Latent Ruthenium Olefin Metathesis Catalysts That Contain an N-Heterocyclic Carbene Ligand

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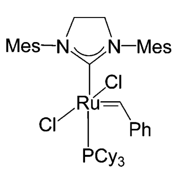
*Summary: A new N-heterocyclic carbene containing olefin metathesis catalyst, (sIMes)$(Cl)_2$Ru$(CH(CH_2)_2$-C,N-2-$C_5H_4N)$ (**4a**), was synthesized from (sIMes)$(PCy_3)(Cl)_2$Ru=CHPh (**1**) or (sIMes)$(py)_2(Cl)_2$Ru=CHPh (**3**). When heated at 40 °C in dichloromethane, **4a** is slowly converted to its isomer **4b**. The X-ray structures of **4a** and **4b** show that the NHC and pyridine ligands are trans in **4a** and cis in **4b**. **4a** is more latent than **1** and **4b** much more latent than **4a** in ring-closing metathesis (RCM) and ring-opening metathesis polymerization (ROMP).*

In recent years, olefin metathesis catalysis has received tremendous attention as a powerful technology for the formation of carbon−carbon bonds and has found numerous applications in organic synthesis and polymer chemistry.[1] The success of olefin metathesis stems from the development of several well-defined transition-metal complexes, such as the Schrock molybdenum catalysts and the Grubbs ruthenium catalysts.[2] Following the discovery of the original Grubbs catalysts $(PR_3)_2(Cl)_2$Ru=CHR′ (where R is an aryl or alkyl group and R′ is an aryl or alkenyl group),[3] much of the research in this area has focused on increasing the stability, selectivity, and particularly the activity of ruthenium olefin metathesis catalysts. These efforts have led to the discovery of highly active and fast-initiating complexes that contain saturated N-heterocyclic carbene (NHC) ligands, such as **1**,[4] **2**,[5] and **3**.[6]



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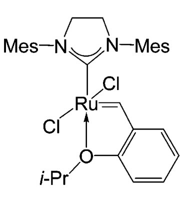

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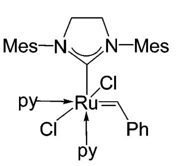

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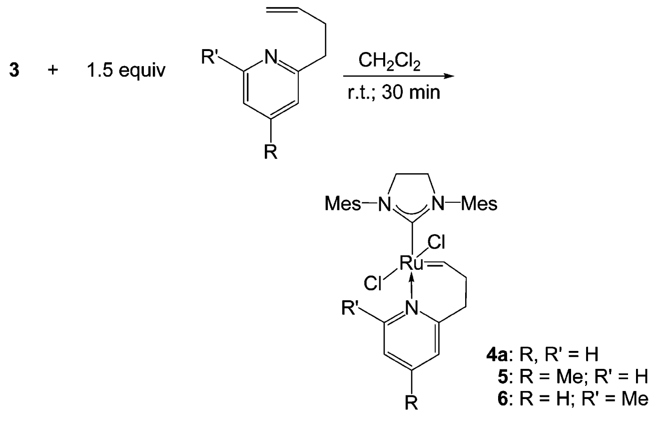
On the other hand, much less work has been aimed at decreasing the initiation rate of the original Grubbs catalysts. van der Schaaf and co-workers prepared the slow olefin metathesis initiator $(PR_3)(Cl)_2$Ru$(CH(CH_2)_2$-*C*,*N*-2-$C_5H_4N)$ by reacting a $(PR_3)_2(Cl)_2$Ru=CHR′ complex with 2-(3-butenyl)pyridine.[7] Catalysts with slower initiation can be particularly beneficial when performing ring-opening olefin metathesis polymerizations (ROMP), because they allow for longer handling of the monomer/catalyst resin before the polymerization starts. Our goal was to prepare an olefin metathesis catalyst that would initiate slowly while maintaining the high activity associated with NHC-based catalysts. Herein we describe the synthesis of a ruthenium complex that contains both a saturated NHC ligand and the 2-pyridylethanyl carbene ligand.

