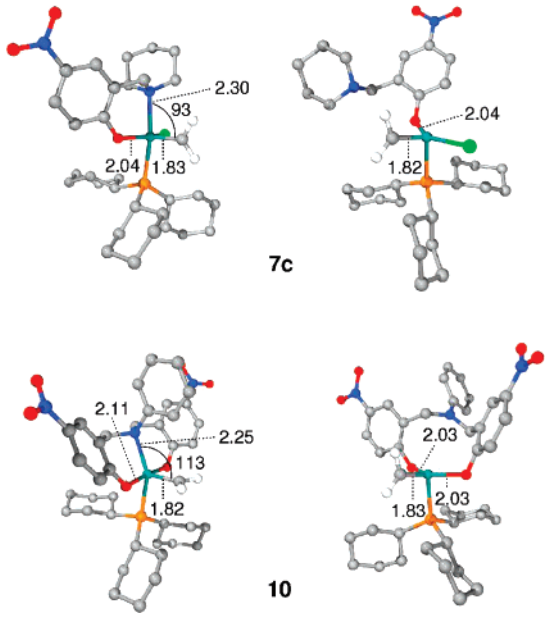


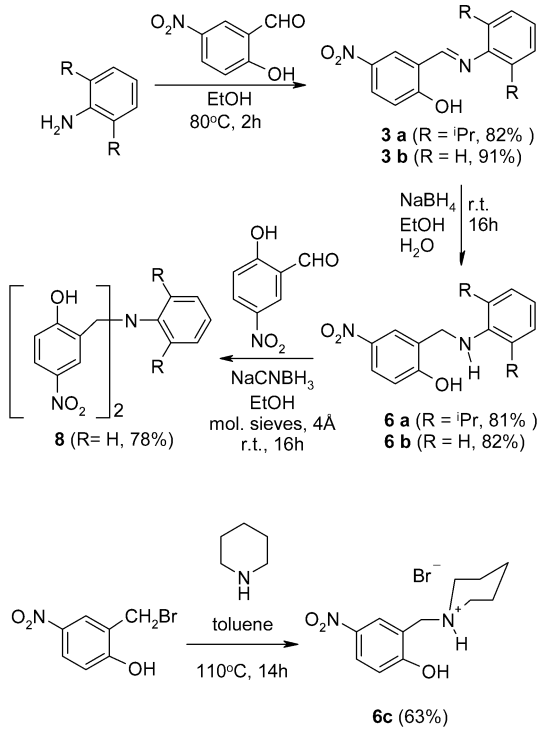
Figure 1. Optimized geometries of complexes **7c** and **10**, with (left) and without (right) the amine donor function bound to Ru: distances in angstroms, angles in degrees. All hydrogen atoms except those of the methylidene group have been omitted for clarity. Color coding: C, dark gray; H, light gray; N, blue; O, red; P, orange; Cl, green; Ru, turquoise.

per mole weaker than the metal−imine bond of **5a**. Moreover, complexes **5a**, **7c**, and **10** have comparable Ru−PCy_3 bond strengths. In other words, the relative strengths of the metal−phosphine and metal−imine/amine bonds are similar for **5a**, **7c**, and **10**, which indicates that the two latter complexes may also prove to be stable and active for olefin metathesis. Furthermore, the geometry-optimized complexes **7a**, **7c**, and **10** all adopt the essential trigonal bipyramidal structure normally seen for the Grubbs family of ruthenium catalyst, show no signs of strain, and feature geometry parameters in their normal ranges (Figure 1). Thus, also the optimized geometries indicate that the new amine complexes could be stable.

Synthesis of Ru Alkylidene Complexes of Chelating Amine Ligands. The chelating N-benzyloxy ligands were prepared according to three different synthetic protocols; see Scheme 1. The first step in the synthesis of **6a**, **6b**, and **8** involved condensation of 5-nitrosalicylaldehyde with 2,6-diisopropylaniline or aniline to give the corresponding Schiff-base ligands **3a** and **3b**, respectively.[9] The reduction of the Schiff-bases to the amines **6a** and **6b** was carried out using a modified version of a protocol previously disclosed by Steevens and Pandit.[28] The bidentate ligands **6a** and **6b** were both obtained in good yields (>80%). Starting from **6b**, the new tridentate amine ligand **8** was obtained in good yield (78%) using a modified version of a previously disclosed procedure.[29] The ammonium salt **6c** was obtained in moderate yield in a straightforward nucleophilic substitution of bromide with piperidine in 2-hydroxy-5-nitrobenzyl bromide.

In the present work the intermediates **3a**,[9] **3b**,[30] and **6b**[31] were characterized and identified by ^{1}H NMR, while all of the other

Scheme 1. Synthetic Pathways to Bidentate (3a,b, 6a−c) and Tridentate (8) Imine and Amine Ligands



ligands were characterized by ^{1}H and ^{13}C NMR. Moreover, compounds **6a** and **8** were also characterized by FTIR spectroscopy and elemental analysis. In addition, the structures of **6a**, **6c**, and **8** were confirmed by single-crystal X-ray analysis; see Figure 2.

Derivatives of amine **6a**, bearing different substituents on the aromatic ring, have previously been disclosed and used as ligands in complexes of Al(III), [32] Cr(II),[33] Cr(III),[33] and Ru-(II).[34] Although the neutral amine of **6c** has been obtained previously,[35] the crystal structure has not yet been reported. Derivatives of amine **6c**, with different substituents on the aromatic ring, have been applied as ligands in complexes of Cu,[36] Al,[37] and V.[38] A compound resembling ligand **8** has been described[39] but has not previously been used as a coordination ligand. However, a pentadentate ligand that contains a derivative of **8** has been synthesized and applied in the preparation of complexes of Fe(III) and Ga(III).[40]

The simplest synthetic strategy to the bi- or tridentate Ru alkylidene complexes involves the direct substitution of one chloride ion (two in the case of the tridentate ligand **8**) and one phosphine ligand from the Grubbs "first-generation" catalyst **1** by a bidentate or tridentate amine ligand salt. Following this

(28) Steevens, J. B.; Pandit, U. K. *Tetrahedron* **1983**, *39*, 1395.
(29) Borch, R. F.; Bernstei, M. D.; Durst, H. D. *J. Am. Chem. Soc.* **1971**, *93*, 2897.
(30) von Auwers, K. *Ber. Deutsch. Chem. Ges.* **1917**, *50*, 1585. Katritzky, A. R.; Ghiviriga, I.; Leeming, P.; Soti, F. *Magn. Reson. Chem.* **1996**, *34*, 518.
(31) Harries, H. J.; Orford, B. F.; Burgess, J. *Inorg. Chim. Acta* **1983**, *68*, 41.
(32) Peng, Y.; Hao, H. J.; Jancik, V.; Roesky, H. W.; Herbst-Irmer, R.; Magull, J. *Dalton Trans.* **2004**, 3548. Hill, M. S.; Atwood, D. A. *Main Group Chem.* **1998**, *2*, 285.
(33) Gibson, V. C.; Newton, C.; Redshaw, C.; Solan, G. A.; White, A. J. P.; Williams, D. J. *J. Chem. Soc., Dalton Trans.* **1999**, 827.
(34) Rath, R. K.; Nethaji, M.; Chakravarty, A. R. *Polyhedron* **2001**, *20*, 2735.
(35) Burckhalter, J. H. *J. Am. Chem. Soc.* **1950**, *72*, 1308.
(36) Schatzschneider, U.; Weyhermuller, T.; Rentschler, E. *Eur. J. Inorg. Chem.* **2001**, 2569.
(37) Dagorne, S.; Lavanant, L.; Welter, R.; Chassenieux, C.; Haquette, P.; Jaouen, G. *Organometallics* **2003**, *22*, 3732.
(38) Hagen, H.; Reinoso, S.; Reijerse, E. J.; van Faassen, E. E.; Lutz, M.; Spek, A. L.; van Koten, G. *Z. Anorg. Allg. Chem.* **2004**, *630*, 2097.
(39) Papa, A. J.; Critchfield, F. E. *J. Cell. Plast.* **1979**, *15*, 258.
(40) Lanznaster, M.; Hratchian, H. P.; Heeg, M. J.; Hryhorczuk, L. M.; McGarvey, B. R.; Schlegel, H. B.; Verani, C. N. *Inorg. Chem.* **2006**, *45*, 955.

