

Syntheses and Activities of New Single-Component, Ruthenium-Based Olefin Metathesis Catalysts

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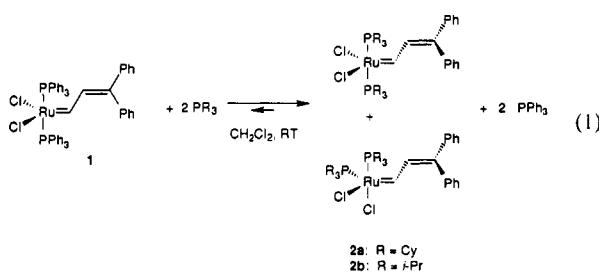
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We recently reported the synthesis of the first well-defined ruthenium-based olefin metathesis catalyst, $(\text{Ph}_3\text{P})_2\text{Cl}_2\text{Ru}=\text{CH}-\text{CH}=\text{CPh}_2$ (**1**), and its activity in the ROMP of norbornene.² Although **1** is also a good catalyst for the ring-opening metathesis polymerization (ROMP) of other highly strained cyclic olefins, such as bicyclo[3.2.0]hept-6-ene^{3a} and *trans*-cyclooctene,^{3b} it is not an efficient catalyst for the ROMP of low-strain cyclic olefins or the metathesis of acyclic olefins. In this paper, we report the synthesis of two new ruthenium carbene derivatives of **1**, $(\text{Cy}_3\text{P})_2\text{Cl}_2\text{Ru}=\text{CHCH}=\text{CPh}_2$ (**2a**) and $[(i\text{-Pr})_3\text{P}]_2\text{Cl}_2\text{Ru}=\text{CH}-\text{CH}=\text{CPh}_2$ (**2b**) which possess much broader metathesis activities.

Although making the metal center more electrophilic by replacing the Cl in **1** with a variety of electron-withdrawing anionic ligands as in examples in early-transition-metal metathesis chemistry^{4,5} does lead to changes in the relative propagation rate of the ruthenium carbene center in the polymerization of norbornene, the resulting anionic derivatives of **1** do not show activity for the metathesis of *cis*-cyclooctene or *cis*-2-pentene.⁶ However, substitution of the triphenylphosphine ligands with better σ -donating alkylphosphines proved to be more fruitful and led to new catalysts with high metathesis activity. The reaction of 2 equiv of either PCy_3 or $\text{P}(i\text{-Pr})_3$ with **1** in CH_2Cl_2 produces the corresponding metal carbene complexes **2a,b** in 90% and 87% yield, respectively (eq 1). Complexes **2a,b** exist in two isomeric



forms: one where the two phosphine ligands are *trans* to each other and one where they are *cis*; the *trans* isomer is the predominant one in the product mixture.^{7,8} In contrast to the case of **1** where the α -proton of the metal carbene moiety appears

as a pseudoquartet in the ^1H NMR spectrum, showing clear spin-coupling to the two equivalent phosphine ligands,² the α -proton of the vinylcarbene moiety of **2a**–*trans* appears only as a doublet at 19.09 ppm, showing no P–H coupling, even at 500 MHz.^{9,10} On the other hand, **2a**–*cis* exhibits a doublet of doublets at 18.89 ppm for H_{α} , showing spin-couplings to two inequivalent phosphines ($^3J_{\text{PH}} = 2.6$ and 7.2 Hz, $J_{\text{HH}} = 10.1$ Hz).^{9,10} Similar ^1H NMR coupling pattern can be observed for the vinylcarbene moiety of **2b**–*cis,trans*.¹⁰ X-ray diffraction data from a single crystal of **2a**–*trans* confirmed the structural assignment. Unfortunately, the vinylcarbene moiety is disordered about a twofold axis, preventing an accurate determination of bond lengths and bond angles for this fragment.¹¹

