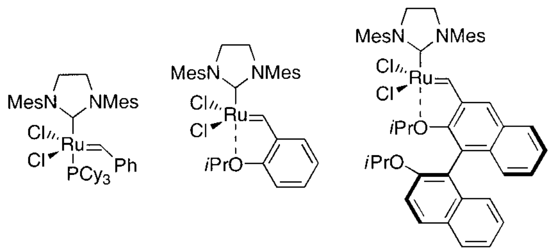
A New Highly Efficient Ruthenium Metathesis Catalyst[**]

Hideaki Wakamatsu and Siegfried Blechert[*]

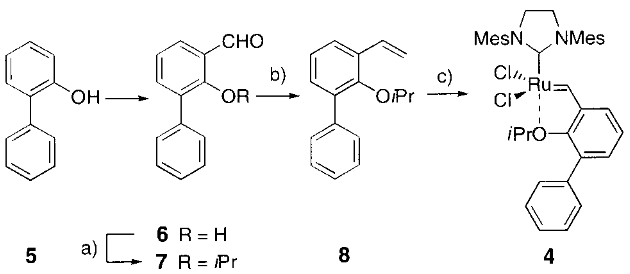
Catalytic olefin metathesis has recently become a powerful tool for carbon—carbon-bond formation in organic chemistry.[1] Over the last three years it has been demonstrated that ruthenium alkylidenes that bear N-heterocyclic carbene ligands, for example, **1** and similar analogues, exhibit extraordinary activity and stability.[2] Studies on the mechanism of olefin metathesis reactions have also been described.[2e,f] Phosphane-free catalyst **2**[3] has also recently been developed and studied. This catalyst possesses superior general reactivity toward electron-deficient olefins[4a,b,d] and is readily modified for attachment to solid supports,[4c,e] thus leading to enhanced recyclability[4c] and even to efficient metathesis in methanol and water.[4e] We have also prepared catalyst **3** with the aim of promoting asymmetric induction in metathesis reactions.[5]



1 **2** **3**

No asymmetric induction was found. However, activity studies[5] demonstrated a relative reactivity order of **3** > **1** > **2**. BINOL-derived **3** also exhibited a similar shelf stability to **1** and **2**. Herein we report the synthesis and catalytic activity of **4** (Scheme 1), a precatalyst with a markedly greater efficiency in metathesis processes than either **1**, **2**, or **3**.

At first, encouraged by the success of the BINOL-based catalyst **3**, we were interested in determining which structural units in the ligand were responsible for the high initiation rates observed. Extensive studies indicated that the presence of steric bulk adjacent to the chelating isopropoxy moiety was critical. Therefore it seemed logical to synthesize complex **4** as shown in Scheme 1. 2-Hydroxybiphenyl-3-carbaldehyde (**6**) was synthesized from commercially available phenol **5**, according to the literature procedure.[6] Ligand **8** was obtained by sequential alkylation and Wittig olefination of **6**. The bright green complex **4** could be produced in good yield by the reaction of **1** with **8** (2 equiv), and was purified by flash chromatography. At this point, the potential of **4** in the ring-closing metathesis (RCM) of tosylamide **9** was tested. When these reactions were carried out at 0 °C in the presence of 1 mol% of catalyst, **4** showed a dramatic improvement in activity over **1** and **3** (Figure 1). At room temperature, the reaction catalyzed by **4** was too fast for convenient accurate measurement. No conversion with catalyst **2** was observed at 0 °C. Consequently in all further metathesis reactions it made more practical sense to compare the new alkylidene **4** with benchmark catalyst **1** instead of with the more sluggish styrene ether based **2**.[5] It was also observed that as little as 0.05 mol% of **4** could induce cyclization of **9** in 80% yield. The catalyst retained the same activity after being exposed to air in the solid state for one week.



Scheme 1. Synthesis of catalyst **4**. a) iPrBr, NaH, DMF, 50 °C, 82%; b) $Ph_3P^+CH_3Br^-$, tBuOK, Et_2O, 0 °C, 88%; c) **1** (1 equiv), **8** (2 equiv), CuCl (1 equiv), CH_2Cl_2, 40 °C, 71%.