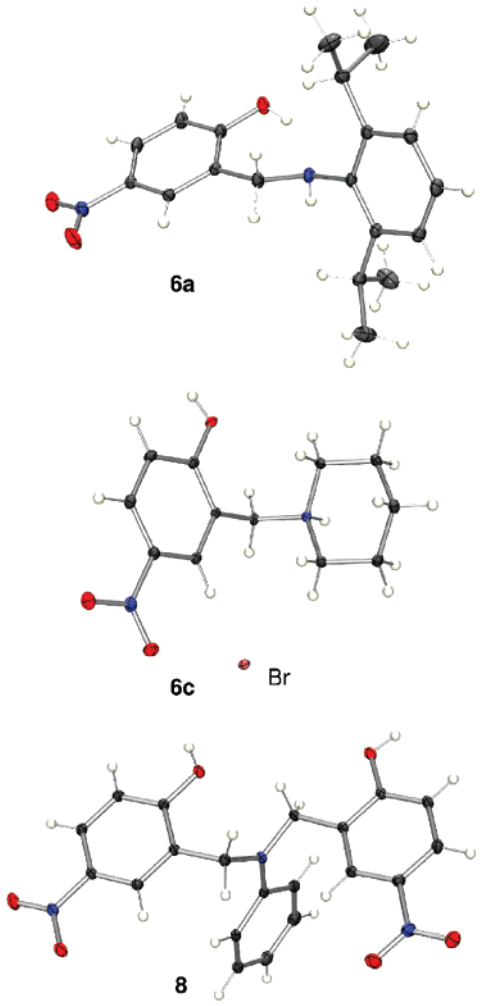
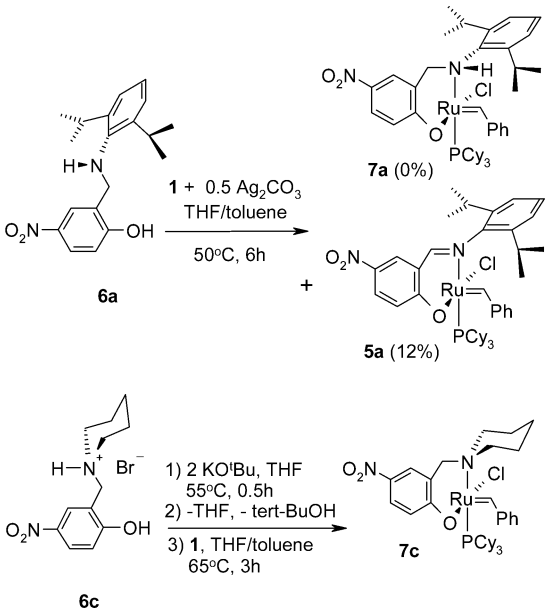


Figure 2. ORTEP diagram of **6a**, **6c**, and **8** with the ellipsoids drawn at the 30% probability level. **6c** is an ammonium bromide salt. The solid-state structure of **8** includes a solvent molecule (THF, not shown). Color coding: C, dark gray; N, blue; O, red; H, wheat; Br, brown.

strategy, 1 equiv of the ammonium bromide salt **6c** was transformed (in situ) to the potassium salt using 2 equiv of *tert*-BuOK and used directly in the next step without further workup. The ligand potassium salt was reacted with 1 equiv of **1** at elevated temperatures for a period of 3−6 h; see Scheme 2. The ^{1}H NMR spectrum of the reaction mixture revealed an alkylidene proton resonance (δ = 20.8, d, 5.1 Hz, 1H). The alkylidene complex was obtained in low yield, is unstable in solution, and decomposed during chromatography using silica gel as well as alumina. Attempts to purify the alkylidene compound failed, and we were thus not able to confirm the structure.

The bidentate ligand **6a** was reacted with **1** in the presence of 0.5 equiv of Ag_2CO_3 to provide a stable complex identified as the bidentate Schiff-base complex **5a** (in a yield of 22%, estimated by ^{1}H NMR).[9] The latter complex may also be obtained, in slightly lower yields, in two steps, via the potassium salt. However, none of the two procedures led to the corresponding amine complex **7a**. This was a surprising observation since ruthenium(II) complexes of derivatives of **6a** already have been obtained.[34] However, ruthenium(III)[41,42] alone, or more

Scheme 2. Attempted Synthesis of Complexes 7a and 7c



efficiently in the presence of Ag(I),[42] have been reported to oxidize primary and secondary amines. It is thus conceivable that ligand **6a** is oxidized by the Grubbs catalyst alone or by the Grubbs catalyst and Ag(I) ions together in the direct and more efficient protocol involving Ag_2CO_3. However, in the absence of Grubbs catalyst and under the same reaction conditions, Ag_2CO_3 alone is unable to oxidize amine **6a** to imine **3a**. If we consider the Grubbs catalyst to contain ruthenium with a formal charge of +4, which seems to be the most realistic representation according to a recent quantum chemical investigation,[27] oxidation of ligand **6a** is brought about by a reduction of the metal to Ru(II). Alternatively, if we consider the Grubbs catalyst to consist of a neutral carbene group bound to Ru(II), oxidation of ligand **6a** is accompanied by carbene reduction.

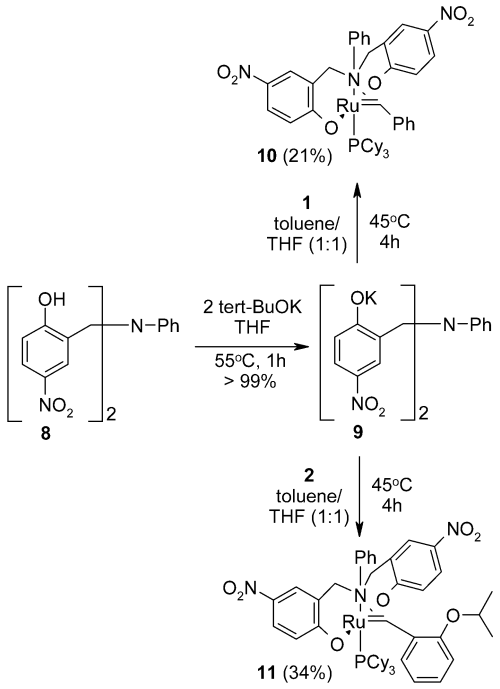
The synthesis of the Ru alkylidene complexes coordinated with the tridentate amine ligand was accomplished by reacting the tridentate bis-potassium salt **9** with the Grubbs "first-generation" catalyst **1** and the Hoveyda−Grubbs first-generation catalyst **2**, to provide the complexes **10** and **11**, respectively, see Scheme 3. The potassium salt **9** was obtained by reacting the tridentate amine ligand and *tert*-BuOK.

Complexes **10** and **11** are both reasonably stable to air and moisture. Moreover, both of these complexes tolerate protic or acidic solvents such as methanol or acetic acid for short periods (<1 h). On the other hand, their thermal stability is rather low. In the solid state, partial decomposition is observed after a few days at 4 °C, whereas no sign of decomposition is observed after several weeks at −20 °C.

Structural Characterization of Ru Alkylidene Complexes of Tridentate Amine Ligands. Compounds **10** and **11** were characterized by ^{1}H and ^{13}C NMR spectroscopy, mass spectrometry, high-resolution mass measurements, and elemental analysis. The ^{1}H NMR and ^{13}C NMR spectra of these complexes contain H (21.20 and 20.75 ppm) and C (303.8 and 301.4 ppm) resonances typical of alkylidene hydrogen and carbon atoms, respectively. Furthermore, the ^{13}C NMR chemical shifts for CH_2 in **10** (66 ppm) and **11** (65 ppm) are downfield-shifted relative to those of ligand **8** (49 ppm) and the corresponding bis-potassium salt **9** (50 ppm), strongly suggesting that the amine group is coordinated to the metal in both the new ruthenium alkylidene complexes.

(41) Fogg, D. E.; James, B. R. *Inorg. Chem.* **1995**, *34*, 2557. Diamond, S. E.; Tom, G. M.; Taube, H. *J. Am. Chem. Soc.* **1975**, *97*, 2661.
(42) Bernhard, P.; Sargeson, A. M. *J. Am. Chem. Soc.* **1989**, *111*, 597.

Scheme 3. Synthesis of Ru Complexes 10 and 11



The NMR spectra also suggest that the two N-benzyloxy bridges of the chelate ligand are perfectly symmetry-related in **10** and essentially symmetry-related in **11**, indicating that, in solution at room temperature, rotation around the Ru−alkylidene bond is fast on the NMR time scale. For example, there is only one resonance (175.4 (**10**) and 175.2 (**11**)) for the quaternary carbon atom bound to the aryloxide oxygen atom (**C**−O−Ru), and only one doublet for the aromatic proton in ortho position to the latter quaternary carbon (6.43 (d, $J = 9.2$ Hz, 2H) (**10**) and 6.50 (d, $J = 9.2$, 2H) (**11**)). The two CH_2 groups of **10** are present with only one peak in the ^{13}C NMR spectrum, and the ^1H NMR spectrum shows only two doublets for the corresponding four protons.