Complexes **2a,b** are moderately stable to air.¹² As for **1**, **2a** is stable in organic solvents in the presence of water, alcohol, acetic acid, or a diethyl ether solution of HCl. These observations indicate that the modification of **1** with alkylphosphines does not increase the susceptibility of the ruthenaolefins center to attack by electrophilic species.¹³ Complex **2a** polymerizes norbornene at room temperature to yield polynorbornene. Because the rate of propagation is much faster than the rate of initiation, very little of the catalyst reacts and the resulting polymer possesses both high molecular weight and broad molecular weight distribution.¹⁴ In contrast to **1**, **2a** catalyzes the ROMP of *cis*-cyclooctene, cyclooctadiene, 7-oxanorbornene derivatives, and cyclopentene.¹⁵ In each of these cases, a propagating species can be observed via ^1H NMR spectroscopy.¹⁵ This propagating species is stable throughout the polymerization reaction. Complexes **2a,b** also catalyze the metathesis of unstrained acyclic olefins such as *cis*-2-pentene. The reaction proceeds at room temperature, and both propagating species (ruthenium ethylidene and ruthenium propylidene) can be observed by ^1H NMR spectroscopy.¹⁵ The data from Table I indicate that CH_2Cl_2 is the best solvent for metathesis by **2a** (entries 1–3). Although the turnover number¹⁶

(7) For example, in the final isolated product mixture used in the experiments reported in this paper, **2a** consists of ca. 16% *cis* and **2b** consists of ca. 20% *cis*. See also supplementary material.

(8) The assignment of *cis*–*trans* isomers is clearest in the ^1H NMR spectrum of **2b**, where for the *trans* isomer, the CH_3 groups of the phosphines appear as a pseudoquartet, and for the *cis* isomer, the CH_3 groups appear as a doublet of doublets, characteristics of *trans*- and *cis*-phosphines, respectively.

(9) (a) The apparent lack of coupling between the phosphines and the α -proton of the vinylcarbene group in **2a,b**–*trans* and the two different $^3J_{\text{PH}}$ values for the corresponding *cis* isomers are surprising. However, depending on the geometry between the phosphine and H_{α} , this coupling can be either large or small (see: Klein, D. P.; Bergman, R. G. *J. Am. Chem. Soc.* 1989, 111, 3079–3080). (b) We note also that the carbene moiety in **2a**–*trans* is orthogonal to the $\text{P}_1\text{–Ru–P}_2$ axis,¹¹ while that in **1** is parallel to the $\text{P}_1\text{–Ru–P}_2$ axis;² this implies that a version of the Karplus relationship may be applicable here.

(10) Selected ^1H NMR spectroscopic data. (a) For **2a**–*trans*: (CD_2Cl_2) δ 19.09 (d, 1 H, $\text{Ru}=\text{CH}$, $J_{\text{PH}} = 11.1$ Hz, $J_{\text{HH}} = 0$ Hz), 8.70 (d, 1 H, $\text{CH}=\text{CPh}_2$, $J_{\text{HH}} = 11.1$ Hz). (b) For **2a**–*cis*: (CD_2Cl_2) δ 18.19 (ddd, 1 H, $\text{Ru}=\text{CH}$, $J_{\text{HH}} = 10.1$ Hz, $J_{\text{PH}} = 2.6$ and 7.2 Hz), 8.28 (d, 1 H, $\text{CH}=\text{CPh}_2$, $J_{\text{HH}} = 10.1$ Hz). (c) **2b**–*trans*: (CD_2Cl_2) δ 19.24 (d, 1 H, $\text{Ru}=\text{CH}$, $J_{\text{HH}} = 11.2$ Hz, $J_{\text{PH}} = 0$ Hz), 8.83 (d, 1 H, $\text{CH}=\text{CPh}_2$, $J_{\text{HH}} = 11.2$ Hz). (d) **2b**–*cis*: (CD_2Cl_2) δ 18.87 (dd, 1 H, $\text{Ru}=\text{CH}$, $J_{\text{HH}} = 10.5$ Hz, $J_{\text{PH}} = 0$ and 8.8 Hz), 8.34 (d, 1 H, $\text{CH}=\text{CPh}_2$, $J_{\text{HH}} = 10.5$ Hz).

(11) X-ray diffraction data for **2a** are reported in the supplementary material.