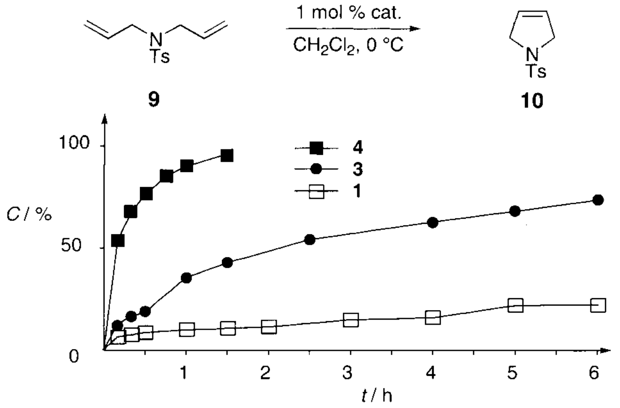
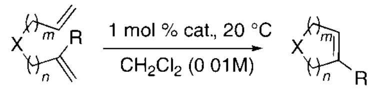


Figure 1. RCM at 0 °C in the presence of catalyst **1**, **3**, and **4**.

The RCM of miscellaneous substrates was also examined and gave impressive results (Scheme 2, Table 1). The superior activity of complex **4** over complex **1** could be established in all cases.

The applicability of **4** in other metathesis reactions was also tested. The results of cross metathesis (CM) of **21** and **22**



11, 12 X = $C(CO_2Et)_2$, R = H, m = 1, n = 1
13, 14 X = $C(CO_2Et)_2$, R = CH_3, m = 1, n = 1
15, 16 X = $C(CO_2Et)_2$, R = H, m = 1, n = 2
17, 18 X = NTs, R = H, m = 2, n = 2
19, 20 X = NTs, R = H, m = 2, n = 3

Scheme 2. Various ring-closing metathesis reactions in the presence of catalyst **1** and **4**.

---

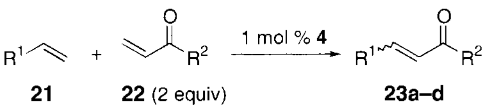
[*] Prof. Dr. S. Blechert, Dr. H. Wakamatsu
Institut für Chemie, Technische Universität Berlin
Strasse des 17. Juni 135, 10623 Berlin (Germany)
Fax: (+49) 30-3142-3619
E-mail: blechert@chem.tu-berlin.de

[**] This work was supported by the Fonds der Chemischen Industrie.

Table 1. Ring-closing metathesis in the presence of **1** and **4**.

Entry	Substrate	Product	Catalyst	time [min]	Yield [%]
1	**9**	**10**	**4**	$\ll$10	99
2	**9**	**10**	**1**	60	99
3	**11**	**12**	**4**	$\ll$10	99
4	**11**	**12**	**1**	90	99
5	**13**	**14**	**4**	40	99
6	**13**	**14**	**1**	240	99
7	**15**	**16**	**4**	$\ll$10	99
8	**15**	**16**	**1**	90	99
9	**17**	**18**	**4**	$\ll$10	99
10	**17**	**18**	**1**	60	99
11	**19**	**20**	**4**	$\ll$10	99
12	**19**	**20**	**1**	240	93

(Scheme 3) are shown in Table 2. These reactions were carried out at 20 °C in the presence of 1 mol% of catalyst. The reaction of **21a** with **22a** in the presence of **4** yielded **23a** after only 15 minutes (Table 2, entry 1). Under identical conditions, the reaction catalyzed by **1** took 3 h to reach completion, and the conversion after 15 minutes was 12% (Table 2, entry 2). The efficiency of **4** relative to **1** in ring-opening cross metathesis processes was also tested (Table 3).



21a: $R^1 = (CH_2)_3OBz$ **22a**: $R^2 = OMe$
21b: $R^1 = (CH_2)_4OTBS$ **22b**: $R^2 = Me$

Scheme 3. Cross metathesis in the presence of catalyst **1** and **4**.

