# Olefin Metathesis Catalysts Containing Acyclic Diaminocarbenes

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# Olefin Metathesis Catalysts Containing Acyclic Diaminocarbenes

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The first examples of ruthenium-based olefin metathesis catalysts containing acyclic diaminocarbene (ADC) ligands are reported. Complexes of the type (ADC)(SIMes)$Cl_2$Ru=CHPh and (ADC)$Cl_2$Ru=CH(2-isopropoxy)Ph (ADC = *N*,*N*′-dimesityl-*N*,*N*′-dimethylformamidin-2-ylidene or *N*,*N*′-bis(2,6-di-isopropylphenyl)-*N*,*N*′-dimethylformamidin-2-ylidene; SIMes = 1,3-dimesitylimidazolin-2-ylidene) were synthesized and studied in solution as well as in the solid state. Depending on their N-substituents and the metal center to which they were coordinated, the aforementioned ADC ligands were found to adopt different conformations. Preliminary investigations revealed that these Ru complexes exhibited high catalytic activities in a variety of olefin metathesis reactions at elevated temperatures and afforded cross-metathesis products with significantly lower *E*:*Z* ratios than catalysts containing analogous N-heterocyclic carbene ligands.

The olefin metathesis reaction[1] has become an indispensible tool for synthesizing small molecules[2] as well as macromolecular materials.[3] Although a variety of catalysts for facilitating this useful transformation are known,[4] those based on late transition metals, particularly ruthenium, often show the highest stabilities toward oxygen, moisture, and a wide range of functional groups.[5] As a bonus, many of these same catalysts also display high activities and react with a broad range of substrates.[6] Representative examples of commercially available Ru-based catalysts that have found widespread utility in a variety of olefin metathesis reactions are shown in Figure 1 (i.e., **1**−**3**).

Realization of the next generation of catalysts that effectively hurdle contemporary challenges, such as those that are able to react with sterically hindered olefins and/or provide products with high diastereo- or enantioselectivities, hinge on the development of new ligands.[7] Although a broad range of ligands for metathesis-active Ru-based catalysts have been studied, N-heterocyclic carbenes (NHCs)[8] are among the most promising.[9] Widely accepted to be stronger electron donors than typical phosphines,[10] NHCs often enhance the activities of Ru-based catalysts upon coordination.[11] In addition to exhibiting favorable electronic properties, the steric properties of NHCs can be modified by varying the nature of their N-substituents using straightforward methods.[10,12] Indeed, efforts toward controlling the stereochemical outcomes of olefin metathesis reactions catalyzed by complexes that contain unsymmetrical NHCs have been reported.[7,13] For example, catalysts **4** and **5** were

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(1) (a) Chauvin, Y. *Angew. Chem., Int. Ed.* **2006**, *45*, 3740. (b) Schrock, R. R. *Angew. Chem., Int. Ed.* **2006**, *45*, 3748. (c) Grubbs, R. H. *Angew. Chem., Int. Ed.* **2006**, *45*, 3760.

(2) Hoveyda, A. H.; Zhugralin, A. R. *Nature* **2007**, *450*, 243.

(3) (a) Buchmeiser, M. R. *Chem. Rev.* **2000**, *100*, 1565. (b) Bielawski, C. W.; Grubbs, R. H. *Prog. Polym. Sci.* **2007**, *32*, 1.

(4) (a) Toreki, R.; Schrock, R. R. *J. Am. Chem. Soc.* **1990**, *112*, 2448. (b) Ivin, K. J.; Mol, J. C. *Olefin Metathesis and Metathesis Polymerization*; Academic Press: San Diego, CA, 1997. (c) Chabanas, M.; Baudouin, A.; Coperet, C; Basset, J. M. *J. Am. Chem. Soc.* **2001**, *123*, 2062. (d) Schrock, R. R. *Chem. Rev.* **2002**, *102*, 145. (d) Schrock, R. R.; Hoveyda, A. H. *Angew. Chem., Int. Ed.* **2003**, *42*, 4592. (e) Katz, T. J. *Angew. Chem., Int. Ed.* **2005**, *44*, 3010. (f) Castarlenas, R.; Esteruelas, M. A.; Onate, E. *Organometallics* **2005**, *24*, 4343.

(5) (a) Schwab, P.; France, M. B.; Ziller, J. W.; Grubbs, R. H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2039. (b) Fraser, C.; Grubbs, R. H. *Macromolecules* **1995**, *28*, 7248. (c) Schwab, P.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1996**, *118*, 100. (d) Trnka, T. M.; Grubbs, R. H. *Acc. Chem. Res.* **2001**, *34*, 18.

(6) Grubbs, R. H. *Handbook of Metathesis*; Wiley-VCH: Weinheim, Germany, 2003.

(7) For selected examples, see: (a) Van Veldhuizen, J. J.; Gillingham, D. G.; Garber, S. B.; Kataoka, O.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2003**, *125*, 12502. (b) Dinger, M. B.; Nieczypor, P.; Mol, J. C. *Organometallics* **2003**, *22*, 5291. (c) Gillingham, D. G.; Kataoka, O.; Garber, S. B.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2004**, *126*, 12288. (d) Vougioukalakis, G. C.; Grubbs, R. H. *Organometallics* **2007**, *26*, 2469. (e) Fournier, P. A.; Collins, S. K. *Organometallics* **2007**, *26*, 2945. (f) Anderson, D. R.; Lavallo, V.; O′Leary, D. J.; Bertrand, G.; Grubbs, R. H. *Angew. Chem. Int. Ed.* **2007**, *46*, 7162. (g) Anderson, D. R.; Ung, T.; Mkrtumyan, M.; Bertrand, G.; Grubbs, R. H.; Schrodi, Y. *Organometallics* **2008**, *27*, 563. (h) Vougioukalakis, G. C.; Grubbs, R. H. *Am. Chem. Soc.* **2008**, *130*, 2234. (i) Kumar, P. S.; Wurst, K.; Buchmeiser, M. R. *Organometallics* **2009**, *28*, 1785. (j) Vorfalt, T.; Leuthäusser, K.; Plenio, H. *Angew. Chem. Int. Ed.* **2009**, *48*, 5191.

(8) (a) Arduengo, A. J.III; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1991**, *113*, 361. (b) Herrmann, W. A.; Köcher, K. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2162.

(9) (a) Colacino, E.; Martinez, J.; Lamaty, F. *Coord. Chem. Rev.* **2007**, *251*, 726. (b) Samojłowicz, C.; Bieniek, M.; Grela, K. *Chem. Rev.* **2009**, *109*, 3708.

(10) Herrmann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1290.

(11) (a) Scholl, M.; Trnka, T. M.; Morgan, J. P.; Grubbs, R. H. *Tetrahedron Lett.* **1999**, *40*, 2247. (b) Scholl, M.; Ding, S.; Lee, C. W.; Grubbs, R. H. *Org. Lett.* **1999**, *1*, 953. (c) Huang, J.; Stevens, E. D.; Nolan, S. P.; Peterson, J. L. *J. Am. Chem. Soc.* **1999**, *121*, 2674. (d) Weskamp, T.; Kohl, F. J.; Hieringer, W.; Gliech, D.; Herrmann, W. A. *Angew. Chem., Int. Ed.* **1999**, *38*, 2416. (e) Briot, A.; Bujard, M.; Gouverneur, V.; Nolan, S. P.; Mioskowski, C. *Org. Lett.* **2000**, *2*, 1517. (f) Trnka, T. M.; Morgan, J. P.; Sanford, M. S.; Wilhelm, T. E.; Scholl, M.; Choi, T.-L.; Ding, S.; Day, M. W.; Grubbs, R. H. *J. Am. Chem. Soc.* **2003**, *125*, 2546.

