A New Ruthenium-Based Olefin Metathesis Catalyst Coordinated with 1,3-Dimesityl-1,4,5,6-tetrahydropyrimidin-2-ylidene: Synthesis, X-ray Structure, and Reactivity

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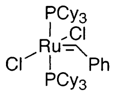
*Summary: The new ruthenium olefin metathesis catalyst **4** bearing a 5,5′-dimethyl-1,3-dimesityl-1,4,5,6-tetrahydropyrimidin-2-ylidene ligand was first synthesized from (PCy$_3$)$_2$(Cl)$_2$Ru═CHPh (**1**). The X-ray crystal structure of complex **4** has been determined and shows that the N-mesityl group of the six-membered carbene ligand and the benzylidene moiety are in close proximity (2.9 Å). This catalyst demonstrates moderate reactivity for both ring-closing olefin metathesis and ring-opening metathesis polymerization.*



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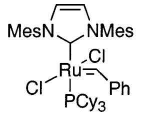

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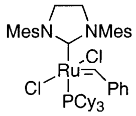

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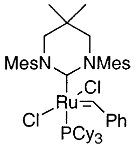

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Since the early 1990s, N-heterocyclic carbenes (NHCs) have become popular ligands in organometallic and inorganic coordination chemistry because of their striking similarity to electron-rich organophosphanes PR$_3$.[1] However, most of the N-heterocyclic metal carbene complexes reported in the literature have been composed of five-membered rings, which include imidazole, triazole, and their saturated analogues.[2] Other cyclic structures, although viable, have remained largely uninvestigated. Recently, a planar, unsaturated six-membered NHC was reported and comparisons to other analogues demonstrated the role of ring size in changing the donor and steric requirements of such ligands.[3]

Our group[4] and others[5] have reported the synthesis of well-defined ruthenium-based olefin metathesis catalysts **2** bearing imidazol-2-ylidene ligands and dihydroimidazol-2-ylidene ligands **3** by replacing one PCy$_3$ in (PCy$_3$)$_2$(Cl)$_2$Ru═CHPh (**1**). The resulting catalysts exhibit higher activity than the parent catalyst **1** toward olefin metathesis. To further investigate the role of subtle changes in the steric environment around the ruthenium-based metathesis catalysts, the six-membered N-heterocyclic carbene ligand was substituted onto catalyst **1**. Here we wish to report the successful synthesis of the new Ru complex **4**, possessing the bulky 5,5′-dimethyl-1,3-dimesityl-1,4,5,6-tetrahydropyrimidin-2-ylidene ligand, and a direct comparison of its structural features and activity relative to five-membered analogues.

The tetrahydropyrimidinium salt **9** was prepared by reacting dimethylmalonyl choride **5** with 2 equiv of mesitylamine **6** to give the bis(amide) **7**, followed by straightforward reduction to **8** and cyclization to **9**, as shown in Scheme 1. Attempts to generate the carbene using KOtBu as base were unsuccessful under a variety of conditions. However, using the base KHMDS in toluene at 100 °C generated the carbene, which was subsequently reacted in situ with (PCy$_3$)$_2$(Cl)$_2$Ru═CHPh at room temperature to produce Ru complex **4** in 30% isolated yield.[6] Complex **4** shows a characteristic singlet for the benzylidene proton at 20.0 ppm in the ^{1}H NMR spectrum as well as a peak at 22.5 ppm for the phosphine ligand in the ^{31}P NMR spectrum.[7]

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(1) Some recent reviews: (a) Herrmann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1290−1309. (b) Fürstner, A. *Angew. Chem., Int. Ed.* **2000**, *39*, 3012−3043. (c) Trnka, T. M.; Grubbs, R. H. *Acc. Chem. Res.* **2001**, *34*, 18−29.

(2) Lappert has described rhodium complexes containing the ligand 1,3-dimethyl-1,4,5,6-tetrahydropyrimidin-2-ylidene: (a) Hitchcock, P. B.; Lappert, M. F.; Pye, P. L. *J. Chem. Soc., Dalton Trans.* **1977**, 2160−2172. (b) Doyle, M. J.; Lappert, M. F.; Pye, P. L.; Terreros, P. *J. Chem. Soc., Dalton Trans.* **1984**, 2355−2364.

(3) Bazinet, P.; Yap, G. P. A.; Richeson, D. S. *J. Am. Chem. Soc.* **2003**, *125*, 13314−13315.

(4) (a) Scholl, M.; Trnka, T. M.; Morgan, J. P.; Grubbs, R. H. *Tetrahedron Lett.* **1999**, *40*, 2247−2250. (b) Scholl, M.; Ding, S.; Lee, C. W.; Grubbs, R. H. *Org. Lett.* **1999**, *1*, 953−956. (c) Morgan, J. P.; Grubbs, R. H. *Org. Lett.* **2000**, *2*, 3153−3155.