Whereas the general similarity between the NMR spectra of **10** and **11** suggests that these complexes have analogous molecular structures, some differences concerning the chemical shifts of the CH_2 groups can be discerned. At room temperature the two CH_2 groups of **11** are present with a relatively broad signal (the half-height width is 13 Hz) in the ^{13}C NMR spectrum, whereas the ^1H NMR spectrum contains a doublet of doublet (2H) and one broad signal (2H) for the four protons. At lower temperature (193 K), the broad resonance appears as two doublets and the doublet of doublet becomes a triplet (see the Supporting Information for more details). The chemical formulas of **10** and **11** are identical except for the isopropyloxy group of the latter, and the isopropyloxy group is not coordinated to ruthenium as judged from the fact that the −O−CH protons (4.66 ppm) and the O−C carbon atoms (71.1 ppm) in **11** are shifted significantly upfield from the corresponding ^1H NMR (5.28 ppm) and ^{13}C NMR (75.5 ppm) chemical shifts in the Hoveyda−Grubbs first-generation catalyst **2**.[6] The availability of the isopropyloxy oxygen suggests that the spectral differences between **10** and **11** can be attributed to a donor−acceptor interaction between this oxygen and the two equatorial protons (oriented essentially parallel to the alkylidene group). This indicates that, at least for complex **11**, the amine phenyl group is directed away from the alkylidene, whereas the CH_2 bridges are pointing toward the alkylidene moiety, that is, implying a conformation different from that assumed in the DFT calculations on complex **10** shown in Figure 1.

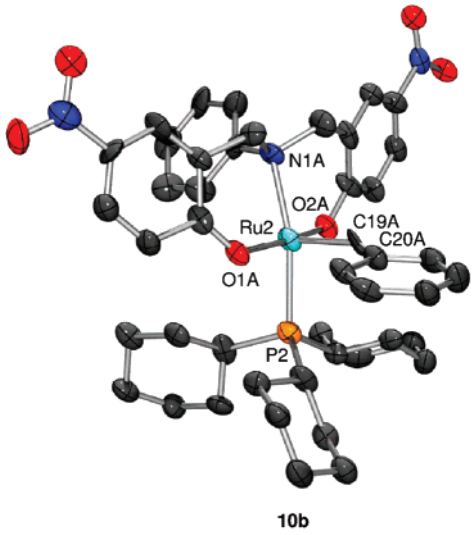


Figure 3. ORTEP diagram of **10** with the ellipsoids drawn at the 30% probability level. The figure shows only one of the three conformers presents in the solid state (conformer **b**). Hydrogen atoms have been removed for clarity. Color coding: C, dark gray; N, blue; O, red; P, orange; Ru, turquoise. Selected geometrical parameters: Ru2−C19A = 1.90 Å, Ru2−N1A = 2.18 Å, Ru2−O1A = 2.07 Å, Ru2−O2A = 2.03 Å, Ru2−P2 = 2.38 Å, C19A−C20A = 1.40 Å, O1A−Ru2−O2A = 170°, P2−Ru2−C19A−C20A = −79°.

Complexes **10** and **11** were crystallized by slow diffusion of *n*-pentane into a concentrated solution of the corresponding complex in CH_2Cl_2 at −34 °C. Whereas the crystal quality of **11** was insufficient for structure determination, a suitable crystal of **10** could be selected and analyzed using an X-ray diffractometer (see Figure 3).

Figure 3 shows one of the three conformers of complex **10** that are present in the solid state. There are significant differences between these conformers, in particular related to the rotational orientation of the alkylidene group (the torsional angle P−Ru−C19−C20 is −110° (**10a**), −79° (**10b**), and 91° (**10c**)) and the R−N bond distance (2.15 Å (**10a**), 2.18 Å (**10b**), and 2.20 Å (**10c**)). Detailed information about the crystal structure of **10** and of the individual conformers is available in the Supporting Information. As also indicated by the NMR spectra of compound **11** (see above), the phenyl group of the amine ligand is directed away from the alkylidene moiety (i.e., anti with respect to the alkylidene), in all three conformers **a**, **b**, and **c**, in contrast to the syn conformation supposed in the initial DFT calculations on complex **10** (Figure 1).

Complex **10** features a rather elongated Ru−alkylidene bond (the average bond distance of the three conformers is 1.88 Å). The long Ru−alkylidene bond may to a large extent be explained by conjugation with the phenyl group as seen from the short alkylidene−phenyl C−C bond (average 1.43 Å). The conjugation effects are at their strongest in **10b** (shown in Figure 3), resulting in a particularly long Ru alkylidene bond (1.90 Å) and a short alkylidene−phenyl bond (1.40 Å). Furthermore, the Ru−N bond distance is longer (average 2.18 Å) than the corresponding Ru−N in the bidentate salicylaldimine Ru-based catalyst **5a** (2.10 Å).[9] The longer Ru−amine bond is mainly due to the negligible π back-donation and the pyramidal and thus sterically more demanding structure of the amine compared to the imine ligand.

The coordination of amine to ruthenium is accompanied by significant elongation of the N−C bonds, from 1.39 Å (N−Ph) and 1.45 Å (average for the two N−CH_2 bonds) in the free ligand **8**, to 1.48 Å (average for N−Ph) and 1.51 Å (average for N−CH_2) in **10**. This remarkable difference is because the nitrogen atom is planar and sp^2-hybridized (the sum of the three C−N−C bond angles is 360°) in the free amine **8**, as previously described for other anilines.[43] Thus, the nitrogen lone pair is delocalized, in particular on the aromatic ring. In contrast, the nitrogen atom in complex **10** is pyramidal, sp^3-hybridized (the average of the sum of C−N−C bond angles is 329°), and bound to the metal.

The fact that the crystal structure (Figure 3) and the initial DFT-optimized structure (Figure 1) of **10** feature two different orientations of the amine phenyl group (anti or syn with respect to the alkylidene group) prompts the question of whether these orientations represent the preferred conformations in the solid state and gas-phase, respectively. Figure 4 shows the DFT optimized structures of the syn (**10d**) and anti (represented by the most stable conformer, **10c**) conformers. The calculated free energies suggest that, also in gas phase, the amine phenyl is preferably oriented away from the alkylidene, although the preference only amounts to ca. 1 kcal/mol relative to **10d** (**10a**, 0.4; **10b**, −0.4; and **10c**, 1.2 kcal/mol). The preference for the anti conformation is somewhat more pronounced (**10a** and **10b** (enantiomers), 0.6; and **10c**, 2.0 kcal/mol) when using the smallest possible alkylidene (methylidene, i.e., R = H in Chart 2) in the calculations. The bond enthalpies initially calculated for **10** (Table 2) were also obtained using methylidene and involved the syn conformer, that is, **10d**. The corresponding enthalpies for **10c** are very similar, 18.4 and 29.1 kcal/mol for the Ru−N and Ru−PCy_3 bonds, respectively, which shows that the initial considerations regarding the similarities between Ru−imine and Ru−amine complexes based on the calculated bond enthalpies of Table 2 are not very dependent on the conformation of the amine.

Metathesis Activity Studies of the Ru Alkylidene Complexes of Tridentate Amine Ligands. Complexes **10** and **11** have been tested as catalysts for ring-closing metathesis (RCM) of diethyl diallylmalonate (DEDAM). The catalytic activity of **10** is very low when the reaction is performed in deuterated benzene or dichloromethane (see entries 1 and 5 of Table 3). However, addition of 1 equiv or an excess of HCl or H_2SO_4 to a solution of **10** in CD_2Cl_2 or C_6D_6 increases the activity dramatically (entries 3, 4 and 6, 7). Similar activation using HCl has been reported previously for other ruthenium alkylidene complexes (see, e.g., refs 44, 45). In $CDCl_3$, the olefin metathesis activity varies from low to high depending on the quality of the solvent (compare, e.g., entries 8 and 9). Moreover, when using the same quality of deuterated chloroform, the relative activity appears to increase with the dilution of the catalyst (entries 9 and 13). Chloroform contains traces of HCl (in variable amounts), and the presence of HCl in various quantities is most probably the reason for the activity of **10** being strongly dependent on the quality of the $CDCl_3$ solvent.