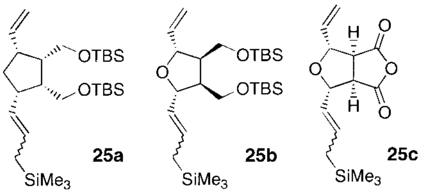
Table 2. Cross metathesis of **21** and **22**.[a]

Entry	21	22	Catalyst	time [min]	Yield [%]	(*E*)-**23**/(*Z*)-**23**
1	**a**	**a**	**4**	15	93	97:3
2	**a**	**a**	**1**	180	86 (12)[b]	97:3
3	**a**	**b**	**4**	20	82	99:1
4[c]	**b**	**a**	**4**	20	91	99:1
5	**b**	**b**	**4**	40	90	99:1

[a] All reactions were carried out at 20 °C in CH_2Cl_2 (0.05 M). [b] Conversion after 15 min in parenthesis. [c] Catalyst (2.5 mol%).

Oxanorbornene derivatives *exo*-4,10-dioxatricyclo[5.2.1.0]-dec-8-ene-dione, protected *exo*-3-hydroxymethyl-(bicyclo-[2.2.1]hept-5-en-2-yl)-methanol, and its *endo* carbocyclic analogue were treated with allyltrimethylsilane (**24**) at 20 °C in the presence of a minute quantity of catalyst (minimum 0.005 mol%) to give ring-opened products **25**. These reactions highlight the vast difference in activity between **1** and **4**, which could also been seen in the ring-opening metathesis polymerization (ROMP) of cyclooctadiene.[7] We found the times taken to reach complete conversion of the monomer depended strongly on the reaction conditions, particularly the extent to which oxygen is excluded, but not on the batch of **1** (either purchased from commercial sources or synthesized in our laboratories). For instance, in ROMP reactions with **1**, times of between 30 to over 60 minutes were required, whereas reaction times for **4** were always significantly shorter. Figure 2 represents an example that clearly demonstrates the difference in terms of reactivity between **1** and **4** in a ROMP reaction under *identical* conditions.

Table 3. Ring-opening cross metathesis with **24** (1 equiv) in the presence of catalysts **4** and **1**.[a]



Entry	25	Catalyst	time [min]	Yield [%]
1[b]	**a**	**4**	30	99
2[b]	**a**	**1**	30	20[c,d]
3	**b**	**4**	5	97
4	**b**	**1**	5	1[c,e]
5	**c**	**4**	10	87
6	**c**	**1**	10	5[c,f]

[a] Conditions: 20 °C, catalyst (0.005 mol%), CH_2Cl_2 (0.05 M). [b] Catalyst (0.025 mol%). [c] Conversions determined by ^1H NMR spectroscopic analysis. [d] Yield = 94% after 2.5 h. [e] Yield = 92% after 3 h. [f] Yield = 75% after 3 h.

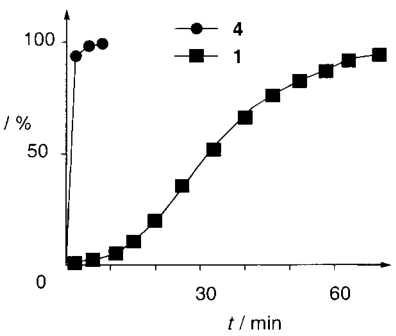


Figure 2. ROMP of cycloocta-1,5-diene in the presence of catalysts **1** and **4**. Conditions: 20 °C, monomer/catalyst ratio 300:1, catalyst = 0.5 mM, CD_2Cl_2 as solvent. Conversion was determined by ^1H NMR.

In an attempt to ascertain the exact cause of the extraordinary activity of precatalyst **4**, the RCM of **9** was monitored under various conditions. At first, parallel experiments were conducted in the presence of **4** (0.01 mol%) in both the presence and absence of ligand **8** (0.1 mol%); however, **10** was obtained in the same yield and reaction time in both cases. Following this, **9** was cyclized by using **4** (1 mol%) in the presence of PCy_3 (1 mol%) and also by using **1** (1 mol%) in the presence of ligand **8** (1 mol%). In the case of the reaction promoted by **4**, the final yield was unchanged, although conversion times were considerably longer. In the latter case, yield and reaction speed were independent of added **8**. We surmise from these results that in the case of catalyst **4**, the active 14-electron species proposed by Grubbs and co-workers[2f] must be speedily produced by relatively fast dissociation of the bulky ligand **8**, and that in the presence of substrate or added PCy_3, reassociation of **8** to ruthenium metal is slow. Therefore, it is thought that a relatively large proportion of the precatalyst is converted into the active species in solution, thus leading to excellent activity.