(12) For recent developments, see: (a) Fürstner, A.; Alcarazo, M.; César, V.; Lehmann, C. W. *Chem. Commun.* **2006**, 2176. (b) Kison, C.; Opatz, T. *Synthesis* **2006**, 3727. (c) Bon, R. S.; Kanter, F. J. J. de; Lutz, M.; Spek, A. L.; Jahnke, M. C.; Hahn, F. E.; Groen, M. B.; Orru, R. V. A. *Organometallics* **2007**, *26*, 3639. (d) Kuhn, K. M.; Grubbs, R. H. *Org. Lett.* **2008**, *10*, 2075. (e) Hirano, K.; Urban, S.; Wang, C.; Glorius, F. *Org. Lett.* **2009**, *11*, 1019.

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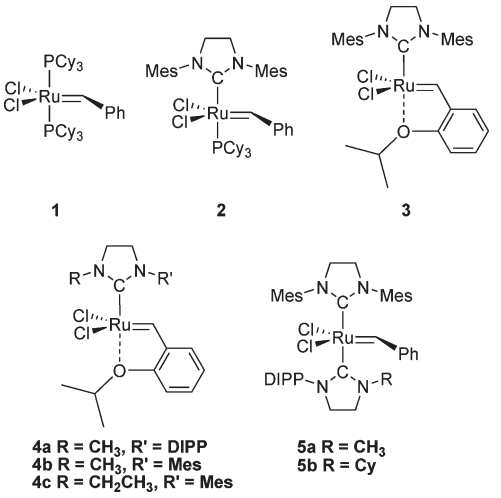


**Figure 1.** Representative examples of commercially available Ru-based catalysts (**1**−**3**) and selected examples of Ru catalysts containing unsymmetrical NHC ligands (**4**, **5**). Cy = cyclohexyl, Mes = 2,4,6-trimethylphenyl, DIPP = 2,6-di-isopropylphenyl.

investigated for their abilities to afford cross-metathesis products with different *E*:*Z* ratios than catalysts containing symmetric NHC ligands, many of which had varying degrees of success.[13] While a Ru-based olefin metathesis catalyst that is universally applicable and provides only cis products has yet to be developed,[14] the use of unsymmetrical NHCs as ligands remains a viable approach.

An emerging class of ligands that may also facilitate the realization of new classes of Ru-based olefin metathesis catalysts with enhanced activities or stereoselectivities is acyclic diaminocarbenes (ADCs).[15] Compared to NHCs, ADCs typically possess wider N−C−N bond angles, are stronger $\sigma$-donors, and can be generated in a straightforward manner via deprotonation of readily accessible formamidinium salts.[16] Furthermore, a broad range of metal complexes containing ADCs are known, some of which have been reported to be

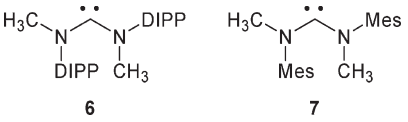


**Figure 2.** Structures of two acyclic diaminocarbenes (ADCs) studied as ligands for Ru alkylidenes. The conformations shown are consistent with their solution state structures.

catalytically active.[17] In addition to their unique electronic and steric properties, another remarkable aspect of ADCs is their structure. Enabled by free rotation about their C−N bonds, ADCs are capable of adopting multiple, unique conformations if their N-substituents are differentially substituted. For example, we reported that the conformations adopted by various ADCs as well as their parent formamidinium salts and derivative metal complexes may be controlled by tuning the steric properties of their N-substituents.[18]

Motivated by the inherent features of ADCs, particularly those that are differentially substituted, we envisioned these ligands enhancing the activities and/or selectivities of Ru-based olefin metathesis catalysts that contain them. With these goals in mind, we describe herein the synthesis of the first examples of olefin metathesis catalysts that contain ADCs and give a preliminary account of their catalytic properties.[19]

Since NHCs with bulky *N*-aryl substituents often result in complexes with superior stabilities due to protection provided by steric shielding about the metal center,[20] efforts were focused on coordinating ADCs **6** and **7** (Figure 2), which feature *N*-DIPP and *N*-Mes substituents, respectively, to various Ru alkylidenes (DIPP = 2,6-di-isopropylphenyl; Mes = 2,4,6-trimethylphenyl). The respective conjugate acids of these ADCs, formamidinium iodides **6**·**HI** and **7**·**HI**, were synthesized by independently treating acetonitrile solutions of *N*,*N*′-bis(2,6-di-isopropylphenyl)formamidine or *N*,*N*′-dimesitylformamidine with excess iodomethane in 69% and 88% yields, respectively. We previously determined that **6**·**HI** adopts a pseudo trans conformation in solution as well as in the solid state;[18] **7**·**HI** appears to follow suit. Two inequivalent signals attributed to the *N*-methyl groups were observed in the $^1$H NMR spectrum of **7**·**HI** at $\delta$ = 3.50 and 2.64 ppm (DMSO-$d_6$), chemical shifts that were nearly identical to those exhibited by **6**·**HI** ($\delta$ = 3.59 and 2.69 ppm in the same solvent). Additionally, two distinct singlets were observed for the *N*-aryl protons of the mesityl groups at $\delta$ = 7.14 and 7.07 ppm. The solid state structure of **7**·**HI** (see Figure S1) was consistent with the solution state assessment, and the key bond lengths and angles exhibited by this complex were similar to those observed in the solid state structure of **6**·**HI**.

(13) (a) Vehlow, K.; Maechling, S.; Blechert, S. *Organometallics* **2006**, *25*, 25. (b) Ledoux, N.; Linden, A.; Allaert, B.; Mierde, H. V.; Verpoort, F. *Adv. Synth. Catal.* **2007**, *349*, 1692. (c) Ledoux, N.; Allaert, B.; Linden, A.; Van Der Voort, P.; Verpoort, F. *Organometallics* **2007**, *26*, 1052.

(14) For recent examples of *Z*-selective catalysts based on Mo, see: (a) Ibrahem, I.; Yu, M.; Schrock, R. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2009**, *131*, 3844. (b) Flook, M. M.; Jiang, A. J.; Schrock, R. R.; Müller, P.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2009**, *131*, 7962. For selected examples of the observation of Z-selectivity in cross-metathesis reactions involving Ru-based catalysts, see: (a) Randl, S.; Gessler, S.; Wakamatsu, H.; Blechert, S. *Synlett* **2001**, 430. (b) Hansen, E. C.; Lee, D. *Org. Lett.* **2004**, *6*, 2035. (c) Sashuk, V.; Samojlowicz, C.; Szadkowska, A.; Grela, K. *Chem. Commun.* **2008**, 2468.

(15) Alder, R. W.; Allen, P. R.; Murray, M.; Orpen, A. G. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1121.

(16) (a) Alder, R. W.; Blake, M. E. *Chem. Commun.* **1997**, 1513. (b) Alder, R. W.; Blake, M. E.; Bortolotti, C.; Bufali, S.; Butts, C. P.; Linehan, E.; Oliva, J. M.; Orpen, A. G.; Quayle, M. J. *Chem. Commun.* **1999**, 241. (c) Alder, R. W.; Blake, M. E.; Bufali, S.; Butts, C. P.; Orpen, A. G.; Schütz, J.; Williams, S. J. *J. Chem. Soc., Perkin Trans. 1* **2001**, 1586. (d) Denk, K.; Sirsch, P.; Herrmann, W. A. *J. Organomet. Chem.* **2002**, *649*, 219. (e) Herrmann, W. A.; Öfele, K.; Preysing, D. V.; Herdtweck, J. *J. Organomet. Chem.* **2003**, *684*, 235. (f) Otto, M.; Conejero, S.; Canac, Y.; Romanenko, V. D.; Rudzevitch, V.; Bertrand, G. *J. Am. Chem. Soc.* **2004**, *126*, 1016. (g) Alder, R. W.; Blake, M. E.; Chaker, L.; Harvey, J. N.; Paolini, F.; Schütz, J. *Angew. Chem., Int. Ed.* **2004**, *43*, 5896. (h) Magill, A. M.; Cavell, K. J.; Yates, B. F. *J. Am. Chem. Soc.* **2004**, *126*, 8717. (i) Lee, M.-T.; Hu, C.-H. *Organometallics* **2004**, *23*, 976. (j) Frey, G. D.; Herrmann, W. A. *J. Organomet. Chem.* **2005**, *690*, 5876. (k) Frey, G. D.; Herdtweck, E.; Herrmann, W. A. *J. Organomet. Chem.* **2006**, *691*, 2465. (l) Wanniarachchi, Y. A.; Slaughter, L. M. *Chem. Commun.* **2007**, 3294. (m) Yoshitha, A.; Wanniarachchi, T. K.; Slaughter, L. M. *Organometallics* **2008**, *27*, 1055.