In additional tests using CD_2Cl_2, or $CDCl_3$ presumed to contain very little HCl, as solvent, the addition of traces of HCl (0.12 M solution of HCl in $CDCl_3$) to the reaction mixture at room temperature leads to instantaneous conversion of the substrate in the corresponding RCM product. A short period of high catalytic activity is followed by rapid decomposition of

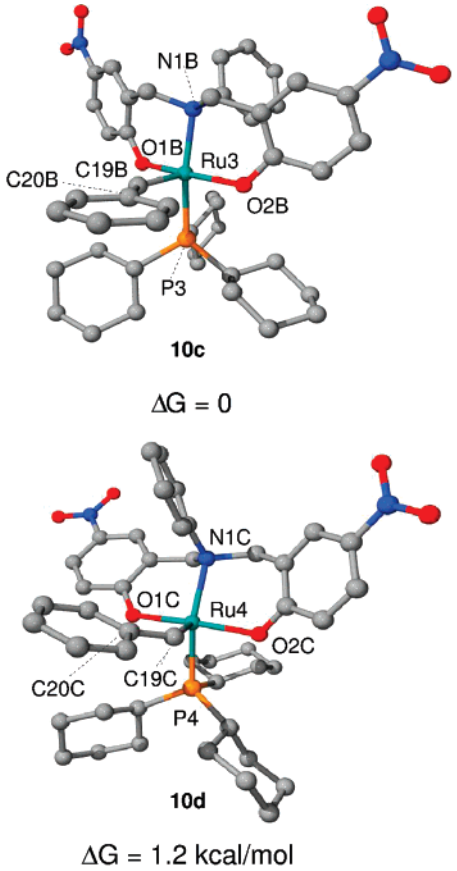


Figure 4. DFT optimized structures of syn (**10d**) and anti (represented by **10c**) conformers of **10** with benzylidene as alkylidene (R = phenyl in Chart 2). Selected distances [Å] and angles [deg] of **10c**: Ru3−N1B = 2.22, Ru3−O1B = 2.10, Ru3−O2B = 2.12, Ru3−C19B = 1.86, Ru3−P3 = 2.53, O1B−Ru3−O2B = 168, N1B−Ru3−C19B = 102, C19B−Ru3−P3 = 92, C19B−Ru3−O1B = 89, C19B−Ru3−O2B = 102, C20B−C19B−Ru3−O1B = −175, P3−Ru3−C19B−C20B = 100. Selected distances [Å] and angles [deg] of **10d**: Ru4−N1C = 2.27, Ru4−O1C = 2.10, Ru4−O2C = 2.14, Ru4−C19C = 1.86, Ru4−P4 = 2.47, O1C−Ru4−O2C = 174, N1C−Ru4−C19C = 113, C19−Ru4−P4 = 95, C19C−Ru4−O1C = 98, C19C−Ru4−O2C = 85, C20C−C19C−Ru4−O1C = −20, P4−Ru4−C19C−C20C = −110. Hydrogen atoms have been omitted for clarity. Color coding: C, gray; N, blue; O, red; P, orange; Ru, turquoise.

an equivalent of the catalyst approximately corresponding to the amount of HCl added. The reaction then continues much more slowly for some minutes and then stops. By continued addition of small amounts of acid, new portions of the catalyst may be activated for short periods until complete decomposition of the entire amount of catalyst is reached. Evaluation of the relative degrees of conversion of the substrate and decomposition of the catalyst has been performed on the basis of integration of the alkylidene proton resonance of complex **10** and the allylic methylene peaks of the substrate and the product. In CH_2Cl_2, the catalytic activity of **11** is slightly higher than that of **10** (see entries 1 and 2), whereas the opposite is true in $CHCl_3$ (see entries 9−12). Moreover, the addition of small amounts of HCl at room temperature does not increase the activity of **11** to any significant extent (entry 17).

The addition of an excess of H_2SO_4 (1−2 μL of a 5 M solution in water) to the reaction mixture dissolved in C_6D_6 (entries 6 and 7) also leads to an increase in the activity of **10**, but not as dramatic as when adding HCl. Moreover, the stability of the resulting catalyst is also higher than that generated by

(43) Vaschetto, M. E.; Retamal, B. A.; Monkman, A. P. *J. Mol. Struct. (THEOCHEM)* **1999**, *468*, 209. Faller, J. W.; Fontaine, P. P. *J. Organomet. Chem.* **2006**, *691*, 5798.

Table 3. RCM of Diethyl Diallylmalonate Using 10 and 11

entry	catal	mol % of catal	added acid	solvent	*T* (°C)	time (h)	yield (%)
1	**10**	8	no	CH_2Cl_2[a]	35	2.5	0.1
2	**11**	8	no	CH_2Cl_2[a]	35	2.5	0.7
3	**10**	1[b]	HCl[c] [1 equiv]	CD_2Cl_2	25	0.1[d]	15
4	**10**	0.6[e]	HCl [excess]	CD_2Cl_2	25	0.1[d]	39
5	**10**	8	no	C_6D_6	35	2	0.1
6	**10**	1[b]	H_2SO_4 [excess]	C_6D_6	25	2[d]	4
7	**10**	0.6[e]	H_2SO_4 [excess]	C_6D_6	45	2	54
8	**10**	8	no	$CDCl_3$[f]	40	24	3
9	**10**	8	no	$CDCl_3$[g]	35	2	85
10	**11**	8	no	$CDCl_3$[g]	35	2	29[h]
11	**10**	8	no	$CDCl_3$[g]	40	22	100
12	**11**	8	no	$CDCl_3$[g]	40	22	98[i]
13	**10**	1[b]	no	$CDCl_3$[g]	35	2	90
14	**10**[j]	1[b]	no	$CDCl_3$[g]	35	2	84
15	**10**	1[b]	no	$CDCl_3$[g]	25	0.1[d]	62
16	**10**	0.6[e]	HCl [excess]	$CDCl_3$[f]	25	0.1[d]	41
17	**11**	8	HCl[c] [1 equiv]	$CDCl_3$[f]	25	10[d]	1.6[k]

[a] The solvent was removed by vacuum at the end of reaction. The residue was dissolved in $CDCl_3$ and transferred to a dry NMR tube using a syringe. [b] Reaction run using 2.4×10^{-4} mmol (1 mol %) of catalyst and 2.4×10^{-2} mmol of DEDAM in 0.5 mL of solvent. [c] Solution of HCl (0.12 M in $CDCl_3$. [d] The reaction was performed in a capped NMR tube that was shaken for few seconds. [e] Reaction run using 3.0×10^{-4} mmol (0.6 mol %) of catalyst and 5.0×10^{-2} mmol of DEDAM in 0.5 mL of solvent. [f] $CDCl_3$ purchased from Sigma-Aldrich (612200-100G). [g] $CDCl_3$ purchased from Sigma-Aldrich (236896-1PAK). [h] The ^{1}H NMR analysis reveals the presence of 0.9 mol % of **2**, which is generated during the reaction. [i] The ^{1}H NMR analysis reveals the presence of 0.04 mol % of **2**, which is generated during the reaction. [j] In the presence of 10 equiv of CuCl. [k] The ^{1}H NMR analysis reveals the presence of traces (~0.01 mol %) of **2**, which are generated during the reaction.

addition of hydrochloric acid. Thus, both the positive and negative effects resulting from the addition of acid are smaller for H_2SO_4 than for HCl, which is probably due to the poor solubility of the sulfuric acid water solution in benzene. At room temperature the activity of **10** is much lower in the presence of H_2SO_4 than in the presence of HCl (see, e.g., entries 3, 4, and 6). However, at higher temperatures, the system benzene/H_2SO_4 appears to give a reasonably high activity as well as turnover number (TON) (entry 7).

These experiments indicate that the reaction of **10** with protic acids instantaneously produces one or more very active and short-lived species, presumably 14-electron ruthenium benzylidene complexes. When an excess of HCl is added to **10**, the color of the solution immediately changes from red to yellow, whereas, as commented upon above, the corresponding decomposition resulting from the addition of H_2SO_4 to a benzene solution of the catalyst is slower.

The short lifetime of the active species prevents their identification. The most obvious alternative involves protonation of the amine group, thus providing the corresponding 14-electron complex of **10**. It is also conceivable that addition of acid leads to protonation of one or both of the benzyloxide groups coordinated to the metal and subsequently to their replacement by chloride or hydrogen sulfate ions. This possibility, at least in the case of chloride ions, is supported by the formation of variable amounts of Hoveyda−Grubbs first-generation catalyst upon dissolution of **11** in $CDCl_3$ (entries 10, 12, and 17). Substitution of alkoxide ligands by Cl upon addition of HCl previously has been reported by Grubbs and co-workers.[45] The corresponding 14-electron complexes derived from **10** are very active but decompose after 15−90 catalytic cycles. The TON seems to depend upon the amount of acid added to the reaction mixture, and the TON continues to increase even beyond addition of 1 equiv of HCl.