1433-7851/02/4113-2404 $ 20.00+.50/0

In conclusion, we have succeeded in the development of the ruthenium-based metathesis catalyst **4**, which exhibits excellent metathesis activity, without any loss of stability in air. These findings once again demonstrate that seemingly small variations in ligand structure can result in significant improvements in catalysis.

Experimental Section

4: CuCl (21 mg, 0.22 mmol) and then **1** (168 mg, 0.20 mmol) in CH_2Cl_2 (4 mL total) were added to a solution of **8** (94 mg, 0.39 mmol) in CH_2Cl_2 (16 mL) in a glove box. This reaction mixture was stirred for 1 h at 40 °C. The reaction mixture was concentrated in vacuo. The residue was dissolved in a minimum volume of CH_2Cl_2, passed through a Pasteur pipette containing a plug of cotton, and concentrated in vacuo. The residue was purified by flash chromatography on silica gel (4:1 hexane/MTBE) to afford **4** (99 mg, 71 %). ^{1}H NMR (CD_2Cl_2): $\delta = 0.81$ (d, $J = 6.2$ Hz, 6H), 2.15–2.72 (br, 18H), 4.16 (s, 4H), 4.36 (septet, $J = 6.2$ Hz, 1H), 6.92 (dd, $J = 0.9$, 7.3 Hz, 1H), 6.99 (t, $J = 7.5$ Hz, 1H), 7.06 (br, 4H), 7.31–7.42 (m, 6H), 16.60 ppm (s, 1H); ^{13}C NMR (CD_2Cl_2): $\delta = 19.6$, 20.5, 51.2, 77.0, 120.9, 123.1, 127.3, 128.1, 128.6, 128.8, 128.9, 131.1, 132.8, 137.8, 138.5, 138.9, 139.3, 147.7, 148.5, 209.8, 297.4 ppm; IR (film): $\tilde{\nu} = 3492$ (br), 1702 (w), 1605 (w), 1481 (m), 1449 (m), 1422 (m), 1263 (s), 1105 (m) cm^{-1}; HRMS *m*/*z* calcd for $C_{37}H_{42}ON_2Cl_2{}^{102}Ru$: [$M^+$] 702.1711, found: 702.1719; elemental analysis calcd (%) for $C_{37}H_{42}ON_2Cl_2Ru \cdot 1/2\,H_2O$: C 62.44, H 6.09, N 3.94; found: C 62.32; H 5.97, N 3.88.

Received: April 22, 2002 [Z19143]

[1] a) M. Schuster, S. Blechert, *Angew. Chem.* **1997**, *109*, 2124; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2036; b) S. K. Armstrong, *J. Chem. Soc. Perkin Trans. 1* **1998**, 371; c) R. H. Grubbs, S. Chang, *Tetrahedron* **1998**, *54*, 4413; d) A. Fürstner, *Angew. Chem.* **2000**, *112*, 3140; *Angew. Chem. Int. Ed.* **2000**, *39*, 3012; e) T. M. Trnka, R. H. Grubbs, *Acc. Chem. Res.* **2001**, 34, 18–29.

[2] a) W. A. Herrmann, M. Speigler, W. C. Schattenmann, T. Westcamp, *Angew. Chem.* **1998**, *110*, 2631; *Angew. Chem. Int. Ed.* **1998**, *37*, 2490; b) W. A. Hermann, T. Westcamp, L. Ackermann, F. J. Kohl, A. Fürstner, *Tetrahedron Lett.* **1999**, *40*, 4787; c) J. Huang, E. D. Stevens, S. P. Nolan, J. L. Pedersen, *J. Am. Chem. Soc.* **1999**, *121*, 2674; d) M. Scholl, S. Ding, C. W. Lee, R. H. Grubbs, *Org. Lett.* **1999**, *1*, 953; e) M. S. Sanford, M. Ulman, R. H. Grubbs, *J. Am. Chem. Soc.* **2001**, *123*, 749; f) M. S. Sanford, J. A. Love, R. H. Grubbs, *J. Am. Chem. Soc.* **2001**, *123*, 6543.