(12) (a) After a microcrystalline sample of **2a** was exposed to air for 1 week, the vinylcarbene could still be detected via ^1H NMR upon solvation. (b) It has been shown that **2a** can be dissolved in air using commercial, reagent-grade solvent on the benchtop and still retains metathesis activity for at least 1 h.²¹ If a solution of **2a** is exposed to air, very slow oxidation of the catalyst can be observed visually as a green layer diffusing from the surface downward into the orange-red solution over a period of hours.

(13) The modification of **1** with alkylphosphines also makes the resulting catalysts more soluble in organic solvents. For example, **1** is only sparingly soluble in benzene and THF, but **2a** is quite soluble in these solvents. Also, **1** is not soluble in alcohols but **2a** is slightly soluble in alcohols.

(14) At room temperature, 2 mg of **2a** polymerizes 142 equiv of norbornene in 0.5 mL of a 1:4 $\text{CD}_2\text{Cl}_2/\text{C}_6\text{D}_6$ solvent mixture in less than 1 min. The polymer was about 86% *trans* by ^1H NMR spectroscopy. M_w (GPC vs polystyrene) = 215 K, PDI = 2.65.

(15) Experimental details for the polymerizations as well as the spectroscopic characteristics of the propagating species may be found in the supplementary material.

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(1) DOD, Office of Army Research NDSEG Predoctoral Fellow.
(2) Nguyen, S. T.; Johnson, L. K.; Grubbs, R. H. *J. Am. Chem. Soc.* 1992, 114, 3974–3975.

(3) (a) Wu, Z.; Benedicto, A. D.; Grubbs, R. H. *Macromolecules* 1993, 26, 4975–4977. (b) Wu, Z.; Grubbs, R. H., unpublished observations.

(4) Schaverien, C. J.; Dewar, J. C.; Schrock, R. R. *J. Am. Chem. Soc.* 1986, 108, 2771–2773.

(5) Feldman, J. R.; Schrock, R. R. *Prog. Inorg. Chem.* 1991, 39, 1–74 and references therein.

(6) Nguyen, S. T.; Johnson, L. K.; Grubbs, R. H., unpublished observations.

Table I. Turnover Numbers¹⁶ and Conditions for the Metathesis of *cis*-2-Pentene Catalyzed by **2a** and **2b**

entry	catalyst	solvent and catalyst concentration	turnover number ¹⁶ (equiv/h)
1	(Cy ₃ P) ₂ Cl ₂ Ru=CHCH=CPh ₂ (2a)	6.06 mM in C ₆ D ₆ ^a	26
2	(Cy ₃ P) ₂ Cl ₂ Ru=CHCH=CPh ₂ (2a)	6.06 mM in THF-d ₈ ^a	11
3	(Cy ₃ P) ₂ Cl ₂ Ru=CHCH=CPh ₂ (2a)	6.06 mM in CD ₂ Cl ₂ ^a	103
4	(Cy ₃ P) ₂ Cl ₂ Ru=CHCH=CPh ₂ (2a)	5.19 mM in (0.29:1) CD ₃ OD/CD ₂ Cl ₂ ^b	67
5	[(i-Pr) ₃ P] ₂ Cl ₂ Ru=CHCH=CPh ₂ (2b)	6.06 mM in C ₆ D ₆ ^a	22

^a Conditions: 0.5 mL of solution, 100 equiv of *cis*-2-pentene, room temperature. The reaction is carried out in an NMR tube with mesitylene as an internal standard. ^b Conditions: 0.59 mL of solution, 100 equiv of *cis*-2-pentene, room temperature. The turnover number is obtained by monitoring the first part of the *cis*-2-pentene metathesis reaction where the rate of metathesis is approximately pseudo-first-order; it is taken as the point at which 40% of the initial *cis*-2-pentene is consumed.