The addition of a phosphine sponge (CuCl, catalyst/CuCl = 1:10) results in slightly reduced stability and activity of **10** (compare entries 13 and 14). This suggests that the amine, not the phosphine, acts as dissociating ligand, in agreement with the calculated ruthenium−amine bond enthalpies in Tables 1 and 2 being lower than the corresponding ruthenium−phosphine bond enthalpies. In conclusion, the highest catalytic activity observed in our experiments has been obtained by the addition of HCl to **10**, thus presumably protonating the amine to produce the short-lived but highly active 14-electron complex.

The lower catalytic activity of **11** (in the presence of HCl) observed in particular at room temperature may be explained by the presence of the pending isopropyloxy function of the alkylidene moiety. This oxygen atom is not coordinated to ruthenium in the catalyst precursor, but may coordinate after protonation of the amine, thereby forming an inactive 16-electron complex.

The low catalytic activity of **10** and **11** without any Brønsted acid present at first glance seems to contradict the prediction that amines should promote catalytic activity to a greater extent than do phosphines and imines.[27] The theoretical screening[27] of the ligand L in catalyst complexes $LL'Cl_2Ru{=}CH_2$ assumed the dissociation of the ligand L′ trans to L as the initiating step of the catalytic cycle. However, as already noted above, most probably the amine, and not the phosphine, constitutes the dissociating ligand in these catalysts. This implies that in the actual 14-electron catalyst, the amine is not coordinated to the metal, just as the imine has been postulated to dissociate from the related catalysts bearing Schiff-base ligands.[14] The bond enthalpies of Table 2 suggest that this initial dissociation should be even more facile for **10**, and would also lead to an active 14-electron complex with an empty coordination site trans to a remaining phosphine ligand. However, owing to the two benzyloxy linkages, the amine moiety is still close to the metal in the dissociated state (cf. Figure 1). The proximity to the metal is expected to ensure fast recoordination of the amine, thus considerably reducing the time available for alkene binding. Ammonium, however, never coordinates to ruthenium, even if close, which thus explains the dramatic effect resulting from the addition of acid.

Conclusions

The novel ruthenium alkylidene complexes **10** and **11** bearing a tridentate amino-benzyloxy ligand have been synthesized and structurally characterized. X-ray crystal structure determination of **10** confirms that this complex has a trigonal bipyramidal structure featuring an essentially symmetrically coordinated tridentate ligand with the oxygen atoms and the alkylidene in equatorial positions, the amine in an apical position, and a tricyclohexyl-phosphine ligand in the second apical position. Spectroscopic results strongly suggest that the molecular structure of **11** is analogous to that of **10**. The isopropyloxy function of the alkylidene group in **11** is not coordinated to the metal. Complexes **10** and **11** are fairly stable to air, moisture, and protic solvents, but display low thermal stability. Only very low catalytic activity has been obtained in RCM of diethyl diallylmalonate using **10** or **11** dissolved in acid-free solvents. Addition of one or more equivalents of a strong protic acid increases the activity dramatically, although at the same time leading to rapid decomposition of the catalyst, resulting in a TON between 15 and 90.

(44) Sanford, M. S.; Henling, L. M.; Grubbs, R. H. *Organometallics* **1998**, *17*, 5384.

(45) Sanford, M. S.; Henling, L. M.; Day, M. W.; Grubbs, R. H. *Angew. Chem., Int. Ed.* **2000**, *39*, 3451.

Novel bidentate amino-benzyloxy ligands have also been obtained and structurally characterized. Unfortunately, we were not able to isolate the corresponding ruthenium alkylidene complexes coordinated by these ligands. The bidentate complexes are unstable and attempts at their synthesis and isolation have resulted in decomposition or oxidation to the corresponding Schiff-base complexes.

The efforts at synthesizing complexes of the bidentate and tridentate amino-benzyloxy ligands were initiated after DFT-based studies had shown that the ruthenium−amine bond strengths of such complexes should be similar to the ruthenium−imine bond strengths of complexes of bidentate Schiff-base ligands.[9,13,14] The latter complexes are both remarkably robust and highly active catalysts for olefin metathesis. The Schiff-base complexes initiate catalysis by dissociation of the pending imine group, and the similar ruthenium−imine and ruthenium−amine bond strengths indicated a similar potential for catalytic activity as well as stability for the ruthenium complexes coordinated by chelating amino-benzyloxy ligands.

Experimental and Computational Section

Experimental Methods. General Procedures. The organic reactions were carried out in oven-dried glassware. All manipulations of organometallic compounds were performed using standard Schlenk techniques, including flame-drying of Schlenkware under argon. Toluene, dichloromethane, and THF were purified in MBraun SPS purification columns.[46] All other chemicals were purchased commercially and used without further purification. F-254 TLC plates were used to follow the progress of the reactions and to check the purity of synthesized products. The spots of substances on the thin-layer were visualized under UV light. ATR-IR spectra [cm^{-1}] were recorded on a Nicolet-Impact 410 FTIR spectrometer. Electrospray mass spectra and high-resolution mass measurements were obtained with a Waters Micromass QTOF 2 W mass spectrometer at the Department of Chemistry, University of Oslo. Thermodynamically corrected melting points were determined using a Büchi B-540 instrument. Elemental analyses were performed with an Elementar Vario EL III analyzer. NMR spectra were recorded on Bruker AV 500 and AV 600 spectrometers. The chemical shifts are reported downfield from tetramethylsilane (TMS) (δ scale) or calibrated to solvent residual peaks as an internal standard ($CDCl_3$, $\delta_C = 77.2$ ppm, residual $CHCl_3$ in $CDCl_3$, $\delta_H = 7.26$ ppm; CD_3OD, $\delta_C = 49.0$ ppm, residual CHD_2OD in CD_3OD, $\delta_H = 3.31$ ppm; $(CD_3)_2SO$, $\delta_C = 39.5$ ppm, residual $(CHD_2)CD_3SO$ in $(CD_3)_2SO$, $\delta_H = 2.50$ ppm; D_2O, residual HOD in D_2O, $\delta_H = 4.79$ ppm; CD_2Cl_2, $\delta_C = 53.8$ ppm, residual $CHDCl_2$ in CD_2Cl_2, $\delta = 5.32$ ppm).[47] Phosphorus resonance spectra were recorded under proton decoupling and calibrated using the Hoveyda−Grubbs first generation catalyst as an internal standard ($\delta = 59.17$).[48]

Synthesis of Bidentate Amine Ligand 6c. 2-Hydroxy-5-nitrobenzyl bromide (0.50 g, 2.2 mmol), was dissolved in 20 mL of warm toluene, followed by the slow addition of a solution of piperidine (0.18 g, 2.2 mmol) in 10 mL of toluene under stirring. The mixture was refluxed and stirred for 14 h. The mixture was cooled to room temperature, followed by addition of 15 mL of ethanol and heating for 2 h at 80 °C. After cooling to room temperature, **6c** was isolated by filtration, washed with diethyl ether, and dried under reduced pressure to provide a yellow solid, 0.44 g (64%). ^{1}H NMR (D_2O, 600 MHz): $\delta = 8.33$ (d, $J = 2.8$ Hz, 1H), 8.27 (dd, $J = 9.1$, 2.8 Hz, 1H), 7.14 (d, $J = 9.1$ Hz, 1H), 4.35 (s, 2H), 3.52 (br d, $J = 12.3$, 2H), 3.05 (br td, $J = 12.5$, 3.0 Hz, 2H), 1.88−2.00 (br m, 2H), 1.65−1.84 (br m, 3H), 1.42−1.56 (br m, 1H). ^{13}C NMR ($(CD_3)_2SO$, 151 MHz): $\delta = 163.1$, 139.4, 129.7. 127.2, 117.1, 116.0, 52.9, 52.1, 22.4, 21.1. An aliquot of the prepared ligand **6c** was further purified by recrystallization by dissolving the solid in warm ethanol followed by slow cooling to room temperature. A suitable crystal was selected and structurally characterized by X-ray diffraction.

Synthesis of Schiff Base 3a. 5-Nitrosalicylaldehyde (1.0 g, 6.0 mmol) and 2,6-diisopropylaniline (1.1 g, 6.0 mmol) were dissolved in ethanol (15 mL) and stirred under reflux for 2 h. The reaction mixture was allowed to cool slowly to room temperature, and then further down to 0 °C. The yellow, crystalline solid was isolated by filtration and dried under reduced pressure to give 1.6 g (82%) of the title product. ^{1}H NMR ($CDCl_3$, 500 MHz): $\delta = 14.29$ (s, 1H), 8.38 (s, 1H), 8.35 (d, $J = 2.8$ Hz, 1H), 8.31 (dd, $J = 9.2$, 2.8 Hz, 1H), 7.20−7.25 (m, 3H), 7.14 (d, $J = 9.2$ Hz, 1H), 2.93 (sept, $J = 6.9$ Hz, 2H), 1.20 (d, $J = 6.9$ Hz, 12H).