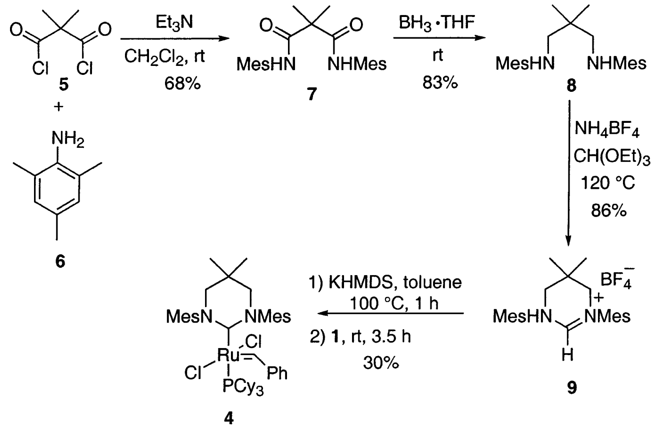
(5) (a) Huang, J.; Stevens, E. D.; Nolan, S. P.; Petersen, J. L. *J. Am. Chem. Soc.* **1999**, *121*, 2674−2678. (b) Weskamp, T.; Kohl, F. J.; Hieringer, W.; Gleich, D.; Herrmann, W. A. *Angew. Chem., Int. Ed.* **1999**, *38*, 2416−2419.

(6) Synthesis of catalyst **4**: in a glovebox, **9** (440 mg, 1.0 mmol) and KHMDS (315 mg, 1.5 mmol) were weighed into a Schlenk flask. After removal from the glovebox, 20 mL of toluene was added and the reaction mixture was stirred at 100 °C for 1 h. This mixture was then cooled to room temperature, and a solution of **1** (412 mg, 0.5 mmol) in toluene (5 mL) was added. The resulting mixture was stirred for 3.5 h at room temperature. The salts generated during the reaction were filtered off under Ar, and the filtrate was concentrated under vacuum to a brown oil. The crude product was purified by column chromatography on TSI silica gel with hexanes and ether (9:1) as eluant and isolated as a brown solid in 30% yield.[7] ^{1}H NMR (300 MHz, C$_6$D$_6$): δ 20.01 (s, 1H), 9.69 (br s, 1H), 7.18−6.97 (m, 6H), 6.60 (s, 1H), 5.85 (s, 1H), 3.01 (s, 3H), 2.83−2.62 (m, 2H), 2.79 (s, 3H), 2.77 (s, 3H), 2.62 (s, 3H), 2.35−2.18 (m, 3H), 2.35 (s, 3H), 2.24 (s, 3H), 1.78 (s, 3H), 1.74−1.04 (m, 32H), 0.69 (s, 3H) ppm. ^{31}P NMR (C$_6$D$_6$): δ 22.53 ppm.

(7) The ^{1}H NMR spectrum of the crude product consistently shows a 50−75% conversion to the desired 4. However, upon purification by column chromatography, significant decomposition occurs.

10.1021/om034369j CCC: $27.50

Scheme 1



Crystals for X-ray diffraction were obtained by slow diffusion of pentane into a concentrated CH_2Cl_2 solution of catalyst **4**.[8] A representation of the X-ray structure is shown in Figure 1, with selected bond lengths and bond angles reported in the caption.

Complex **4** has a distorted square-pyramidal geometry with the benzylidene group at the vertex and the L and X type ligands in trans-configured basal positions. The bond lengths and bond angles around the Ru are nearly identical with those in **3**. However, the steric interactions of the mesityl moieties in the larger 5,5′-dimethyl-1,3-dimesityl-1,4,5,6-tetrahydropyrimidin-2-ylidene ligand are more pronounced than in catalyst **3**. In a comparison of the proximity of the C atom of the benzylidene to the *ipso*-C atom of the mesityl nearest to it, the distance is shorter in complex **4** (2.9 Å) than in **3** (3.0 Å). The deviation from planarity around the *ipso*-C atom of the mesityl groups is particularly noteworthy. In complex **4**, the angle $\angle N_2-C_{23}-C_{26}$ is 169° for the mesityl group adjacent to the benzylidene and the other angle, $\angle N_1-C_{14}-C_{17}$, is 171°. The corresponding angles for catalyst **3** are more nearly coplanar (177 and 175°, respectively). This large deviation shows that the proximal mesityl group is significantly bent away from Cl and the alkylidene ligand in general. Consequently, the 5,5′-dimethyl-1,3-dimesityl-1,4,5,6-tetrahydropyrimidin-2-ylidene ligand in **4** exerts a significantly larger steric influence on the benzylidene than does the imidazolyl ligand in catalyst **3**. In addition, unlike the imidazolyl NHC's, which exhibit a flat backbone, the tetrahydropyrimidinyl NHC **4** adopts a half-chair conformation in which C_{10} is out of the plane.