(17) (a) Kremzow, D.; Seidel, G.; Lehmann, C. W.; Fürstner, A. *Chem.—Eur. J.* **2005**, *11*, 1833. (b) Moncada, A. I.; Manne, S.; Tanski, J. M.; Slaughter, L. M. *Organometallics* **2006**, *25*, 491. (c) Dhudshia, B.; Thadani, A. N. *Chem. Commun.* **2006**, 668. (d) Wanniarachchi, Y. A.; Kogiso, Y.; Slaughter, L. M. *Organometallics* **2008**, *27*, 21. (e) Hirsch-Weil, D.; Snead, D. R.; Inagaki, S.; Seo, H.; Abboud, K. A.; Hong, S. *Chem. Commun.* **2009**, *18*, 2475.

(18) Rosen, E. L.; Sanderson, M. D.; Saravanakumar, S.; Bielawski, C. W. *Organometallics* **2007**, *26*, 5774.

(19) Attempts to prepare a Ru-based catalyst containing an ADC via treatment of $(PCy_3)_2Cl_2Ru$=CHPh with *N*,*N*,*N*′,*N*′-tetra(isopropyl)-formamidin-2-ylidene were reported to result in decomposition; see: Herrmann, W. A.; Öfele, K.; Preysing, D. V.; Herdtweck, E. *J. Organomet. Chem.* **2003**, *684*, 235.

(20) (a) Díez-González, S.; Nolan, S. P. *Coord. Chem. Rev.* **2007**, *251*, 874. (b) Cavallo, L.; Correa, A.; Costabile, C.; Jacobsen, H. *J. Organomet. Chem.* **2005**, *690*, 5407.

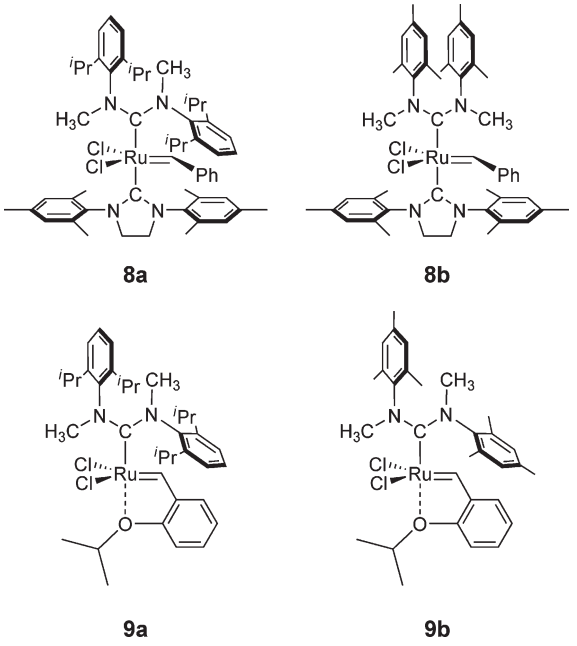


**Figure 3.** Structures of Ru alkylidenes containing ADC ligands. The conformations shown are consistent with their structures observed in solution and, for **8b**, **9a**, and **9b**, in the solid state.

With the aforementioned formaminidinum salts in hand, efforts shifted toward synthesizing Ru alkylidenes that contained the respective ADCs as ligands. Initial attempts to synthesize (ADC)($PCy_3$)$Cl_2$Ru=CHPh-type complexes by treating independent benzene solutions of **6·HI** or **7·HI** with $NaN(SiMe_3)_2$ (to generate their respective ADCs *in situ*) followed by the addition of ($PCy_3$)$_2Cl_2$Ru=CHPh were promising. In addition to the observation of free $PCy_3$, new diagnostic signals were observed in the NMR spectra of the crude product mixtures and tentatively assigned to (**6**)($PCy_3$)$Cl_2$Ru=CHPh ($^1$H: 19.20 and $^{31}$P: 31.90 ppm, $CDCl_3$) and (**7**)($PCy_3$)$Cl_2$Ru=CHPh ($^1$H: 18.91 and $^{31}$P: 32.26 ppm, $CDCl_3$), respectively. Unfortunately, pure materials could not be isolated from analogous preparation-scale reactions in reasonable quantities, despite numerous attempts using various techniques and conditions, including chromatographic methods (using silica or alumina with hexanes/ethyl acetate, hexanes/ether, hexanes/$CH_2Cl_2$, etc.), precipitations, and triturations.

We reasoned that the apparent instabilities of the aforementioned (ADC)($PCy_3$)$Cl_2$Ru=CHPh-type complexes could be related to the lability of the phosphine ligands trans to the ADCs. As such, efforts shifted toward preparing mixed NHC-ADC Ru complexes since analogous bis-(NHC)-type Ru complexes are known to be relatively stable.[13,27] Gratifyingly, addition of (SIMes)(pyridine)$_2Cl_2$-Ru=CHPh[21] (SIMes = 1,3-dimesitylimidazolin-2-ylidene) to a solution of the ADC (generated *in situ* via deprotonation of **6·HI** or **7·HI** with $NaN(SiMe_3)_2$) afforded the desired complexes, **8a** and **8b**, in 35% and 66% isolated yields, respectively, after purification by column chromatography. The characteristic benzylidene signals in these complexes were observed at $\delta$ = 18.59 and 19.16 ppm ($CDCl_3$) in their respective $^1$H NMR spectra. To elucidate the solution structures adopted by complexes **8a** and **8b**, a series of NOESY experiments were performed in $CDCl_3$. Irradiation of the benzylidene proton at $\delta$ = 18.60 ppm ($CDCl_3$) in **8a** led to enhancement of signals that were attributed to both *N*-DIPP and *N*-Mes substituents present in this complex. This result suggested to us that the benzylidene moiety was positioned in between these two aromatic systems. Irradiation of the *N*-methyl signal at $\delta$ = 3.62 ppm in **8a** led to enhancement of two singlets at 6.87 and 6.82 ppm, which were assigned to the *N*-mesityl's aryl protons. Collectively, these spectroscopic results were consistent with the ADC ligand in **8a** adopting a pseudo trans conformation, which was similar to the structure of its respective free ADC and **6·HI**.[18]

