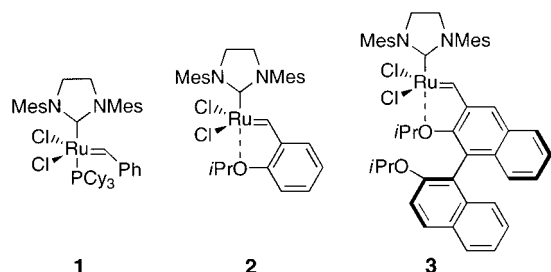




A New Highly Efficient Ruthenium Metathesis Catalyst**

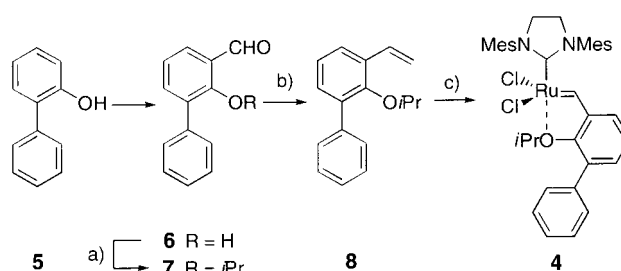
Hideaki Wakamatsu and Siegfried Blechert*

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.^[4c] We have also prepared catalyst **3** with the aim of promoting asymmetric induction in metathesis reactions.^[5]



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



Scheme 1. Synthesis of catalyst **4**. a) *i*PrBr, NaH, DMF, 50 °C, 82 %; b) $\text{Ph}_3\text{P}^+\text{CH}_3\text{Br}^-$, *t*BuOK, Et_2O , 0 °C, 88 %; c) **1** (1 equiv), **8** (2 equiv), CuCl (1 equiv), CH_2Cl_2 , 40 °C, 71 %.

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

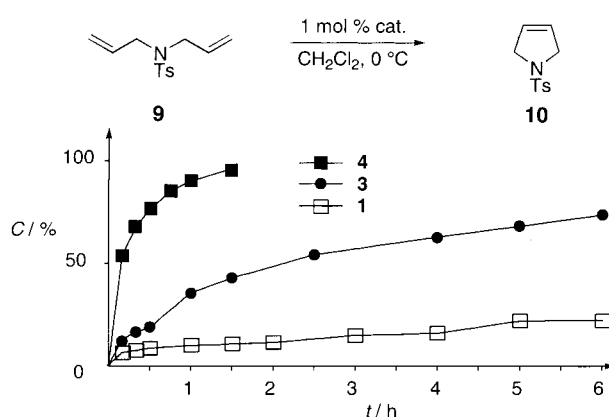
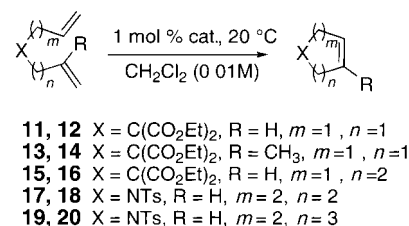


Figure 1. RCM at 0 °C in the presence of catalyst **1**, **3**, and **4**.

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.

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**



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

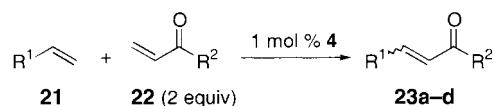
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Table 1. Ring-closing metathesis in the presence of **1** and **4**.

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



21a: R¹ = (CH₂)₃OBz **22a:** R² = OMe
21b: R¹ = (CH₂)₄OTBS **22b:** R² = 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 [%]	(<i>E</i>)- 23 / <i>(Z)</i> - 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 CH₂Cl₂ (0.05 M). [b] Conversion after 15 min in parenthesis. [c] Catalyst (2.5 mol %).

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).

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 be 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

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 %), CH₂Cl₂ (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.

represents an example that clearly demonstrates the difference in terms of reactivity between **1** and **4** in a ROMP reaction under identical conditions.

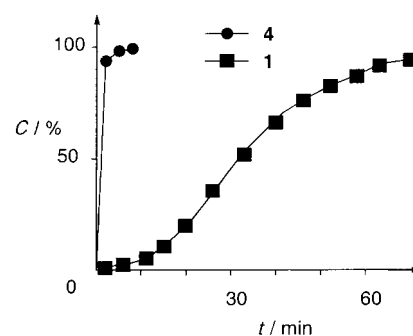


Figure 2. ROMP of cycloocta-1,5-diene in the presence of catalysts **1** and **4**. Conditions: 20 °C, monomer/catalyst ratio 300:1, catalyst = 0.5 mM, CD₂Cl₂ as solvent. Conversion was determined by ¹H NMR.

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 PCy₃ (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 PCy₃, 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.



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 CH₂Cl₂ (4 mL total) were added to a solution of **8** (94 mg, 0.39 mmol) in CH₂Cl₂ (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 CH₂Cl₂, 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 %). ¹H NMR (CD₂Cl₂): δ = 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); ¹³C NMR (CD₂Cl₂): δ = 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 C₃₇H₄₂ON₂Cl₂Ru: [M⁺] 702.1711, found: 702.1719; elemental analysis calcd (%) for C₃₇H₄₂ON₂Cl₂Ru · 1/2 H₂O: C 62.44, H 6.09, N 3.94; found: C 62.32; H 5.97, N 3.88.

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Photochemical Sensing of NO₂ with SnO₂ Nanoribbon Nanosensors at Room Temperature**

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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 NO₂ sensors that work at room temperature and are based on individual single-crystalline SnO₂ nanoribbons.

Tin dioxide is a wide-bandgap (3.6 eV) semiconductor. For n-type SnO₂ 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 SnO₂ depends strongly on surface states produced by molecular adsorption that results in space-charge layer changes and band modulation.^[6] NO₂, a combustion product that plays a key role in tropospheric ozone and smog formation, acts as an electron-trapping adsorbate on SnO₂ crystal faces and can be sensed by monitoring the electrical conductance of the material. Because NO₂ chemisorbs strongly on many metal oxides,^[7] commercial sensors based on particulate or thin-film SnO₂ 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 SnO₂ 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 SnO₂ bandgap. The active desorption process is thus photoinduced molecular desorption (Figure 1).^[9]

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