Synthesis of Schiff Base 3b. 5-Nitrosalicylaldehyde (1.0 g, 6.0 mmol) and aniline (0.56 g, 6.0 mmol), were dissolved in ethanol (15 mL) and stirred under reflux for 2 h. The reaction mixture was allowed to cool slowly to room temperature, and then further down to 0 °C. The yellow, crystalline solid was isolated by filtration and dried under reduced pressure to give 1.3 g (91%). ^{1}H NMR ($CDCl_3$, 600 MHz): $\delta = 14.45$ (s, 1H), 8.72 (s, 1H), 8.40 (d, $J = 2.8$ Hz, 1H), 8.27 (dd, $J = 9.2$, 2.8 Hz, 1H), 7.44−751 (m, 2H), 7.32−7.39 (m, 3H), 7.10 (d, $J = 9.2$ Hz, 1H).

Synthesis of Bidentate Amine Ligand 6a. A mixture of Schiff-base **3a** (1.6 g, 4.9 mmol) and $NaBH_4$ (1.6 g, 42 mmol) in 160 mL of EtOH/water (90:10) was stirred overnight at room temperature. Diluted HCl (10%) was added to the mixture until the yellow color disappeared and a clear and almost colorless solution was obtained. Next, a saturated solution of Na_2CO_3 was added until pH 8−9, providing a pale, yellow solution. The solution was subsequently extracted twice with $CHCl_3$ (using in total ca. 50 mL). The organic phase was dried with Na_2SO_4 and filtered through a welted filter paper. The solvent was removed using a rotary evaporator at room temperature, and the residue was further dried under reduced pressure to provide the target product, a crystalline, pale, yellow solid, 1.3 g (yield 81%). ^{1}H NMR (CD_3OD, 600 MHz): $\delta = 8.11$ (d, $J = 2.9$ Hz, 1H), 8.07 (dd, $J = 8.9$, 2.9 Hz, 1H), 7.02−7.10 (m, 3H), 6.93 (d, $J = 8.9$ Hz, 1H), 4.05 (s, 1H), 3.34 (sept, $J = 6.9$ Hz, 2H), 1.21 (d, $J = 6.9$ Hz, 12H). ^{13}C NMR (CD_3OD, 151 MHz): $\delta = 163.5$, 144.0, 143.2, 141.5, 128.5, 126.3, 125.8, 125.4, 124.7, 116.0, 52.4, 28.7, 24.7. IR (film): 3645 (br, w), 3345 (w), 3327 (w), 2960 (m), 2865 (w), 1623 (w), 1600 (m), 1548 (w), 1518 (m), 1487 (w), 1459 (m), 1441(m), 1406 (m), 1379 (m), 1363 (w), 1336 (m), 1305 (s), 1288 (s), 1244 (s), 1213 (w), 1187 (w), 1167 (m), 1127 (w), 1109 (w), 1091 (m), 1055 (w), 1044 (w), 1034 (w), 999 (w), 974 (w), 925 (w), 909 (m), 842 (m), 832 (w), 813 (m), 798 (w), 712 (m), 746 (s), 734 (w), 714 (w), 684 (w). Anal. Calcd for $C_{20}H_{17}N_3O_6$: C, 69.49; H, 7.37; N, 8.53. Found: C, 69.41; H, 7.38; N, 8.40. An aliquot of **6a** was further purified by recrystallization in ethyl acetate by allowing the solvent to evaporate in air at room temperature. A suitable crystal was selected and structurally characterized by X-ray diffraction.

Synthesis and Characterization of Amine 6b. A mixture of Shiff-base **3b** (1.3 g, 5.4 mmol) and $NaBH_4$ (1.3 g, 35 mmol) in 130 mL EtOH/water (95:5) was stirred overnight (14 h) at room temperature. Diluted HCl (10%) was added until pH = 1, and the reaction was then stirred for 30 min at room temperature until the solution was totally clear and the yellow color had disappeared. The solution was neutralized (pH 7−8) with a saturated solution of Na_2CO_3. The product was extracted twice with $CHCl_3$. The organic phase was dried with Na_2SO_4 and filtered through a welted filter paper. The solvent was removed using a rotary evaporator at room temperature. The residue, a crystal yellow pale solid, was

(46) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.

(47) Gottlieb, H. E.; Kotlyar, V.; Nudelman, A. *J. Org. Chem.* **1997**, *62*, 7512.

(48) Garber, S. B.; Kingsbury, J. S.; Gray, B. L.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2000**, *122*, 8168.

the intended product, 1.1 g (yield 82%). ^{1}H NMR ($CDCl_3$, 500 MHz): $\delta = 10.11$ (br s, 1H), 8.06−8.18 (m, 2H), 7.27 (t, $J = 7.9$ Hz, 2H), 6.99 (d, $J = 7.4$ Hz, 1H), 6.93 (d, $J = 8,5$ 1H), 6.87 (d, $J = 7.9$ Hz, 2H), 4.54 (s, 2H), 4.11 (br s, 1H).

Synthesis and Characterization of the Tridentate Ligand 8. Amine **6b** (1.1 g, 4.5 mmol), 5-nitrosalicylaldehyde (0.75 g, 4.5 mmol), $NaCNBH_3$ (0.28 g, 4.5 mmol) and 3.0 g of 4-Å molecular sieves were transferred to a 250 mL Schlenk flask. Methanol (50 mL) and formic acid (4 mL) were added to the flask and the mixture was stirred for 21 h at room temperature. The mixture was filtered to remove the molecular sieves. Diluted HCl (10%) was added to the filtrate until pH = 1, followed by stirring for 30 min until the solution was clear and the yellow color had disappeared. The solution was neutralized (pH 7−8) with a saturated solution of Na_2CO_3. The product was extracted twice with $CHCl_3$ (total volume 150 mL). The organic phase was dried with $NaSO_4$ and filtered through a welted filter paper. The solvent was removed under reduced pressure and the residue, a yellow-orange solid was the crude amine **5**, 1.7 g (95%). A reddish impurity was easily removed by suspending the solid in a few milliliters of cold methanol and isolating the pure product (yellow solid) by filtration, 1.4 g (78%). ^{1}H NMR ($(CD_3)_2SO$, 600 MHz): $\delta = 11.41$ (br s, 2H), 8.04 (dd, $J = 9.0$, 2.9 Hz, 2H), 7.84 (d, $J = 2.9$ Hz, 2H), 7.11−7.17 (m, 2H), 7.00 (d, $J = 9.0$ Hz, 1H), 6.61−6.68 (m, 3H), 4.66 (s, 2H). ^{13}C NMR ($(CD_3)_2SO$, 151 MHz): $\delta = 161.8$, 147.7, 139.6, 129.3, 125.8, 124.5, 123.0, 116.7, 115.3, 111.9, 49.2. IR (film): 3295 (br), 1616 (w), 1590 (m), 1504 (m), 1488 (m), 1436 (w), 1382 (w), 1322 (s), 1278 (s), 1268 (s), 1257 (s), 1231 (m), 1193 (m), 1181 (w), 1126 (w), 1088 (m), 1076 (m), 1057 (w), 990 (w), 961 (w), 933 (w), 922 (w), 910 (w), 893 (w), 864 (w), 829 (m), 804 (w), 773 (w), 748 (s), 723 (m), 715 (w), 695 (m), 666 (w). Anal. Calcd for $C_{20}H_{17}N_3O_6 \cdot C_4H_8O$ (THF): C, 61.39; H, 5.15; N, 8.95. Found: C, 61.74; H, 5.18; N, 9.01. An aliquot of **8** was crystallized by slow diffusion of hexane into a concentrated solution of **8** in THF at room temperature. A suitable crystal was selected and structurally characterized by X-ray diffraction.

Synthesis and Characterization of Tridentate Ligand Potassium Salt 9. Tridentate ligand **8** (0.15 g, 0.38 mmol) and potassium *tert*-butoxide (0.085 g, 0.76 mmol) were transferred to a 25 mL Schlenk flask. THF (5 mL) was added to the mixture, and the suspension was heated at 55 °C for 1 h. Next, the mixture was cooled to room temperature, and the solvent was removed in reduced pressure. The Schlenk flask was heated to 80 °C under vacuum until constant weight. The orange solid was identified as the bis-potassium salt and was obtained in quantitative yield (0.20 g).[49] ^{1}H NMR ($(CD_3)_2SO$, 500 MHz): $\delta = 7.71$ (dd, $J = 9.4$, 3.2 Hz, 2H), 7.52 (d, $J = 3.2$ Hz, 2H), 6.99−7.06 (m, 2H), 6.41−6.54 (m, 3H), 5.93 (d, $J = 9.4$ Hz, 1H), 4.27 (s, 2H). ^{13}C NMR ($(CD_3)_2SO$, 151 MHz): $\delta = 179.6$, 148.9, 128.9, 127.4, 126.5, 125.6, 122.8, 118.4, 114.6, 111.1, 50.2. IR (film): 2864 (w), 2363 (w), 1595 (m), 1541 (w), 1505 (m), 1478 (w), 1399 (w), 1381 (w), 1336 (m), 1268 (s), 1221 (s), 1126 (s), 1087 (m), 1049 (m), 990 (w), 957 (w), 928 (w), 902 (w), 821 (w), 821 (m), 785 (w), 756 (m), 724 (w), 693 (w).