Different spectroscopic results were obtained with **8b**. When the benzylidene signal (found at $\delta$ = 19.16 ppm; $CDCl_3$) was irradiated, a positive enhancement to a signal found at $\delta$ = 2.22 ppm was observed, suggesting the presence of a juxtaposed *N*-methyl group. This interaction was confirmed after irradiating that same group ($\delta$ = 2.22 ppm), which, in addition to enhancing the signal attributed to the benzylidene moiety, also enhanced the signals found at $\delta$ = 2.00 and 1.62 ppm. These latter chemical shifts were assigned to the 2,6-dimethyl groups on the *N*-mesityl substituent connected to same nitrogen atom as the *N*-methyl group under interrogation. Irradiation of the signal at $\delta$ = 3.10 ppm, which was assigned to the other *N*-methyl substituent, led to enhancement of the aromatic *N*-mesityl protons found at $\delta$ = 6.90 ppm as well as two singlets at 2.08 and 1.86 ppm. This interaction was attributed to a NOE contact with a mesityl group on the SIMes fragment. Collectively, these results were consistent with the ADC ligand in **8b** adopting a pseudo cis conformation where both *N*-methyl substituents were oriented toward the Ru center. This geometry differs from its respective free ADC[22] and formamidinium salt, and indicated that **7** underwent a C−N bond rotation either prior to or after metallation.[23]

Additional support for the unique conformation adopted by the ADC ligand in **8b** was obtained using X-ray crystallography. X-ray quality crystals were obtained by vapor diffusion of hexanes into a benzene solution saturated with this complex.[24] The ORTEP diagram shown in Figure 4 revealed that the ADC ligand in **8b** adopted a pseudo cis conformation in the solid state, a result that was consistent with the aforementioned assessment of its solution state structure. Close inspection of the crystal data revealed that the distance between the adjoining[25] arenes of the

(21) Sanford, M. S.; Love, J. A.; Grubbs, R. H. *Organometallics* **2001**, *20*, 5314.

(22) Upon *in situ* deprotonation of **7·HI** using NaHMDS, ADC **7** appears to adopt a pseudo trans conformation in solution, as determined by NMR spectroscopy. $^1$H NMR (75 MHz, $C_6D_6$): $\delta$ 6.78 (s, 2H), 6.64 (s, 2H), 3.48 (s, 3H), 2.28 (s, 6H), 2.24 (s, 6H), 2.18 (s, 3H), 2.15 (s, 3H), 2.08 (s, 3H). $^{13}$C NMR (75 MHz, $C_6D_6$): $\delta$ 248.7, 149.1, 144.9, 136.6, 134.8, 134.1, 132.5, 129.4, 128.8, 48.8, 35.5, 20.9, 18.5, 18.4. HRMS: calcd for $C_{21}H_{29}N_2$ [(M + H$^+$)] 309.2331; found 309.2332.

(23) As noted in the text, the ADC ligand found coordinated to the Ru center in **8b** adopted a different ground state conformation than its respective formidinium precursor, both in solution and in the solid state. To determine if this complex was capable of displaying multiple conformations, a solution of **8b** in toluene-$d_8$ was examined by variable-temperature $^1$H NMR spectroscopy. Unfortunately, no changes were observed, even at 100 °C. Furthermore, the lack of Overhauser effects between the benzylidene protons in **8** and **9** and the *N*-methyl groups pointing toward the Ru centers in these complexes suggest that rotation about the Ru-ADC bond may be relatively slow on the NMR timescale.

(24) Unfortunately, all efforts to obtain X-ray quality crystals of **8a** have been unsuccessful.

(25) The angle between the planes of these arenes was calculated to be 19.4°.

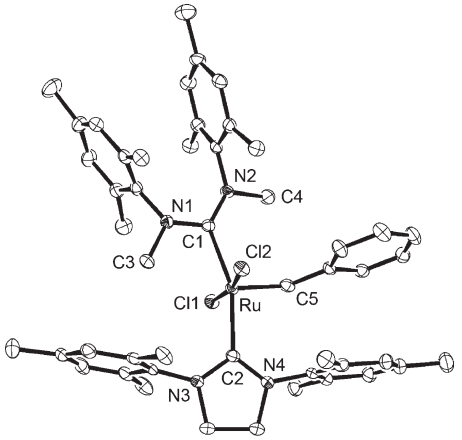


**Figure 4.** ORTEP diagram of (**7**)(SIMes)$Cl_2$Ru=CHPh (**8b**) showing 50% probability ellipsoids. H atoms and solvent molecules have been removed for clarity. Selected bond lengths (Å) and angles (deg): Ru−C1, 2.112(3); Ru−C2, 2.132(3); Ru−C5, 1.840(3); N1−C1, 1.356(3); N2−C1, 1.356(4); N3−C2, 1.360(4); N4−C2, 1.343(3); N1−C1−Ru, 110.6(2); N2−C1−Ru, 130.6(2); N3−C2−Ru, 125.4(2); N4−C2−Ru, 128.3(2); C1−Ru−C5, 104.0(1); C2−Ru−C5, 95.7(1); C1−Ru−C2, 160.1(1); Cl1−Ru−Cl2, 170.76; N1−C1−N2, 118.7(3); N3−C2−N4, 106.3(2).

*N*-mesityl substituents in the ADC (3.58 Å) was in accord with a favorable $\pi-\pi^*$ interaction,[26] which may facilitate formation of the unusual conformation observed. Regardless, the ADC ligand possessed a relatively wide N−C−N angle (118.7(3)°), which may impose additional steric constraint on the Ru center than may be otherwise expected and explain why the observed $C_{NHC}-Ru-C_{ADC}$ bond angle (C1−Ru−C2: 160.1(1)°) in **8b** was significantly more acute than the analogous angles observed in other reported bis(NHC) Ru complexes (162.0(2)−171.2(1)°).[27,28] The other structural metrics of **8b** were relatively similar to those found in reported bis(NHC) Ru complexes. For example, the $Ru-C_{benzylidene}$ bond distance (Ru−C5, 1.840(3) Å) was comparable to the analogous bond distances reported for related bis(NHC) Ru complexes (1.818(4)−1.835(2) Å).[13,27] The $Ru-C_{NHC}$ bond distance (Ru−C2, 2.132(3) Å) observed in **8b**, however, was slightly longer than analogous distances observed in a range of other bis(NHC) Ru complexes (2.115(3)−2.122(3) Å).[13,27]

With catalytic applications in mind, efforts were directed toward determining whether the ADC or the NHC ligand in **8a** and **8b** was more likely to dissociate. It has been previously reported that the addition of excess $PCy_3$ to $(NHC)_2Cl_2Ru$=CHPh-type complexes can be used to determine ligand lability.[13c] Heating a mixture of either **8a** or **8b** (20 mg in 0.8 mL of $C_6D_6$) in the presence of a 10-fold molar excess of $PCy_3$ at 100 °C (sealed tube) resulted in a dramatic color change from olive green to tan-red and resulted in the formation of (SIMes)($PCy_3$)$Cl_2$Ru=CHPh (**2**). $^1$H and $^{31}$P NMR spectroscopic analysis of the crude reaction mixtures showed the formation of new signals at $\delta$ = 19.60 and 30.54 ppm and $\delta$ = 19.62 and 30.54 ppm for the reactions involving **8a** and **8b**, respectively. These signals were nearly identical to those observed in $C_6D_6$ solutions of **2** ($\delta$ = 19.63 and 30.53 ppm). While the exchange reaction between **8a** and $PCy_3$ was complete within 2 h, the analogous reaction with **8b** took nearly 8 h. The rate difference may be related to the increased sterics associated with **6** as compared to **7**, facilitating dissociation of the former. Regardless, these results suggested to us that the relatively bulky ADC ligands in **8a** and **8b** were dissociating from their respective metal centers in preference to SIMes. As such, the catalytically active species generated from these catalysts would be effectively the same as those generated from commercially available catalyst **2** or **3**.

