A Highly Active and Air-Stable Ruthenium Complex for Olefin Metathesis**

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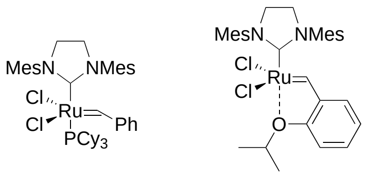
Over the past ten years, olefin metathesis has made rapid progress in the field of synthetic organic chemistry.[1] In 1999 a major step forward has been made with the development of ruthenium alkylidene **1** (Scheme 1).[2] Studies on the mechanism of olefin metathesis reactions promoted by **1** and its bisphosphane analogue[3] have revealed that a low ratio of phosphane reassociation to substrate binding was necessary for high activity. Recently, a phosphane-free *N*-heterocyclic carbene complex **2** (Scheme 1) has been described[4, 5] and an immobilized version is also known.[6] Precatalyst **2** has a superior stability to **1** and is even recoverable by column chromatography. We have found though, that in general this comes hand in hand with longer reaction times. Herein, we report the discovery of a variant of **2** with a similar stability, but with an activity that significantly surpasses that of **1**. The advantages associated with the use of **2** over **1** in cross-metathesis (CM) reactions involving highly electron-deficient olefins are becoming apparent,[7] especially for CM with challenging substrates such as acrylonitrile and fluorinated olefins.

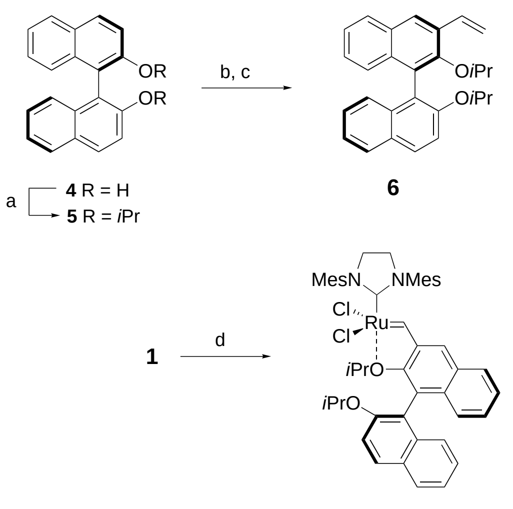


1 **2**

Scheme 1. Ruthenium precatalysts **1** and **2**.

Given this difference in reactivity, a stabilizing interaction between the isopropoxy group and the metal center during metathesis could not be excluded. This presumption prompted us to prepare a chiral chelating isopropoxystyrene ligand for possible asymmetric ring-closing metathesis (ARCM). Only quite recently, the first ruthenium-catalyzed ARCM was described.[8] We planned to prepare complex **3** (see Scheme 2). The C_2-symmetric, chiral 2,2′-dihydroxy-1,1-binaphthyl (binol) **4** is useful for asymmetric synthesis,[9] and we expected that **3** would have a similar stability as **2**.

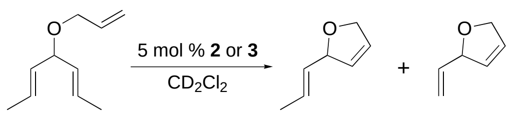
The synthetic route to **3** is shown in Scheme 2. Ligand **6** was readily prepared from commercially available **4** by treatment with *i*PrBr followed by monoformylation and Wittig olefination. Complex **3** could be produced in good yield by reaction of **1** with **6** in the presence of CuCl as a phosphane scavenger in CH_2Cl_2, and isolated by column chromatography.



3

Scheme 2. Synthesis of **3**. a) 1) NaH, DMF, 2) *i*PrBr, RT, 80%; b) 1) *n*BuLi, THF, 0°C, 2) DMF, RT, 28%, (**5** (49%) recovered); c) $Ph_3P^+CH_3Br^-$, *t*BuOK, Et_2O, 0°C, 96%; d) **6** (2 equiv), CuCl (1 equiv), CH_2Cl_2, 40°C, 76%.

The potential of **3** in ARCM was tested with ether **7** [Eq. (1)]. This reaction was carried out at room temperature in CD_2Cl_2 and monitored by ^1H NMR spectroscopy. In addition to **8**, vinyl dihydrofuran **9** was also obtained in all cases (**8**:**9** = 7:3, determined by GC). We postulate that **9** arises as a result of the reaction between **8** and a methylenecarbene complex. Disappointingly, no asymmetric induction was observed by GC on a chiral column.