Attempts at Synthesis and Characterization of Ru Complex 7c. Ammonium bromide **6c** (0.0038 g, 0.012 mmol) and potassium *tert*-butoxide (0.0027 g, 0.024 mmol) were transferred to a 25 mL Schlenk flask. To this mixture was added THF (2 mL), and the suspension was heated for 30 min at 55 °C, resulting in the dissolution of the solid and a yellow solution. The solution was cooled to room temperature, followed by removal of the solvent under reduced pressure. Subsequently, 10 mg (0.012 mmol) of **1** was added to the Schlenk flask, which was then evacuated and then filled again with argon. Dry THF (0.20 mL) and dry toluene (2.0 mL) were added, and the mixture was stirred and heated at 65 °C for 3 h. Next, the mixture was cooled, and the solvent was removed under reduced pressure. The ^{1}H NMR spectrum contains peaks, for example, a doublet at 20.8 ppm ($J = 5.1$ Hz), indicative of an alkylidene proton, which are compatible with the target ruthenium alkylidene complex. Unfortunately, all attempts at further isolation and purification have resulted in complete decomposition of the complex.

Attempts at Synthesis and Characterization of Ru Complex 7a. Amine **6a** (0.040 g, 0.12 mmol), Ag_2CO_3 (0.017 g, 0.060 mmol), and **1** (0.10 g, 0.12 mmol) were added to a 25 mL Schlenk flask. The flask was evacuated and then again filled with argon, followed by addition of dry and degassed toluene (5.0 mL). The mixture was stirred at 50 °C for 6 h and then cooled to room temperature. The solvent was removed under vacuum, and the product, 12 mg (12%), was isolated by chromatography (silica gel, 1:9 solvent mixture of diethyl ether/hexane). ^{1}H NMR (CD_2Cl_2, 500 MHz): $\delta = 19.77$ (d, $J = 3.5$ Hz, 1H), 8.25 (d, $J = 2.9$ Hz, 1H), 8.12 (d, $J = 5.4$ Hz, 1H), 8.10 (dd, $J = 9.5$, 2.9 Hz, 1H), 7.92 (dd, $J = 8.3$, 1.1 Hz, 2H), 7.58 (tt, $J = 7.4$, 1.1 Hz, 1H), 7.28 (t, $J = 7.9$ Hz, 2H), 7.20 (m, 2H), 7.07 (dd, $J = 7.4$, 1.8 Hz, 1H), 6.96 (d, $J = 9.5$ Hz, 1H), 3.23 (sept, $J = 6.8$ Hz, 1H), 2.49 (q, $J = 11.8$ Hz, 3H), 2.11 (sept, $J = 6.6$ Hz, 1H), 1.73 (bs, 20H), 1.39 (d, $J = 6.8$ Hz, 3H), 1.23 (m, 10H), 1.13 (d, $J = 6.8$ Hz, 3H), 0.78 (dd, $J = 25.2$, 6.8 Hz, 6H). Analysis of the ^{1}H NMR spectrum reveals that the isolated complex is the Schiff-base Ru complex **5a**, previously disclosed by Chang et al.,[9] and not the target amine complex **7a**.

Synthesis and Characterization of Ru Complex 10. Potassium salt **9** (0.070 g, 0.15 mmol), Grubbs "first generation" catalyst **1** (0.12 g, 0.15 mmol), and AgCl (0.019 g, 0.13 mmol) were added to a 25 mL Schlenk flask. The flask was evacuated and back-filled with argon. Dry THF (3.0 mL) and toluene (3.0 mL) were added to the Schlenk flask under argon. The mixture was stirred at 45 °C for 4 h and cooled to room temperature followed by removal of the solvent under reduced pressure. The residue, a dark-brown solid, was passed through a silica gel column using diethyl ether/hexane (1:1) as eluent. The red fraction was collected and concentrated to afford the title product **10** as a red solid, 0.027 g (21%), mp 127−129 °C (dec). ^{1}H NMR ($CDCl_3$, 600 MHz): $\delta = 21.20$ (d, $J = 7.2$ Hz, 1H), 8.20 (d, $J = 8.3$ Hz, 2H), 7.85 (d, $J = 8.3$ Hz, 2H), 7.74−7.81 (m, 3H), 7.53 (d, $J = 2.8$ Hz, 2H), 7.42 (t, $J = 7.7$ Hz, 2H), 7.30 (t, $J = 7.7$ Hz, 2H), 7.19 (t, $J = 7.4$ Hz, 1H), 6.43 (d, $J = 9.2$ Hz, 2H), 4.54 (d, $J = 13.1$ Hz, 2H), 3.84 (d, $J = 13.1$ Hz, 2H), 2.16 (q, $J = 11.9$ Hz, 3H), 1.45−1.95 (m, 20H), 1.14−1.30 (m, 10H). ^{13}C NMR (($CDCl_3$, 151 MHz): $\delta = 303.82$ (d, 15.2 Hz), 175.2, 155.6, 144.7, 135.2, 130.9, 130.2, 129.8, 128.9(4), 128.8-(7), 126.1, 122.3, 120.7, 120.4, 66.0, 33.3, 33.1, 28.9, 27.9, 27.8, 26.5. ^{31}P NMR (202.5 MHz, $CDCl_3$) $\delta = 46.07$. IR (film): 2926 (m), 2850 (w), 1596 (m), 1566 (m), 1481 (m), 1445 (w), 1434 (w), 1287 (s), 1254 (m), 1173 (m), 1128 (w), 1092 (m), 1029 (w), 1004 (w), 960 (w), 929 (w), 901 (w), 848 (w), 826 (w), 773 (m), 752 (m), 721 (w), 689 (w), 663 (m). HRMS (ESI), *m/z*: $[M]^+$ calculated for $C_{45}H_{54}N_3O_6PRu(99)$, 862.2804; found, 862.2798. Anal. Calcd for $C_{45}H_{54}N_3O_6PRu \cdot 0.55C_6H_{14}$: C, 63.58; H, 6.82; N, 4.61. Found: C, 63.90; H, 6.51; N, 4.53.

Synthesis and Characterization of Ru Alkylidene Complex 11. Potassium salt **9** (0.047 g, 0.10 mmol), **2** (0.060 g, 0.10 mmol), and AgCl (0.019 g, 0.132 mmol) were added to a 25 mL Schlenk flask. The flask was evacuated and back-filled with argon. Dry THF (3 mL) and toluene (3 mL) were added to the Schlenk flask under argon. The mixture was stirred at 40 °C for 3 h and cooled to room temperature followed by removal of the solvent under reduced pressure. The residual, a dark-brown solid was passed through a silica gel column using diethyl ether/hexane (4:6) as eluent. The red fraction was collected and concentrated and afforded the title product as an orange-red solid, 31 mg (34%), mp 118−120 °C (dec). It was difficult to separate the complexes **2** and **11** completely by chromatography because of their similar polarities. ^{1}H NMR (CD_2Cl_2, 500 MHz): $\delta = 20.75$ (d, $J = 11.2$ Hz, 1H), 8.08 (dd, $J = 7.8$, 1.7 Hz, 1H), 7.80 (d, $J = 8.4$ Hz, 2H), 7.69−7.78 (m, 3H),

7.53 (d, $J = 3.0$ Hz, 2H), 7.31 (t, $J = 7.9$ Hz, 2H), 7.20 (t, $J = 7.4$ Hz, 1H), 6.96 (d, $J = 8.4$ Hz, 1H), 6.84 (t, $J = 7.5$ Hz, 1H), 6.50 (d, $J = 9.2$, 2H), 4.66 (br, 2H), 4.62 (septet, $J = 6.0$), 3.77 (dd, $J = 13.5$, 2.4 Hz, 2H), 2.23 (q, $J = 11.8$ Hz, 3H), 1.48−2.06 (m, 20H), 1.20−1.36 (m, 10H), 1.14 (d, $J = 6.0$ Hz, 6H). ^{13}C NMR ($(CD_2Cl_2$, 125.8 MHz): $\delta = 301.4$ (m), 175.4, 148.8, 147.6, 145.6, 135.6, 130.0, 129.8, 129.7, 128.6, 128.5, 125.7, 122.8, 122.3, 121.3, 121.0, 115.0, 71.1, 65.0, 33.3, 33.2, 29.2, 28.2, 28.1, 26.9, 22.0. ^{31}P NMR (202.5 MHz, $CDCl_3$) $\delta = 45.90$. IR (film): 2927 (m), 2851 (w), 1596 (m), 1566 (m), 1480 (m), 1449 (w), 1433 (w), 1385 (w), 1288 (s), 1255 (m), 1231 (m), 1174 (w), 1159 (w), 1114 (w), 1092 (m), 1041 (w), 1005 (w), 951 (w), 929 (w), 901 (w), 848 (w), 827 (w), 773 (m), 753 (m), 731 (w), 698 (w), 664 (m). HRMS (ESI), *m/z*: $[M]^+$ calculated for $C_{48}H_{60}N_3O_7PRu$(99), 920.3222; found, 920.3234. Anal. Calcd for $C_{48}H_{60}N_3O_7PRu\cdot 0.4C_6H_{14}$: C, 63.22; H, 6.91; N, 4.39. Found: C, 63.56; H, 6.61; N, 4.23.