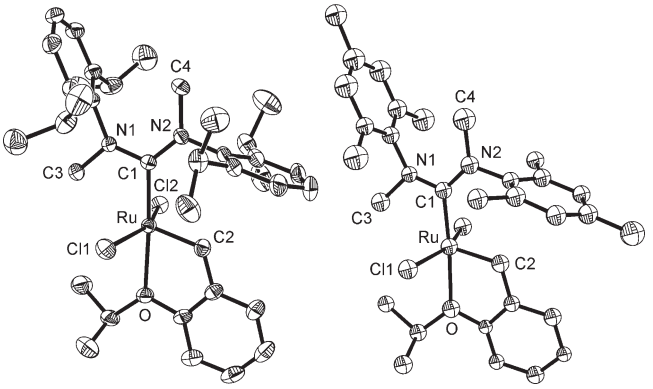


**Figure 5.** (Left) ORTEP diagram of **9a** showing ellipsoids at 50% probability. H atoms have been removed for clarity. Key bond lengths (Å) and angles (deg): Ru−C1, 2.015(2); Ru−C2, 1.834(2); Ru−O, 2.333(2); N1−C1, 1.359(3); N1−C2, 1.350(3); N1−C1−Ru, 110.4; N2−C1−Ru, 130.2(2); C1−Ru−C2, 106.56(9); C1−Ru−O, 175.75(7); Cl1−Ru−Cl2, 155.70(2); N1−C1−N2, 119.4(2). (Right) ORTEP diagram of **9b** showing ellipsoids at 50% probability. H atoms and solvent molecules have been removed for clarity. Key bond lengths (Å) and angles (deg): Ru−C1, 2.012(2); Ru−C2, 1.838(1); Ru−O, 2.307(1); N1−C1, 1.355(2); N1−C2, 1.481(3); N1−C1−Ru, 110.2(1); N2−C1−Ru, 130.1(1); C1−Ru−C2, 107.361(7); C1−Ru−O, 174.47(6); Cl1−Ru−Cl2, 158.97(2); N1−C1−N2, 119.6(2).

Although the catalytic activities of **8a** and **8b** were still investigated (see below), efforts were also directed toward the synthesis of ADC-containing derivatives with more labile ligands. In particular, efforts focused on synthesizing Hoveyda−Grubbs-type catalysts, which contain a weakly bound aryl ether trans to either an NHC or phosphine.[29] (ADC)$Cl_2$Ru=CH(2-isopropoxy)Ph-type complexes, **9a** and **9b**, were synthesized via treatment of ($PCy_3$)-$Cl_2$Ru=CH(2-isopropoxy)Ph with **6** or **7** (generated *in situ* from their respective formamidinium salts), respectively. As observed with **8a** and **8b**, complexes **9a** and **9b** were stable toward column chromatography, which facilitated their isolation. On the basis of a series of NOESY measurements, the ADCs in these complexes were determined to adopt pseudo trans conformations in which one *N*-aryl ring was juxtaposed with the benzylidene moieties. This assessment was confirmed by analyzing single crystals of the aforementioned complexes using X-ray diffraction (see Figure 5). Compared to NHC analogues **4**,[13a,b] the N−C−N bond angles observed in the solid state structures of **9** were significantly more obtuse (119.4(2)−119.6(2)° versus

(26) Hunter, C. A.; Sanders, J. K. M. *J. Am. Chem. Soc.* **1990**, *112*, 5525.

(27) (a) Weskamp, T.; Schattenmann, W. C.; Spiegler, M.; Herrmann, W. A. *Angew. Chem., Int. Ed.* **1998**, *37*, 2490. (b) Conrad, J. C.; Yap, G. P. A.; Fogg, D. E. *Organometallics* **2003**, *22*, 1986.

(28) This angle is similar to that observed for (1-methyl-3-(2,6-diisopropylphenyl)imidazolinylidene)$_2Cl_2$Ru=CHPh (162.0(2)°).[13c]

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

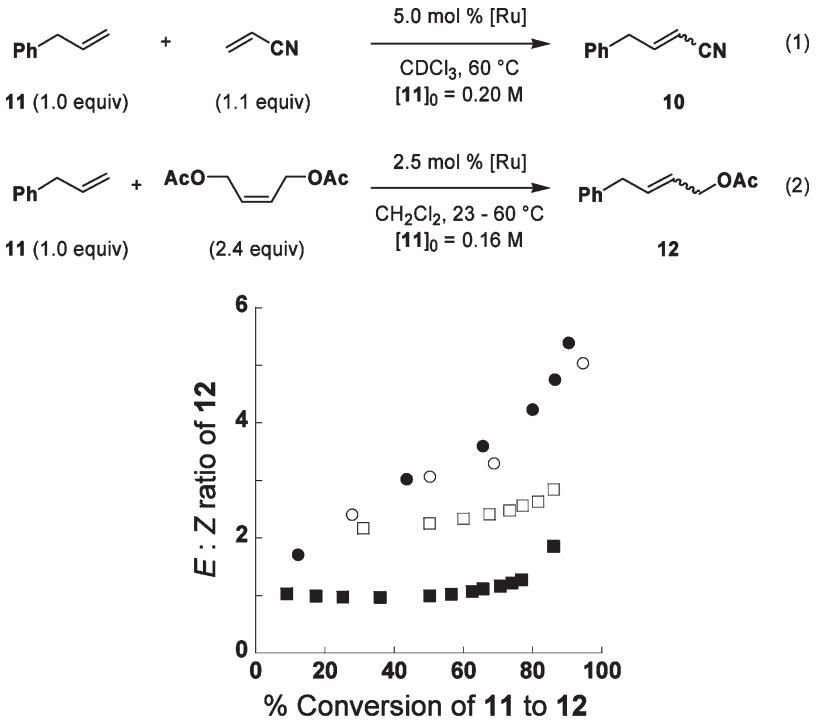


**Figure 6.** *E*:*Z* ratio of **12** versus conversion of **11** to **12** using **3** (○), **4a** (□), **9a** (■), and **9b** (●) as catalysts. Conditions are shown in eq 2. The reaction using **9a** was performed at 60 °C; all other reactions were run at 23 °C. Ratios and conversions were determined by gas chromatography.[31]

107.2(5)−107.6(3)°). These relatively large angles may impose additional steric constraints on the ligated metal centers[30] and explain why the $^1$H NMR signals attributed to the benzylidene moieties of these complexes ($\delta$ = 15.94 and 15.92 ppm, respectively; $CDCl_3$) were upfield compared to those observed in **4** ($\delta$ = 16.13−16.22 ppm).[13a,b] In addition, the Ru−O bond lengths in **9** were longer than analogous distances found in the crystal structures of **4** (2.307(1)−2.333(2) Å versus 2.269(3)−2.281(4) Å),[13] which may reflect the relatively strong electron donicities of the ADCs as compared to NHCs.

After the synthesis and characterization of **8** and **9**, a preliminary investigation of their catalytic activities was conducted.[31] Under standardized conditions,[32] these complexes showed relatively low catalytic activities in various ring-closing metathesis (RCM) reactions, compared to **1** and **2**. Although the highest activity in the RCM of diethyl diallyl malonate (DDM) was observed when **9b** was used (23% conversion after 1 h), this catalyst was less active than **2** (~100% conversion within 30 min)[32] (conditions: $[DDM]_0$ = 0.1 M, 1.0 mol % catalyst, $CD_2Cl_2$, 30 °C). In accord with results observed with Ru complexes containing exceptionally bulky NHC ligands (e.g., 1-(1-adamantyl)-3-mesityl-4,5-dihydroimidazol-2-ylidene), the relatively slow kinetics displayed by **8** and **9** may be due to the increased steric bulk of the ADCs interfering with olefin coordination or the catalytic mechanism.[33]

However, significantly enhanced catalytic activities were observed at elevated temperatures. For example, at 40 °C, conversions of DDM to its cyclic product were determined to be 89%, 62%, 100%, and 100%, for **8a**, **8b**, **9a**, and **9b**, respectively, after 12 h (conditions: $[DDM]_0$ = 0.1 M, 1.0 mol % catalyst, $CD_2Cl_2$). More impressively, diethyl bis(2-methylallyl)malonate, a sterically encumbered olefin, was quantitatively converted to the expected product in less than 1 h when the reactions were performed at 100 °C using catalysts **9a** and **9b** (conditions: $[substrate]_0$ = 0.1 M, 5.0 mol % catalyst, toluene-$d_8$). Under otherwise identical conditions, the analogous RCM reaction involving **8a** or **8b** required up to 12 h to reach similar conversions.