at room temperature is modest compared to that observed for the most active catalysts in the tungsten- and molybdenum-based systems,^{4,5} this is the first time that the metathesis of an acyclic olefin has been reported with well-defined ruthenium carbene complexes.¹⁷ Among other factors, the modest turnover number for complexes **2a,b** can be attributed to the slow initiation of the parent vinylcarbene complex.^{18–20} In contrast to early-transition-metal metathesis catalysts, where functional group tolerance is limited, **2a** is an extremely robust catalyst. Neither a protic solvent (entry 4 and ref 21) nor a coordinating solvent (entry 2) significantly affected the metathesis rate of *cis*-2-pentene. Complex **2a** also catalyzes the metathesis of functionalized substrates such as allyl ether, allyl alcohol, 3-buten-1-ol, and methyl oleate⁶ and the ring-closing metathesis of functionalized dienes.²¹

The role of the phosphine ligand in activating the vinylcarbene moiety appears to be mainly electronic, not steric, in origin. Complex **1**² (cone angle PPh₃ = 145°²²) does not metathesize acyclic olefins, while complexes **2a,b**, with bulky, electron-rich, alkylphosphine ligands, catalyze the metathesis of *cis*-2-pentene. Although PCy₃ (cone angle = 170°²²) and P(i-Pr)₃ (cone angle = 160°²²) are sterically somewhat different,²³ **2a** and **2b** are equally active (Table I, entries 1 and 5). On the other hand, the vinylcarbene derivative resulting from the reaction of P(CH₂-Ph)₃ with **1** does not metathesize unfunctionalized acyclic olefins.⁶

(16) Because of the nature of the kinetics and the slow initiation of the parent catalyst, the reported turnover numbers are lower-limit values.

(17) Ivin, K. J. *Olefin Metathesis*; Academic Press: London, 1983; p 34.

(18) Preliminary experiments indicate that at higher concentrations of olefin it is possible to eventually convert all of **2a** into the “propagating” species.

(19) After 1 day, >90% of the total starting vinylcarbene is still present in various forms, including the starting vinylcarbene.

(20) Previous works have shown that optimal activity for Ru-based catalysts is often obtained at temperature > 55 °C: (a) Novak, B. M.; Grubbs, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 7542–7543. (b) Foltynowicz, Z.; Marciniec, B.; Pietraszuk, C. *J. Mol. Catal.* **1991**, *65*, 113–125.

(21) Fu, G. C.; Nguyen, S. T.; Grubbs, R. H. *J. Am. Chem. Soc.*, preceding paper in this issue.

(22) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313–348.

(23) The difference between P(i-Pr)₃ and PCy₃ is more steric than electronic. See ref 22.

This result clearly suggests that electronic factors are more important than steric effects since the cone angle of P(CH₂Ph)₃ (165°²²) is intermediate between that of P(i-Pr)₃ and PCy₃ but the phosphine is much less electron-rich. In contrast to the catalysts developed from d⁰ early-transition-metal centers,⁵ where increasing the electron-withdrawing ability of the ancillary ligands leads to increased turn over numbers, it appears that the d⁶ Ru^{II} metal center²⁴ requires electron-rich ancillary ligands for increased metathesis activity.²⁵

Complexes **2a,b** represent the first examples of a new generation of robust, well-defined, single-component catalysts for the metathesis of acyclic olefin. Even with the present level of activity, the remarkable functional tolerance of **2a,b** makes these catalysts very attractive for the synthesis of a variety of useful substrates.²¹

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Supplementary Material Available: Experimental details and spectroscopic data for complexes **2a,b**, data on ROMP and olefin metathesis catalyzed by **2a**, a description of the X-ray diffraction experiment, thermolecular drawings of **2a**, and tables of crystal data, atomic coordinates, thermal parameters, distances and angles, and torsion angles (35 pages); listing of observed and calculated structure factor amplitudes (16 pages). Ordering information is given on any current masthead page.

(24) When the oxidation state for the Ru center was assigned the vinylcarbene moiety was considered to be neutral. See: Bohle, D. S.; Clark, G. R.; Rickard, C. E. F.; Roper, W. R.; Wright, L. J. *J. Organomet. Chem.* **1988**, *358*, 411–447.

(25) This enhanced activity can be explained if the formation of a metallacyclobutane is assumed to be the rate-determining step in the metathesis cycle. In the metallacyclobutane intermediate, the metal center is formally Ru(IV), and a better σ donor will stabilize this intermediate better.