[3] a) S. B. Garber, J. S. Kingsbury, B. L. Gray, A. H. Hoveyda, *J. Am. Chem. Soc.* **2000**, *122*, 8168; b) S. Gessler, S. Randl, S. Blechert, *Tetrahedron Lett.* **2000**, *41*, 9973.

[4] a) S. Randl, S. Gessler, H. Wakamatsu, S. Blechert, *Synlett* **2001**, 430; b) S. Imhof, S. Randl, S. Blechert, *Chem. Commun.* **2001**, 1692; c) S. Randl, N. Buschmann, S. J. Connon, S. Blechert, *Synlett* **2001**, 1547; d) S. Randl, S. J. Connon, S. Blechert, *Chem. Commun.* **2001**, 1796; e) S. J. Connon, S. Blechert, *Bioorg. Med. Chem. Lett.* **2002**, in press.

[5] H. Wakamatsu, S. Blechert, *Angew. Chem.* **2002**, 114, 832; *Angew. Chem. Int. Ed.* **2002**, 41, 794.

[6] M. M. G. Antonisse, B. H. M. Snellink-Ruël, A. C. Ion, J. F. J. Engbersen, D. N. Reinhoudt, *J. Chem. Soc. Perkin Trans. 2*, **1999**, 1211.

[7] C. W. Bielawski, R. H. Grubbs, *Angew. Chem.* **2000**, 112, 3025; *Angew. Chem. Int. Ed.* **2000**, 39, 2903.

Photochemical Sensing of NO_2 with SnO_2 Nanoribbon Nanosensors at Room Temperature[**]

Matt Law, Hannes Kind, Benjamin Messer, Franklin Kim, and Peidong Yang[*]

A major area of application for nanowires and nanotubes is likely to be the sensing of important molecules, either for medical or environmental health purposes. The ultrahigh surface-to-volume ratios of these structures make their electrical properties extremely sensitive to surface-adsorbed species, as recent work has shown with carbon nanotubes,[1, 2] functionalized silicon nanowires and metal nanowires.[3, 4] Chemical nanosensors are interesting because of their potential for detecting very low concentrations of biomolecules or pollutants on platforms small enough to be used in vivo or on a microchip. Here we report the development of photochemical NO_2 sensors that work at room temperature and are based on individual single-crystalline SnO_2 nanoribbons.

Tin dioxide is a wide-bandgap (3.6 eV) semiconductor. For n-type SnO_2 single crystals, the intrinsic carrier concentration is primarily determined by deviations from stoichiometry in the form of equilibrium oxygen vacancies, which are predominantly atomic defects.[5] The electrical conductivity of nanocrystalline SnO_2 depends strongly on surface states produced by molecular adsorption that results in space-charge layer changes and band modulation.[6] NO_2, a combustion product that plays a key role in tropospheric ozone and smog formation, acts as an electron-trapping adsorbate on SnO_2 crystal faces and can be sensed by monitoring the electrical conductance of the material. Because NO_2 chemisorbs strongly on many metal oxides,[7] commercial sensors based on particulate or thin-film SnO_2 operate at 300–500 °C to enhance the surface molecular desorption kinetics and continuously "clean" the sensors.[8] The high-temperature operation of these oxide sensors is not favorable in many cases, particularly in an explosive environment. We have found that the strong photoconducting response of individual single-crystalline SnO_2 nanoribbons makes it possible to achieve equally favorable adsorption–desorption behavior at room temperature by illuminating the devices with ultraviolet (UV) light of energy near the SnO_2 bandgap. The active desorption process is thus photoinduced molecular desorption (Figure 1).[9]

---

[*] Prof. P. Yang, M. Law, Dr. H. Kind, B. Messer, F. Kim
Department of Chemistry
University of California, Berkeley
Berkeley, CA 94720-1460 (USA)
Fax: (+1) 510-642-7301
E-mail: p_yang@uclink.berkeley.edu

[**] This work was supported by the Camille and Henry Dreyfus Foundation, 3M Corporation, the National Science Foundation, and the University of California, Berkeley. P.Y. is an Alfred P. Sloan Research Fellow. Work at the Lawrence Berkeley National Laboratory was supported by the Office of Science, Basic Energy Sciences, Division of Materials Science of the US Department of Energy. We thank the National Center for Electron Microscopy for the use of their facilities.

1433-7851/02/4113-2405 $ 20.00+.50/0