We briefly screened the reactivity of catalyst **4** in an olefin metathesis reaction. The ring-closing metathesis (RCM) of diethyl diallylmalonate at 50 °C results in 72% conversion after 30 min and 83% after 1 h. In comparison, the reaction goes to completion with catalysts **3**[4b] and **2**[4a] after 10 and 30 min, respectively, which indicates that the increased steric interactions evident in **4** result in a slower RCM catalyst, as compared to its imidazolyl counterparts. We next checked the reactivity of **4** for the ring-opening metathesis polymerization (ROMP) of 1,5-cyclooctadiene (COD). The polymerization proceeds to a conversion of 85% after 10 min and 96% after 20 min at room temperature (a monomer to catalyst ratio of 300). Under similar conditions, catalyst **3** goes to completion in 10 min, while catalyst **2** proceeds to 35% after 10 min and to 60% after 20 min.[9] Overall, catalyst **4** exhibits similar but significantly lower reactivity in comparison to **3**. We assume that the lower reactivity of **4** is due to a larger steric environment around the metal atom, which may disfavor olefin binding or metallacyclobutane formation.

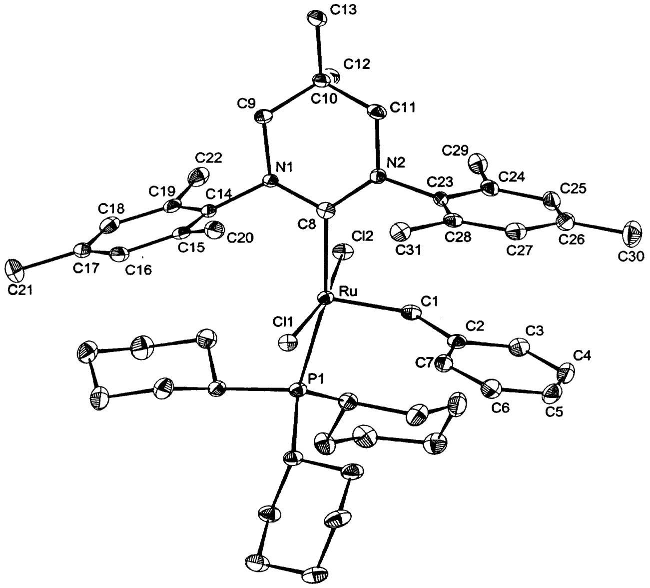


Figure 1. X-ray structure of **4** with 50% displacement ellipsoids. Selected bond distances (Å): Ru−C(1) = 1.835, Ru−Cl(1) = 2.390, Ru−Cl(2) = 2.415, Ru−P(1) = 2.447, Ru−C(8) = 2.106, C(1)−C(2) = 1.475. Selected angles (deg): C(8)−Ru−P(1) = 163.7, Cl(2)−Ru−Cl(1) = 169.1, C(8)−Ru−C(1) = 99.6, N(1)−C(9)−C(10) = 112.1, N(2)−C(11)−C(10) = 112.9, C(9)−C(10)−C(11) = 105.7, N(2)−C(8)−N(1) = 115.1, C(8)−N(2)−C(11) = 124.4, C(8)−N(1)−C(9) = 125.1.

The tetrahydropyrimidinyl NHC-coordinated Ru complex **4** has been synthesized. Although catalyst **4** is less reactive than **3** for the reactions studied, the increased steric interactions open new possibilities for catalyst selectivities.

Acknowledgment. We acknowledge financial support for this work from the National Institutes of Health and BP Amoco. We thank Dr. Michael W. Day for determining the X-ray crystal structure.

Supporting Information Available: Details of the synthesis and spectroscopic characterization of compounds **7**−**9** and of the X-ray structure determination of **4** and tables of atomic coordinates, bond distances and angles, anistropic thermal parameters, and calculated mean planes for **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[8] Crystal data for **4**: $C_{49}H_{71}Cl_2N_2PRu$; $M_r = 891.02$; crystal size 0.26 × 0.22 × 0.07 mm^3; space group $P2_1/n$, monoclinic, $a = 18.3317(7)$ Å, $b = 12.5852(5)$ Å, $c = 19.9966(7)$ Å, $\beta = 104.3240(10)$°; $V = 4470.0(3)$ Å^3, $T = 98(2)$ K, $Z = 4$, $d_{calcd} = 1.324$ Mg/m^3; Mo Kα radiation, $\lambda = 0.710\,73$ Å; 90 760 reflections collected, 10 676 independent reflections ($R_{int} = 0.0580$). Full-matrix least-squares refinement on $|F|^2$ yielded a final R1 value of 0.0305 and wR2 value of 0.0521. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K., and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number 186478.

[9] Bielawski, C. W.; Grubbs, R. H. *Angew. Chem., Int. Ed.* **2000**, *39*, 2903−2906.