Having established that **8** and **9** showed reasonable activities at elevated temperatures, subsequent efforts focused on determining if the unsymmetrical conformations adopted by their ADC ligands would affect the inherent *E*:*Z* selectivities displayed by these complexes in various metathesis reactions. Emphasis was placed on catalysts **9a** and **9b** since it was concluded from the aforementioned phosphine exchange experiments that the ADC ligands in **8** likely dissociate in preference to the NHC ligands present.

Catalysts **9a** and **9b** were studied in two representative cross-metathesis (CM) reactions to allow comparison of their inherent *E*:*Z* selectivities to those exhibited by the analogous NHC catalysts **4a** and **4b**. Under the conditions summarized in eq 1, **9a** and **9b** afforded **10** with *E*:*Z* ratios = 1.2:1 and 0.6:1, respectively, at relatively early stages of the reaction (30% and 32% conversion of allylbenzene (**11**) to the desired CM product, respectively). For comparison, catalysts **4a** and **4b**, which contain NHCs analogous to the ADCs in **9a** and **9b**, were reported to afford the same product with higher *E*:*Z* ratios (*E*:*Z* = 2.8:1 and 1.8:1, respectively) at similar conversions (< 33%) and under similar conditions.[13b] Analogous results were obtained when the CM of **11** with 1,4-diacetoxy-2-butene to afford **12** was explored (see eq 2). As shown in Figure 6, **9a** afforded **12** in a nearly 1:1 ratio of its *E* and *Z* isomers to conversions that exceeded 75%.

(30) The distances between the benzylidene proton and the centroid of the juxtaposed arenes are significantly shorter for **9a** and **9b** (2.321 and 2.365 Å, respectively) than for **3** (**3**: 2.489 Å, **4a**: 2.567 Å, **4b**: 2.595 Å).

(31) See the Supporting Information for additional details.

(32) Ritter, T.; Hejl, A.; Wenzel, A. G.; Funk, T. W.; Grubbs, R. H. *Organometallics* **2006**, *25*, 5740.

(33) Dinger, M. B.; Nieczypor, P.; Mol, J. C. *Organometallics* **2003**, *22*, 5291.

For comparison, **4a** also afforded **12**, but with an *E*:*Z* ratio = 2.5:1 at similar conversions. Likewise, catalyst **9b** yielded **12** with a lower *E*:*Z* ratio (ca. 4:1) than that reported[13] for **4b** (6:1) under otherwise identical conditions and conversions (80%).[34]

While the origin of the selectivities observed in the reactions described above is presumed to be due to the increased sterics of the ADC-containing catalysts as compared to their NHC analogues, it may also be related to a reduced ability of the former to facilitate olefin isomerization and other secondary metatheses. To investigate, a CM reaction involving **11** and 1,4-diacetoxy-2-butene was performed as described in eq 2 (60 °C), using **9a** as the catalyst. When the conversion of **11** to **12** reached 95% (24 h; *E*:*Z* of product = 1.5:1), the reaction mixture was split into two fractions. One fraction was left untreated and a second bolus of catalyst was added to the other ($[Ru]_{final}$ = 5.0 mol %). After heating both fractions to 60 °C for an additional 24 h, they were analyzed. The *E*:*Z* of **12** found in these fractions increased to 3.0:1 and 7.0:1, respectively. Hence, while **9a** facilitates secondary metathesis reactions, these processes appear to be relatively slow.

In summary, the first examples of Ru-alkylidene olefin metathesis catalysts containing acyclic diaminocarbene ligands have been prepared. Compared to related NHC analogues, the ADCs imposed unique steric and electronic constraints on the metal centers to which they were ligated, as evidenced by relatively wide N−C−N bond angles, long Ru−O bond lengths, and other spectroscopic data. Furthermore, ADCs exhibited unsymmetrical conformations when coordinated to Ru, except for complex **8b**, for which, surprisingly, its ADC ligand **7** underwent a C−N rotation prior to or after complexation. This resulted in a pseudo cis conformation of the ADC ligand with the *N*-methyl substituents oriented toward the coordinated metal. The conformations of the ADC moieties were assigned in solution and found to be consistent with their solid state structures, where applicable. Finally, Ru-based catalysts containing ADCs afforded CM products with lower *E*:*Z* ratios than analogous NHC-containing catalysts.

## Experimental Section

**Materials and Methods.** Benzene was distilled from sodium and benzophenone under an atmosphere of nitrogen. Dichloromethane ($CH_2Cl_2$) and toluene were distilled from $CaH_2$ under an atmosphere of nitrogen. All solvents were degassed by three, consecutive freeze−pump−thaw cycles. Allylbenzene (**11**), acrylonitrile, *cis*-1,4-diacetoxy-2-butene, and *n*-octane were purchased from Aldrich and degassed using three consecutive freeze−pump−thaw cycles before use. $(PCy_3)_2Cl_2Ru{=}CHPh$ (**1**) and $(SIMes)(PCy_3)Cl_2Ru{=}CHPh$ (**2**) were generously donated by Materia, Inc. The Hoveyda−Grubbs first-generation catalyst, $(PCy_3)Cl_2Ru{=}CH$(2-isopropoxy)Ph, was purchased from Aldrich. $(SIMes)(pyridine)_2Cl_2Ru{=}CHPh$,[21] *N*,*N*′-bis(DIPP)-*N*,*N*′-dimethylformamidinium iodide (**6**·**HI**),[18] *N*,*N*′-dimesitylformamidine,[35] $(SIMes)Cl_2Ru{=}CH$(2-isopropoxy)Ph (**3**),[29] and (1-DIPP-3-methylimidazolin-2-ylidene)-$Cl_2Ru{=}CH$(2-isopropoxy)Ph (**4a**)[13c] were synthesized according to literature procedures. All other materials and solvents were of reagent quality and were used as received. Unless otherwise noted, all manipulations were performed under an atmosphere of nitrogen using drybox or Schlenk techniques.

**Instrumentation.** $^1H$ and $^{13}C\{^1H\}$ NMR spectra were recorded using a Varian 300, 400, 500, or 600 MHz spectrometer. Chemical shifts $\delta$ (in ppm) were referenced to tetramethylsilane using the residual solvent as an internal standard. For $^1H$ NMR: $CDCl_3$, 7.24 ppm; $C_6D_6$, 7.15 ppm; toluene-$d_8$, 2.09 ppm; $CD_2Cl_2$, 5.32 ppm; DMSO-$d_6$, 2.49 ppm. For $^{13}C$ NMR: $CDCl_3$, 77.0 ppm; DMSO-$d_6$, 39.5 ppm. Coupling constants (*J*) are expressed in hertz (Hz). $^{31}P$ NMR spectra were recorded using a Varian 300 MHz spectrometer, with chemical shifts $\delta$ (in ppm) referenced to $H_3PO_4$. To determine the proton-decoupled chemical shift corresponding to the benzylidene $^{13}C$ nuclei in complexes **8** and **9**, the decoupling frequencies were set to the $^1H$ chemical shifts of their respective benzylidene signals. High-resolution mass spectra (HRMS) were obtained with a VG analytical ZAB2-E or a Karatos MS9 instrument (ESI or CI) and are reported as *m*/*z* (relative intensity). Gas chromatography (GC) was performed on an Agilent 6850 gas chromatograph. Elemental analyses were performed by Midwest Microlabs, LLC (Indianapolis, IN).