(1)

7 **8** **9**

Interestingly, with precatalyst **3**, RCM required only 5 min to reach completion, compared to 30 min using **2**. This enhanced reactivity prompted us to undertake a more systematic study to compare the performance of catalysts **1**–**3** in RCM reactions. Thereupon, the RCM of **10** to **11** promoted by **1**, **2**, or **3** was controlled by HPLC, and conversions were determined (Figure 1). All reactions were carried out at room temperature in CH_2Cl_2 in the presence of 1 mol% of precatalyst. Surprisingly, the activity of complex **3** was drastically higher than that of not only **2** but also of the phosphane-based catalyst **1**. In general, an increased reactivity in metathesis catalyst is coupled with a decreased stability. To our delight, complex **3** retained all of its activity after being exposed to air for one week.

Subsequently, the performance of **3** compared to that of the benchmark complex **1** was tested in RCM reactions with various substrates (Table 1). The superiority of complex **3** compared to complex **1** over shorter reaction times (turnover frequencies) could be demonstrated in all cases. For example, the reaction of **18** yielded azepin **19** in nearly quantitative

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

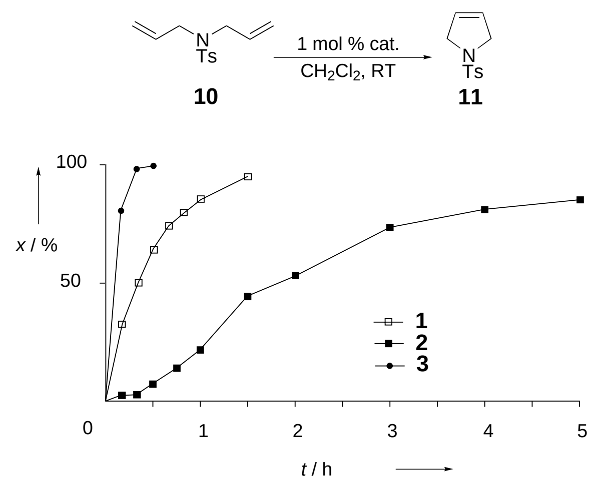
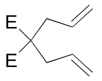
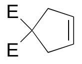
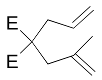
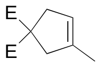
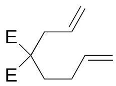
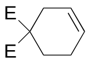
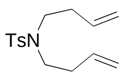
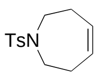
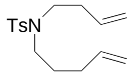
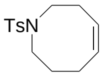


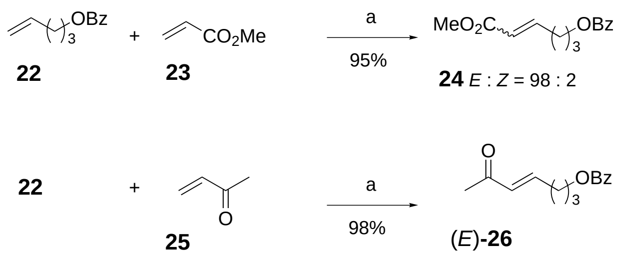
Figure 1. RCM of **10** using catalysts **1, 2**, or **3**. x = conversion.

Table 1. Results of RCM using **1** or **3** (1 mol %).[a]

Entry	Substrate	Product	t [min]	Yield using **3**[b] [%]	Yield using **1**[c] [%]
1	**10**	**11**	30	99	71
2[d]	 **12**	 **13**	30	98	51
3[d]	 **14**	 **15**	90	99	69
4[d]	 **16**	 **17**	20	99	40
5	 **18**	 **19**	10	99	18
6	 **20**	 **21**	20	99	4

[a] All reactions were carried out at room temperature in $\mathrm{CH_2Cl_2}$ (0.01M). [b] Yield of isolated product after column chromatography. [c] Conversions determined by ^{1}H NMR spectroscopy. [d] E = $\mathrm{CO_2Et}$.

yield after only 10 min (Table 1, entry 5), whereas under identical conditions, **1** gave only 18 % conversion. The greater activity of **3** is especially evident in eight-membered ring formation, which is known to be difficult (Table 1, entry 6). However, the products generated by using **1** were obtained in similar yields if the reaction time was prolonged to a maximum of 4 h. Furthermore, the potential of catalyst **3** for CM reactions was examined (Scheme 3). Catalyst **3** exhibited a high activity in this reaction, even with electron-deficient olefins (**23**, **25**), and the products (**24**, **26**) were obtained in excellent yield after only 20 min.



Scheme 3. CM using **3** (1 mol %). a) $\mathrm{CH_2Cl_2}$, RT, 20 min.

In summary, the novel binol-based ruthenium alkylidene catalyst **3** exhibits excellent activity and stability in various metathesis reactions. It is clear that the replacement of the isopropoxystyrene ligand in **2** by binol-based styrene **6** results in a large improvement in catalyst activity. We assume that this increase in steric bulk improves the leaving group ability of the ligand, thus facilitating formation of the catalytically active 14-electron species, and suppressing reassociation to the metal center, which supposedly deactivates the catalyst.