Olefin Metathesis Activity of Ru Complexes 10 and 11. In a representative procedure, 6.9×10^{-4} mmol (8%) of the Ru-complex and diethyl diallylmalonate (8.6×10^{-3} mmol) were transferred to a 25 mL Schlenk flask and dissolved in 0.5 mL of the solvent. The reactions were performed under inert atmosphere, and the reaction mixtures were magnetically stirred. At the end of reaction the solution was transferred to a dry NMR tube using a syringe, and the reaction was monitored by integration of the allylic methylene peaks.

X-ray Crystallography and Crystal Structure Determination of 6a, 6c, 8, and 10. Crystals suitable for diffraction experiments were mounted in Paratone-N inside a nylon loop (Hampton research). Data collection for **6a**, **6c**, and **8** was done on a Bruker AXS SMART 2K CCD diffractometer using graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) performing ω scans in four φ positions, employing the SMART software package.[50] The collected images (1888) were processed using SAINT.[51] Numerical absorption correction was done using SHELXTL.[52] The structures were solved by direct methods and refined with standard difference Fourier techniques.[52]

The extremely thin crystals of compound **10** diffracted very poorly, and data collection on **10** was therefore done on a Bruker AXS MICROSTAR microfocus rotating anode system (2.7 kW anode power on a 100×100 μm^2 anode focal spot) with focusing optics, using a Platinum 135 CCD detector, with Cu Kα radiation ($\lambda = 1.54178$ Å) at 100 K. A total of 42 data collection runs (4780 images) in various ω scans and φ settings yielded 268 662 reflections of which 267 228 remained (20 688 unique) after scaling with SADABS.[53] The SQUEEZE routine, as implemented in PLATON[54] was employed to subtract the scattering contribution of the solvent molecules, 683 electrons in the unit cell, which roughly equals to nine pentane solvent molecules (disordered) per unit cell. $Z' = 12$ ($Z'/Z = 3$) with respect to the Ru-complex.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no's CCDC-662806 (**6a**), CCDC-662807 (**6c**), CCDC-662808 (**8**), and CCDC-662809 (**10**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (Fax: (+44)1223-336-033. E-mail: deposit@ccdc.cam.ac.uk.)

(49) The weight (200 mg) is 10 % higher than the theoretical weight (179 mg). The excess is due to the presence of 0.7 equiv of residual THF, as discernible in the ^{1}H-NMR spectrum.

(50) *SMART, Data Collection Software for Bruker AXS CCD*, version 5.504; Bruker AXS Inc.: Madison, WI, 1999.

(51) *SAINT, Data Integration Software for Bruker AXS CCD*, version 6.45a; Bruker AXS Inc.: Madison, WI, 2002.

(52) *SHELXTL, Structure Determination Software Suite*, version 6.14; Bruker AXS Inc.: Madison, WI, 2000.

Computational Details

Initial conformational searches were performed using a semiempirical method (PM3) implemented in Spartan'02.[55] In the case of the Grubbs first generation catalyst **1**, and Schiff base bidentate ruthenium complex **5a**, the available X-ray structures were used as starting geometries after modification of the alkylidene groups. The thus located low-energy conformers were taken as input structures for geometry optimization in the Gaussian 03[56] suite of programs using the OLYP density functional. All located stationary points were characterized by calculation of the Hessian matrix. The OLYP functional contains Handy's OPTX modification[57] of Becke's exchange[58] and correlation due to Lee, Yang, and Parr.[59] This functional has been reported to be superior to the related BLYP functional and other pure density functionals in general[60] and also in applications involving transition metals.[61] Numerical integrations were performed using the default "fine" grid of Gaussian 03, and the Gaussian 03 default values were chosen for the self-consistent-field (SCF) and geometry optimization convergence criteria. Thermochemical values were computed within the harmonic-oscillator, rigid-rotor, and ideal-gas approximations.

Hay and Wadt effective core potentials (ECPs) in combination with their accompanying valence double-ζ basis sets were applied for phosphorus, chlorine, and ruthenium.[62,63] For ruthenium, the ECP replaced the 1s, 2s, 2p, 3s, 3p, and 3d electrons whereas the 4s, 4p, 4d, 5s, and 5p orbitals were represented by the Hay and Wadt primitive basis set[63] (5s, 6p, 4d) contracted to [3s, 3p, 2d]. Carbon, nitrogen, oxygen, and hydrogen atoms were described by standard Dunning and Hay valence double-ζ basis sets.[64]

Total energies and properties were obtained in single point (SP) energy evaluations using the three-parameter hybrid density functional method of Becke (termed "B3LYP"),[65] as implemented in the Gaussian 03 set of programs.[56] The SP calculations involved basis sets that were improved compared to those used in the geometry optimizations. For ruthenium, the Hay and Wadt primitive basis set,[63] (5s, 6p, 4d), was contracted to [4s, 4p, 3d]. A diffuse s function was added to the basis sets of all elements except ruthenium, whereas a diffuse p function was added to all elements except ruthenium and hydrogen. The diffuse s function for hydrogen

(53) *SADABS, Bruker AXS Area Detector Scaling and Absorption Correction*, version 2006/1; Bruker AXS Inc.: Madison, WI, 2006.

(54) Spek, A. L. *J. Appl. Crystallogr.* **2003**, *36*, Part 1, 7.

(55) *Spartan'02*; Wavefunction, Inc.: Irvine, CA, 2002.

(56) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision B.04; Gaussian, Inc.: Wallingford, CT, 2004.

(57) Handy, N. C.; Cohen, A. J. *Mol. Phys.* **2001**, *99*, 403.

(58) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.

(59) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(60) Xu, X.; Goddard, W. A. *J. Phys. Chem. A* **2004**, *108*, 8495. Baker, J.; Pulay, P. *J. Chem. Phys.* **2002**, *117*, 1441. Hoe, W. M.; Cohen, A. J.; Handy, N. C. *Chem. Phys. Lett.* **2001**, *341*, 319.

(61) Baker, J.; Pulay, P. *J. Comput. Chem.* **2003**, *24*, 1184.

(62) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 284.

(63) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299.

(64) Dunning Jr., T. H.; Hay, P. J. In *Methods of Electronic Structure Theory*; Schaefer H. F., III, Ed.; Plenum Press: New York, 1977; p 1.

(65) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

and the diffuse p functions were taken from ref 66. For the other elements, the diffuse s functions were added in an even-tempered manner. For hydrogen, a p polarization function was added, whereas a d polarization function was added to the basis sets of carbon, nitrogen, oxygen, phosphorus, and chlorine.[66] These diffuse and polarization functions were added to the standard valence double-ζ basis sets described above and contracted to [4s, 1p] for hydrogen and [4s, 4p, 1d] for first-row elements as well as for the valence of phosphorus and chlorine.

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(66) Check, C. E.; Faust, T. O.; Bailey, J. M.; Wright, B. J.; Gilbert, T. M.; Sunderlin, L. S. *J. Phys. Chem. A* **2001**, *105*, 8111.

Supporting Information Available: Calculated energies and Cartesian coordinates of the optimized structures; IR-, ^{1}H NMR-, ^{13}C NMR-, and MS-spectra for all isolated ligands and ruthenium alkylidene complexes; tables of crystal and intensity collection data; positional and displacement parameters; complete bond distances and angles for **6a**, **6c**, **8**, and **10**; X-ray crystallographic file for compounds **6a**, **6c**, **8**, and **10** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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