***N*,*N*′-Dimesityl-*N*,*N*′-dimethylformamidinium Iodide (7·HI).** Under an atmosphere of air, a 30 mL pressure vessel equipped with a stir bar was charged with *N*,*N*′-dimesitylformamidine (2.79 g, 9.96 mmol), $NaHCO_3$ (4.20 g, 49.8 mmol), and $CH_3CN$ (20 mL). Methyl iodide (4.24 g, 29.9 mmol) was added to the resulting suspension, and the vessel was sealed with a Teflon-lined cap. The reaction mixture was stirred for 12 h at 85 °C. After the mixture was allowed to cool to ambient temperature, it was filtered. The filtrate was concentrated to dryness and then triturated with diethyl ether. The resulting solid was recovered via vacuum filtration and dried under high vacuum to afford the desired product as a pale yellow powder (3.82 g, 88% yield). Crystals of **7**·**HI** were grown as colorless prisms by slow evaporation from ethyl acetate. Mp: 220−222 °C. $^1H$ NMR (300 MHz, DMSO-$d_6$): $\delta$ 8.46 (s, 1H), 7.12 (s, 2H), 7.04 (s, 2H), 3.52 (s, 3H), 2.61 (s, 3H), 2.36 (s, 6H), 2.26 (s, 9H), 2.24 (s, 3H). $^{13}C$ NMR (100 MHz, DMSO-$d_6$): $\delta$ 156.0, 140.7, 139.7, 138.8, 134.3, 134.0, 133.8, 129.4, 129.3, 45.8, 37.4, 20.5, 20.4, 17.4, 17.0. HRMS: calcd for $C_{21}H_{29}N_2$ ($[M^+]$) 309.2329; found 309.2325. Anal. Calcd (%) for $C_{21}H_{29}N_2I$: C, 57.80; H, 6.70; N, 6.42. Found: C, 57.77; H, 6.73; N, 6.47.

**(*N*,*N*′-Bis(2,6-di-isopropylphenyl)-*N*,*N*′-dimethylformamidin-2-ylidene)(SIMes)$Cl_2Ru{=}CHPh$ (8a).** A 6 mL glass vial equipped with a stir bar was charged with **6**·**HI** (213 mg, 0.409 mmol) and $NaN(SiMe_3)_2$ (85 mg, 0.464 mmol). Toluene (5 mL) was added to the mixture, and the vial was sealed with a Teflon-lined cap. The solution was stirred for 30 min at ambient temperature and then filtered through a 0.2 $\mu$m PTFE filter into a second clean vial equipped with a stir bar. $(SIMes)(pyridine)_2Cl_2Ru{=}CHPh$ (85 mg, 0.117 mmol) was then added, and the vial was sealed with a Teflon-lined cap. The reaction was allowed to stir for 1.5 h at 60 °C. The solvent was then removed under reduced pressure. Hexanes (2 mL) was added to the resulting green solid, which resulted in the formation of a yellow-brown precipitate that was later removed by filtration. The green filtrate was then loaded onto a short column of silica gel. The silica gel was washed with hexanes (20 mL) followed by ethyl acetate (10 mL), and the green band which eluted was collected. The green solution was concentrated under reduced pressure and dried under high vacuum to afford the desired

(34) We also monitored the ring-opening metathesis polymerization of 1,5-cyclooctadiene (COD) over time using **4a** and **9a** as catalysts by quantitative $^1H$ and $^{13}C$ NMR spectroscopy (conditions: $C_6D_6$ as solvent, 75 °C (sealed tube), $[COD]_0$ = 0.50 M, $[catalyst]_0$ = 0.016 M).[31] At low monomer conversions (< 35%), both catalysts afforded predominantly cis polybutadiene (*E*:*Z* = 1.0:4.8 for **9a** at 32% monomer conversion and 1.0:3.2 for **4a** at 34% were observed). At conversions approaching 50%, **9a** afforded polymer with a higher cis content (*E*:*Z* = 1.0:4.0 at 49% monomer conversion) than **4a** (*E*:*Z* = 1.0:2.8 at 48%).

(35) Taylor, E. C.; Ehrhart, W. A. *J. Org. Chem.* **1963**, *28*, 1108.

product as a green solid (73.6 mg, 66% yield). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 18.59 (s, 1H), 8.97 (d, 1H, $J$ = 7.8), 7.27−7.22 (m overlapping with solvent, 1H, $J$ = 15.3), 7.09−7.03 (m, 3H), 6.94 (s, 1H), 6.87−6.74 (m, 3H), 6.66−6.61 (m, 2H), 6.36 (t, 1H, $J$ = 7.5), 5.99 (t, 2H, $J$ = 6.0), 5.52 (s, 1H), 4.02−3.92 (m, 2H), 3.79−3.74 (m, 2H), 3.61 (s, 3H), 3.57−3.50 (m, 3H), 2.88−2.83 (m, 1H), 2.62 (s, 3H), 2.56 (s, 3H), 2.45 (s, 3H), 2.35 (s, 3H), 2.19 (s, 3H), 1.88 (s, 3H), 1.84 (s, 3H), 1.40 (d, 3H, $J$ = 6.6), 1.25 (d, 6H, $J$ = 6.6), 1.18 (d, 3H, $J$ = 6.9), 1.13 (d, 3H, $J$ = 6.3), 1.05 (d, 3H, $J$ = 6.9), 0.81 (d, 3H, $J$ = 6.6), 0.62 (d, 3H, $J$ = 6.6). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 296.1, 222.9, 216.6, 149.8, 148.8, 146.5, 146.0, 145.8, 143.8, 143.2, 139.5, 138.3, 137.9, 137.71, 137.66, 137.3, 136.8, 136.1, 132.6, 130.9, 129.4, 128.94, 128.90, 128.5,128.3, 128.2, 126.8, 126.3, 125.6, 123.5, 123.42, 123.39, 40.7, 27.8, 27.7, 27.6, 27.4, 27.2, 26.5, 26.0, 25.6, 25.2, 24.1, 22.5, 22.4, 22.3, 20.95, 20.94, 19.8, 19.1, 18.6, 18.4. HRMS: calcd for $C_{55}H_{72}Cl_2N_4Ru$ ([$M^+$]) 960.4178; found 960.4163. Anal. Calcd (%) for $C_{55}H_{72}Cl_2N_4Ru$: C, 68.73; H, 7.55; N, 5.83. Found: C, 68.63; H, 7.41; N, 5.94.