Experimental Section

3: CuCl (11 mg, 0.11 mmol) was added to a solution of **6** (83 mg, 0.21 mmol) in dry $\mathrm{CH_2Cl_2}$ (8 mL), then under $\mathrm{N_2}$ **1** (88 mg, 0.10 mmol) in $\mathrm{CH_2Cl_2}$ (2 mL) was added. The mixture was stirred for 1 h at 40 °C, and then concentrated in vacuo. The residue was dissolved in a minimal volume of $\mathrm{CH_2Cl_2}$ and passed through a Pasteur pipette containing a plug of cotton wool. After concentration in vacuo, the residue was purified by column chromatography on silica gel (hexane/methyl *tert*-butyl ether, 4:1) to afford **3** as a green solid (68 mg, 76 %).[10]

General procedure for the metathesis reaction using catalyst **3** at room temperature: 1) RCM: Compound **3** (2.0 mg, 2.32 μmol, 1 mol %) was added to a stirred solution of substrate (0.23 mmol, see Table 1) in dry $\mathrm{CH_2Cl_2}$ (23 mL, 0.01M) under $\mathrm{N_2}$. After TLC analysis showed that the substrate was consumed, the volatiles were removed in vacuo. The residue was purified by column chromatography on silica gel (hexane/methyl *tert*-butyl ether).[11] 2) CM: Compound **3** (2.0 mg, 2.32 μmol, 1 mol %) was added to a stirred solution of substrate **22** (0.23 mmol) and methyl acrylate (**23**) or methyl vinyl ketone (**25**) (0.46 mmol) in dry $\mathrm{CH_2Cl_2}$ (4.6 mL, 0.05M) under $\mathrm{N_2}$. After 20 min the solution was worked up as described under RCM.[11]

Received: November 15, 2001 [Z18224]

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[10] Spectral data for **3**: ^{1}H NMR (500 MHz, CD_2Cl_2): $\delta = 0.64, 0.99, 1.02, 1.15$ (4 d, $J = 6$ Hz; $2 \times Me_2$CH), 2.26, 2.37 (2 br. s; 2 *Me*-Ar), 2.53 (br.s; $3 \times$ *Me*-Ar), 2.62 (br. s; *Me*-Ar), 4.09–4.17 (m, $2 \times CH_2$; *C*HMe$_2$), 4.64 (septet, $J = 6$ Hz; *C*HMe$_2$), 6.91 (d, $J = 8$ Hz; CH), 6.99 (br. s; CH), 7.20–7.26 (m, 6H), 7.31 (dd, $J = 6.5, 6.5$ Hz; CH), 7.35 (d, $J = 8$ Hz; CH), 7.38 (d, $J = 9$ Hz; CH), 7.59 (s; CH), 7.82 (d, $J = 8$ Hz; CH), 7.96 (d, $J = 9$ Hz; CH), 8.02 (d, $J = 8$ Hz; CH), 16.77 (s; CH=Ru); ^{13}C NMR (125 MHz, CD_2Cl_2): $\delta = 17.8, 19.9, 20.3$ ($3 \times CH_3$), 20.6 ($4 \times CH_3$), 21.0, 21.4, 21.7 ($3 \times CH_3$), 50.6, 51.6 ($2 \times CH_2$), 69.6, 78.0, 113.4 ($3 \times$ CH), 117.7, 117.8 ($2 \times$ C), 120.6, 123.3, 125.1, 125.3, 126.2, 126.3, 126.7, 127.4 ($11 \times$ CH), 127.9 (C), 128.6, 128.7, 129.3, 129.9 ($4 \times$ CH), 130.2, 133.6, 133.7, 134.0, 137.9, 138.5, 139.6, 147.3, 147.8, 152.7, 210.2 ($14 \times$ C), 297.1 (CH); HRMS *m/z* calcd for $C_{48}H_{52}O_2N_2Cl_2{}^{102}Ru$ [M^+]: 860.2443, found: 860.2451; elemental analysis calcd (%) for $C_{48}H_{52}O_2N_2Cl_2Ru$: C 66.97, H 6.09, N 3.25; found: C 66.65, H 6.11, N 3.48.