Catalyst (sIMes)$(PCy_3)(Cl)_2$Ru=CHPh (**1**) was reacted with 1.5 equiv of 2-(3-butenyl)pyridine in dichloromethane at 40 °C for 5 h to afford (sIMes)$(Cl)_2$Ru$(CH(CH_2)_2$-*C*,*N*-2-$C_5H_4N)$ (**4a**) in 80% yield. **4a** can also be easily prepared by reaction of (sIMes)$(py)_2(Cl)_2$Ru=CHPh (**3**) with 1.5 equiv of 2-(3-butenyl)pyridine in dichloromethane at room temperature for 30 min. In addition, this method is amenable to the synthesis of complexes (sIMes)$(Cl)_2$Ru$(CH(CH_2)_2$-*C*,*N*-2-(4-Me)-$C_5H_3N)$ (**5**) and Ru$(CH(CH_2)_2$-*C*,*N*-2-(6-Me)-$C_5H_3N)$ (**6**) (Scheme 1).

Scheme 1



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10.1021/om0493210 CCC: $27.50

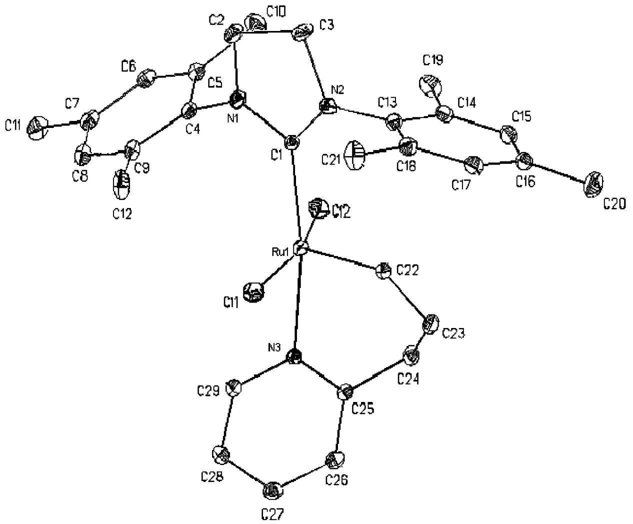
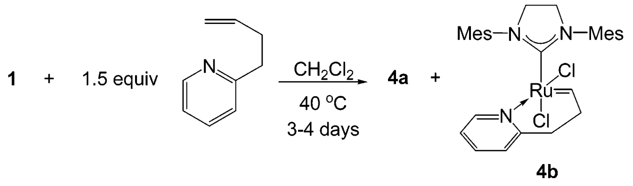


Figure 1. Structure of **4a** represented by thermal ellipsoids drawn at the 50% probability level. Selected bond distances (Å) and angles (deg): Ru(1)–C(1) = 2.0459(10), Ru(1)–C(22) = 1.8185(11), Ru(1)–N(3) = 2.1355(9), Ru(1)–Cl(1) = 2.3973(3), Ru(1)–Cl(2) = 2.3662(3); Cl(1)–Ru(1)–Cl(2) = 164.406(11), C(1)–Ru(1)–N(3) = 170.21(4), C(22)–Ru(1)–N(3) = 88.32(4).

The ^{1}H NMR spectra for **4a**, **5**, and **6** are consistent with complexes of C_s symmetry, where the resonances for each of the *p*-methyl groups of the mesityl rings, the *o*-methyl groups of the same rings, and the ethylene bridge of the sIMes ligand appear as singlets.[8] The alkylidene proton resonances near 18 ppm appear as triplets, due to coupling to the methylene protons ($^3J_{HH}$ = 2.7–3.6 Hz).

Monitoring the reaction of **1** and 2-(3-butenyl)pyridine by ^{1}H NMR spectroscopy showed that the production of **4a** is followed by the slow formation of a different complex, **4b**. When the mixture is stirred for 4 days at 40 °C, the reaction yields a ~3:7 mixture of **4a** and **4b** (Scheme 2).

Scheme 2



4b appears as a ruthenium carbene of C_1 symmetry, displaying six inequivalent methyl groups on the mesityl rings, four inequivalent protons on the ethylene bridge of the sIMes ligand, and four inequivalent protons on the ethylene bridge of the pyridyl ligand in the ^{1}H NMR spectrum. The carbene resonance of **4b** also appears as a triplet (δ 19.14 ppm; $^3J_{HH}$ = 3.3 Hz). Pure isolated **4a**, dissolved in CD_2Cl_2 (0.1 M), is slowly converted to a 22:78 mixture of **4a** and **4b** at 40 °C over the course of 96 h, and pure isolated **4b** forms a similar mixture under the same conditions. Therefore, we conclude that **4a** and **4b** are isomers in equilibrium, where **4b** is the thermodynamically favored species and K_{eq} = 0.28.[9]