**(*N,N′*-Dimesityl-*N,N′*-dimethylformamidin-2-ylidene)(SIMes)-$Cl_2$Ru=CHPh (8b).** A 6 mL glass vial equipped with a stir bar was charged with **7·HI** (158 mg, 0.363 mmol), $NaN(SiMe_3)_2$ (66.0 mg, 0.363 mmol), and toluene (4 mL) and then sealed with a Teflon-lined cap. The reaction mixture was stirred for 30 min at ambient temperature. A cloudy mixture formed, which was subsequently filtered through a 0.2 $\mu$m PTFE filter into a clean glass vial equipped with a stir bar (in a drybox). (SIMes)-$(pyridine)_2Cl_2$Ru=CHPh (251 mg, 0.346 mmol) was added, and the vial was sealed with a Teflon-lined cap. The solution was stirred at ambient temperature for 12 h and then concentrated under reduced pressure to afford a green solid. The solid was triturated with pentane and filtered. The recovered solid was then dissolved in ethyl acetate and filtered through a short column of silica gel. Removal of residual solvent under high vacuum afforded the desired product as a light green solid (104.9 mg, 35% yield). Crystals of **8b**·$C_5H_{12}$ were grown as green plates by slow evaporation from pentane. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 19.16 (s, 1H), 9.50 (br s, 2H), 7.31 (t, 1H, $J$ = 7.3), 7.07 (br s, 2H), 6.90 (s, 2H), 6.85 (s, 1H), 6.43 (s, 1H), 6.30 (s, 1H), 6.18 (s, 1H), 6.07 (s, 1H), 5.87 (s, 1H), 4.06−3.89 (m, 3H), 3.78−3.73 (m, 1H), 3.11 (s, 3H), 2.77 (s, 3H), 2.62 (s, 3H), 2.53 (s, 3H), 2.22 (s, 3H), 2.19 (s, 3H), 2.07 (s, 3H), 2.02 (s, 3H), 1.99 (s, 3H), 1.97 (s, 3H), 1.94 (s, 3H), 1.86 (s, 3H), 1.62 (s, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ 295.8, 227.4, 222.7, 152.0, 144.0, 142.1, 139.2, 139.0, 138.3, 138.0, 137.6, 137.5, 136.8, 136.6, 135.6, 135.1, 135.0, 134.4, 133.9, 133.8, 129.4, 129.3, 129.1, 128.9, 128.2, 128.0, 127.9, 127.8, 127.4, 51.8, 51.6, 47.4, 40.6, 21.1, 21.0, 20.6, 20.4, 19.8, 19.66, 19.63, 19.5, 18.8, 18.65, 18.57, 18.3. HRMS: calcd for $C_{49}H_{60}Cl_2N_4Ru$ ([$M^+$]) 876.3239; found 876.3237. Anal. Calcd (%) for $C_{49}H_{60}Cl_2N_4Ru$: C, 67.11; H, 6.90; N, 6.39. Found: C, 66.82; H, 6.83; N, 6.40.

**(*N,N′*-Bis(2,6-di-isopropylphenyl)-*N,N′*-dimethylformamidin-2-ylidene)$Cl_2$Ru=CH(2-isopropoxy)Ph (9a).** A 6 mL glass vial equipped with a stir bar was charged with **6·HI** (185 mg, 0.355 mmol), $NaN(SiMe_3)_2$ (65.0 mg, 0.355 mmol), and benzene (4 mL) and then sealed with a Teflon-lined cap. The mixture was stirred for 30 min at ambient temperature, after which it was filtered through a 0.2 $\mu$m PTFE filter into a second clean glass vial containing a stir bar. $(PCy_3)Cl_2$Ru=CH(2-isopropoxy)Ph (100 mg, 0.166 mmol) was added, and the vial was sealed with a Teflon-lined cap. The resulting purple-red solution was then stirred for 5 h at ambient temperature, after which the color had changed to green-brown. The solution was then concentrated under reduced pressure to afford a dark green solid. The solid was dissolved in a minimal amount of dichloromethane (ca. 2 mL) and then filtered through a short column of silica gel with the aid of additional dichloromethane (ca. 4 mL). The filtrate was then evaporated to a volume of approximately 1 mL, and pentane (5 mL) was added, which caused a green precipitate to form. The green precipitate was collected and dried under vacuum to afford the desired product as a dark green microcrystalline solid (34 mg, 28% yield). Crystals of **9a** were grown as green prisms by vapor diffusion of pentane into a $C_6H_6$ solution of the complex. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 15.94 (s, 1H), 7.58−7.48 (m, 2H), 7.37−7.33 (m, 3H), 7.20 (d, 2H, $J$ = 7.5), 6.95 (d, 1H, $J$ = 7.2), 6.85 (t, 2H, $J$ = 7.5), 5.05−5.01 (m, 1H), 4.97 (s, 3H), 3.98−3.90 (m, 2H), 3.30−3.21 (m, 2H), 2.88 (s, 3H), 1.69 (d, 6H, $J$ = 6.0), 1.36−1.34 (2 overlapping d, 12H), 1.06 (d, 6H, $J$ = 6.9), 0.94 (d, 6H, $J$ = 6.6). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ 299.3, 202.1, 152.0, 148.4, 146.6, 146.1, 145.3, 144.9, 129.5, 129.0, 128.7, 124.9, 124.2, 122.9, 122.4, 133.0, 74.5, 46.9, 46.8, 28.0, 27.7, 26.2, 26.1, 23.6, 23.0, 22.4. HRMS: calcd for $C_{37}H_{52}Cl_2N_2ORu$ ([$M^+$]) 712.2500, found 712.2500. Anal. Calcd (%) for $C_{37}H_{52}Cl_2N_2ORu$: C, 62.35; H, 7.35; N, 3.93. Found: C, 62.41; H, 7.29; N, 4.03.

**(*N,N′*-Dimesityl-*N,N′*-dimethylformamidin-2-ylidene)$Cl_2$Ru=CH(2-isopropoxy)Ph (9b).** A 6 mL glass vial equipped with a stir bar was charged with **7·HI** (191 mg, 0.438 mmol), $NaN(SiMe_3)_2$ (80.0 mg, 0.438 mmol), and benzene (4 mL) and then sealed with a Teflon-lined cap. The solution was stirred for 30 min at ambient temperature, after which it was filtered through a 0.2 $\mu$m PTFE filter into a second clean glass vial containing a stir bar. $(PCy_3)Cl_2$Ru=CH(2-isopropoxy)Ph (105 mg, 0.175 mmol) was added, and the vial was sealed with a Teflon-lined cap. The reaction mixture was stirred at 50 °C for 3 h. The solution was then concentrated under reduced pressure to afford a dark green solid. The resulting solid was purified by column chromatography on silica gel using hexanes/ethyl acetate (5:1 v/v) as the eluent. A dark green band eluted first, which was determined to be an intermediate where $PCy_3$ had displaced the coordinating isopropoxy moiety.[36] This solution was concentrated, dissolved in 5 mL of $CHCl_3$, and then stirred at ambient temperature for 10 h to induce phosphine dissociation. A second band was eluted from the aforementioned column, which contained the desired product. After the first band had finished stirring, it was combined with the second band and the resulting solution was concentrated under reduced pressure. Diethyl ether (5 mL) was then added, which caused a light green solid to precipitate upon standing. After decanting the mother liquor, the residual solids were collected by vacuum filtration and washed with hexanes (5 mL). The solids were then dried under high vacuum to afford the desired product as a light green powder (59 mg, 54% yield). Crystals of **9b**·1.5($C_6H_6$) were grown as green needles by vapor diffusion of pentane into a $CH_2Cl_2$ solution of the complex. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 15.92 (s, 1H), 7.52 (t, 1H, $J$ = 8.7), 7.04 (s, 2H), 7.00−6.97 (m, 1H), 6.93 (s, 2H), 6.89−6.86 (m, 2H), 5.06 (h, 1H, $J$ = 6.0), 4.80 (s, 3H), 2.82 (s, 3H), 2.54 (s, 6H), 2.46 (s, 3H), 2.30 (s, 3H), 2.26 (s, 6H), 1.67 (d, 6H, $J$ = 6.00). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ 302.8, 201.2, 151.7, 148.4, 145.4, 144.9, 138.0, 137.5, 136.7, 135.6, 129.9, 129.8, 129.0, 123.3, 122.6, 113.0, 74.4, 44.6, 42.7, 22.2, 21.1, 21.0, 18.7, 18.3. HRMS: calcd for $C_{31}H_{40}Cl_2N_2ORu$ ([$M^+$]) 628.1561, found 628.1559. Anal. Calcd for $C_{31}H_{40}Cl_2N_2ORu$: C, 59.23; H, 6.41; N, 4.46. Found: C, 58.91; H, 6.29; N, 4.60.

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**Supporting Information Available:** $^1$H and $^{13}$C NMR spectra, crystallographic data, and kinetics details are available free of charge via the Internet at http://pubs.acs.org.

(36) An analogous intermediate has been reported in the synthesis of related NHC-containing Hoveyda−Grubbs-type catalysts; see ref 13b.