[11] ^{1}H NMR data for the new compounds **21** and (*E*)-**26**; **21**: ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.74$ (tt, $J = 6, 7$ Hz, 2H), 2.22 (dt, $J = 6, 7$ Hz, 2H), 2.29 (dt, $J = 4, 7$ Hz, 2H), 2.40 (s, 3H), 3.08 (t, $J = 6$ Hz, 2H), 3.13–3.15 (m, 2H), 5.66–5.73 (m, 2H), 7.27 (d, $J = 8$ Hz, 2H), 7.66 (d, $J = 8$ Hz, 2H); HRMS *m/z* calcd for $C_{14}H_{19}O_2NS$ [M^+] : 265.1137, found: 265.1133; (*E*)-**26**: ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.92–1.97$ (m, 2H), 2.20 (s, 3H), 2.38 (dt, $J = 7, 7$ Hz, 2H), 4.34 (t, $J = 6$ Hz, 2H), 6.11 (d, $J = 16$ Hz, 1H), 6.81 (dt, $J = 16, 7$ Hz, 1H), 7.42 (dd, $J = 7, 7.5$ Hz, 2H), 7.54 (t, $J = 7$ Hz, 1H), 8.01 (d, $J = 7.5$ Hz, 2H); HRMS *m/z* calcd for $C_7H_{11}O_2$ [$M^+ - $COPh]: 127.0759, found: 127.0753.

Characterization and Photochemistry of the Gallium and Indium Subhydrides Ga_2H_2 and In_2H_2**

Hans-Jörg Himmel,* Laurent Manceron,
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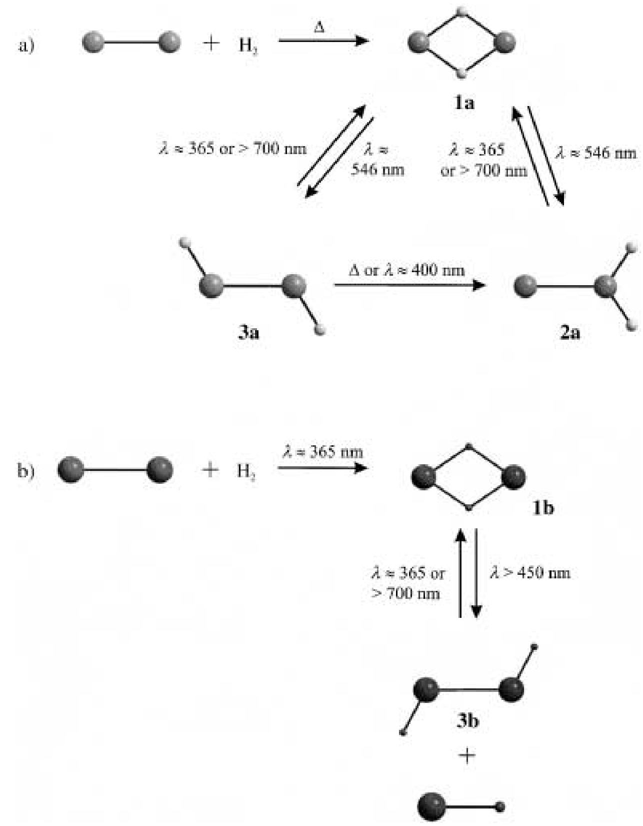
Herein we describe the cocondensation of Ga or In vapor with H_2 in an excess of Ar at 10–12 K, and the subsequent irradiation of the resulting matrix with light of different wavelengths. We show that the reaction of Ga_2 or In_2 with H_2 directly or indirectly gives rise to three isomers of Ga_2H_2 and two isomers of In_2H_2, namely the bis(μ-hydrido) species Ga(μ-H)$_2$Ga (**1a**) and In(μ-H)$_2$In (**1b**), the *trans*-bent species HGaGaH (**3a**) and HInInH (**3b**), and $GaGaH_2$ (**2a**) with two terminal Ga–H bonds (Scheme 1). All these molecules have been identified and characterized by IR spectroscopy, and by a comparison of the measured spectra with those calculated by quantum-chemical methods as well as with spectra of known gallium and indium hydrides. The findings show that the isomers can be interconverted by selective photolysis.



Scheme 1. Thermally and photolytically activated reactions taking place in argon matrices a) between Ga_2 and H_2, and b) between In_2 and H_2.

The Group 13 subhydrides are of interest not only because of the possibility of metal–metal bonding in M(μ-H)$_2$M species and even of multiple bonding in HMMH species (M = Ga or In), but also because of the potential role of gallium and indium hydrides as precursors or intermediates in chemical vapor deposition (CVD) processes designed to produce metallic or semiconductor materials. Although such compounds have attracted considerable attention from theorists,[1–4] experimental information is available only for linear HBBH[5] and for Al(μ-H)$_2$Al,[6] both identified in matrix experiments. Similar experiments with thermally evaporated gallium have suggested[7] that Ga_2 reacts spontaneously with H_2 to form **1a** which, like Al(μ-H)$_2$Al has the planar structure motif **A**. Of other possible M_2H_2 isomers (structure motifs **B**–**D**), only HAl(μ-H)Al (with structure motif **D**) has been identified, albeit somewhat tentatively.[6]

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[**] This work was supported by the Deutsche Forschungsgemeinschaft (Habilitation grant to H.-J. H.), the CNRS (L. M.), and the EPSRC (A. J. D.).