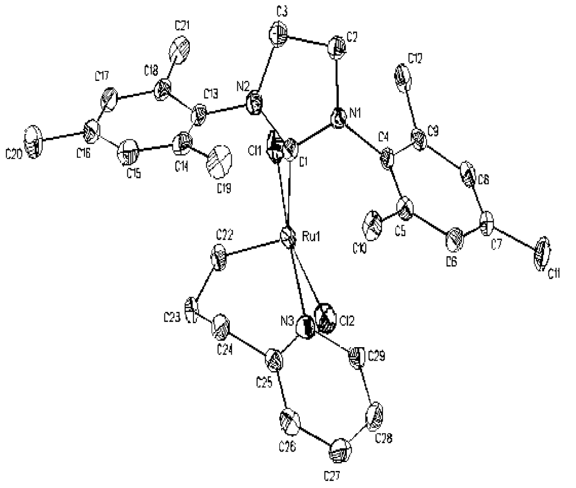


Figure 2. Structure of **4b** represented by thermal ellipsoids drawn at the 50% probability level. Selected bond distances (Å) and angles (deg): Ru(1)–C(1) = 2.024(2), Ru(1)–C(22) = 1.811(2), Ru(1)–N(3) = 2.0977(19), Ru(1)–Cl(1) = 2.4000(6), Ru(1)–Cl(2) = 2.3883(6); Cl(1)–Ru(1)–Cl(2) = 85.93(2), C(1)–Ru(1)–N(3) = 98.04(8), C(22)–Ru(1)–N(3) = 92.35(10), C(1)–Ru(1)–Cl(1) = 88.62(6), C(1)–Ru(1)–Cl(2) = 153.74(6).

Crystals suitable for X-ray analysis were obtained for **4a** and **4b**. Figures 1 and 2 give ORTEP views of **4a** and **4b**, respectively. Both complexes display square-pyramidal geometries, where the chloride, pyridine, and NHC ligands occupy the equatorial positions and the alkylidene occupies the axial position. In **4a**, the chloride ligands are trans to one another (Cl(1)–Ru(1)–Cl(2) = 164.41(1)°), as are the neutral ligands (C(1)–Ru(1)–N(3) = 170.21(4)°). This geometry is typical for ruthenium olefin metathesis catalysts and is consistent with the ^{1}H NMR spectrum of **4a**. On the other hand, **4b** possesses cis chloride ligands (Cl(1)–Ru(1)–Cl(2) = 85.93(2)°) and cis neutral ligands (C(1)–Ru(1)–N(3) = 98.04(8)°), which explain the C_1 symmetry deduced from the spectroscopic data. This type of ligand arrangement is relatively rare for ruthenium carbene complexes, although it has been observed in a few cases.[10–13] The Ru(1)–N(3) distance of 2.1355(9) Å in **4a** is significantly longer than that of 2.098(2) Å in **4b**, due to the trans influence of the NHC ligand. Similarly, the Ru(1)–Cl(2) distance in **4b** (2.3883(6) Å) is longer than that in **4a** (2.3662(3) Å).

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(8) The ^{1}H NMR singlets described are consistent with a C_s symmetry *and* free rotation of the sIMes ligand around the Ru–C bond (on the NMR time scale).

(9) Attempts to measure the kinetics of the approach to equilibrium were hampered by a decomposition process concurrent with the **4a** ↔ **4b** isomerization process.

(10) Ruthenium complexes containing chelating bis-phosphine ligands and cis chlorides have been described: (a) Hansen, S. M.; Volland, M. A. O.; Rominger, F.; Eisenträger, F.; Hofman, P. *Angew. Chem., Int. Ed.* **1999**, *38*, 1273–1276. (b) Hansen, S. M.; Rominger, F.; Metz, M.; Hofman, P. *Chem. Eur. J.* **1999**, *5*, 557–566. (c) Volland, M. A. O.; Straub, B. F.; Gruber, I.; Rominger, F.; Hofman, P. *J. Organomet. Chem.* **2001**, *617*, 288–291. (d) Nieczypor, P.; van Leeuwen, P. W. N. M.; Mol, J. C.; Lutz, M.; Spek, A. L. *J. Organomet. Chem.* **2001**, *625*, 58–66.

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(12) A related complex with cis neutral ligands and cis anionic pentafluorophenoxide ligands has been reported: Conrad, J. C.; Amoroso, D.; Czechura, P.; Yap, G. P. A.; Fogg, D. E. *Organometallics* **2003**, *22*, 3634–3636.

(13) A related vinylcarbene ruthenium complex containing cis chlorides has also been reported: Trnka, T. M.; Day, M. W.; Grubbs, R. H. *Organometallics* **2001**, *20*, 3845–3847.

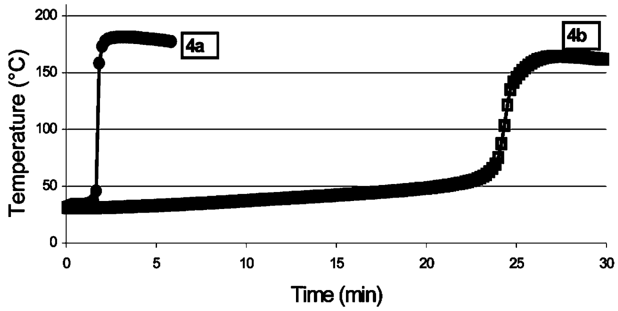

Figure 3. Exotherm graph of DCPD ROMP started at 30 °C using **4a** and **4b** (30 000:1).

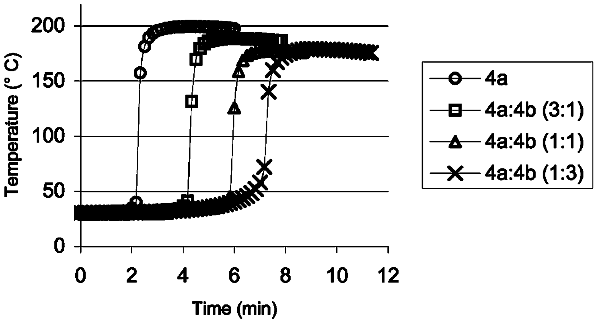

Figure 4. Exotherm graph of DCPD ROMP started at 30 °C using **4a/4b** mixtures (40 000:1).

The reactivity of **4a**, **4b**, **5**, and **6** was tested in the ring-closing metathesis (RCM) of diethyl diallylmalonate and the ROMP of dicyclopentadiene (DCPD). In RCM, **4a** is much slower than **1** (<20% conversion after 100 min versus ~100% conversion, respectively, under the conditions used) and **4b** is much slower than **4a** (<2% conversion after 100 min under the conditions used) (see the Supporting Information). In the same way, **4b** initiates the ROMP of DCPD more slowly than **4a**. Indeed, a ROMP of DCPD using **4a** reaches its exotherm within 3 min, while the same polymerization catalyzed by **4b** requires more than 25 min (Figure 3). We attribute the difference in reactivity between **4a** and **4b** to the fact that the pyridine ligand in **4a** is trans to the strongly σ-donating NHC ligand and therefore dissociates to give the active 14-electron species much more quickly than in **4b**. We believe that the difference in activity between **4a** and **4b** is purely due to a disparity in initiation rates and does not give any clues regarding the conformation of the metallacyclobutane metathesis intermediates. In other words, the fact that **4a** is a faster catalyst than **4b** does not imply that the olefin approaching the 14-electron species must necessarily bind trans to the NHC ligand.[14] Substitution on the pyridine ring has a much less dramatic effect on catalytic activity. **4a** and **5** show similar reactivity in RCM, but **6** proved to initiate faster than **4a** and **5**, presumably due to steric crowding of the *o*-methyl group on the pyridine ligand (see the Supporting Information). In the ROMP of DCPD, a reaction less sensitive to small reactivity differences, the three complexes **4a**, **5**, and **6** were found to have similar catalytic properties.

Finally, one can envision using the slow isomerization process and large activity difference between **4a** and **4b** to tune this catalytic system by partially isomerizing **4a** to a **4a/4b** mixture with the desired initiation rate. Indeed, the use of varying **4a/4b** mixtures for the ROMP of DCPD allowed for the control of the times to exotherm, as shown in Figure 4.

In conclusion, the reaction of **1** with 2-(3-butenyl)-pyridine has yielded two different isomers: **4a** of C_s symmetry and **4b** of C_1 symmetry. While **4a** and **4b** are both slow initiators relative to complexes **1**–**3**, **4b** is much slower than **4a**.

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Supporting Information Available: Detailed synthetic procedures and crystallographic data are available as text, tables, and figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) See ref 13 for a discussion on the conformation of olefin metathesis intermediates.