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Journal of Organometallic Chemistry 691 (2006) 5172–5180
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

The activity of covalently immobilized Grubbs–Hoveyda type catalyst is highly dependent on the nature of the support material

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Received 25 April 2006; received in revised form 20 June 2006; accepted 20 June 2006
Available online 30 June 2006

Abstract

A Hoveyda-type catalyst for olefin metathesis was synthesized and covalently attached via an amide bond to four different solid supports. One of these supports was a home-made hybrid silica support, where an ultra-thin copolymer of poly(styrene) and poly(acrylamide) was grafted on. The three other supports were commercially available, namely HypoGel 400, PEGA and Trisoperl. It was demonstrated that the catalysts were active in ring closing metathesis (RCM) reactions as well as in cross metathesis (CM) and ring opening metathesis (ROM) reactions, but the activity of the catalyst was highly dependent on the nature of the support.

Keywords: Alkenes; Immobilization; Olefin metathesis; Ruthenium; Supported catalysts

1. Introduction

One of the most impressive reactions developed in the last years is olefin metathesis with all its synthetic manifoldness like ring closing metathesis (RCM), ring opening metathesis (ROM), cross metathesis (CM) or enyne metathesis [1–5]. The now widely available Ru-complexes developed by Grubbs (Fig. 1) allow the construction of highly diverse molecules or materials [6–9]. These complexes show high activity along with relatively high stability and they tolerate a broad spectrum of functional groups. Hoveyda discovered a modified version of the Grubbs-type catalyst, bearing a styrenyl ether (Fig. 1) [10,11]. The ether chelate improved the stability towards air and moisture even more, so that purification on silica gel and recycling of these complexes became feasible. However, the observed leaching of Ru into the products is a disadvantage and makes additional purification necessary [12–16].

The most common method to overcome this problem is immobilization of the transition metal catalyst on a solid phase, which also allows for an easy separation from the products. With the Grubbs – as well as with the Hoveyda – type catalysts, immobilization proved to be, to a certain degree, efficient in reducing the Ru-leaching. Meanwhile, various alternative applications were developed using solid phases, soluble polymers, ionic liquids or perfluoro-tagged complexes [17–24].

2. Results and discussion

Here, we report the synthesis and application of new, immobilized Hoveyda-type catalysts on amino-functionalized solid supports of different nature. One of these materials was a hybrid silica gel which consisted of porous silica gel as matrix, on which an ultra-thin layer (≈10 nm) of an acrylamide-styrene copolymer was grafted (Fig. 2). The organic layer mediates the contact with organic solvents but shows no swelling. The loading of the support by amino groups can be adjusted by the ratio of acrylamide to styrene.

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doi:10.1016/j.jorganchem.2006.06.030

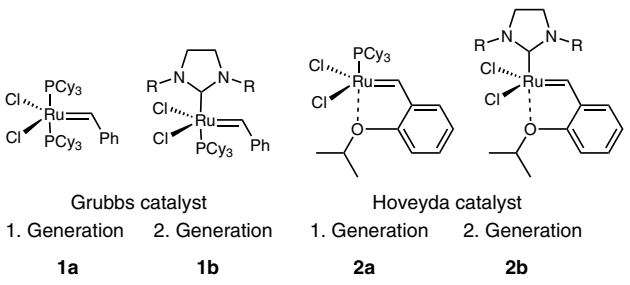


Fig. 1. Olefin metathesis catalysts.

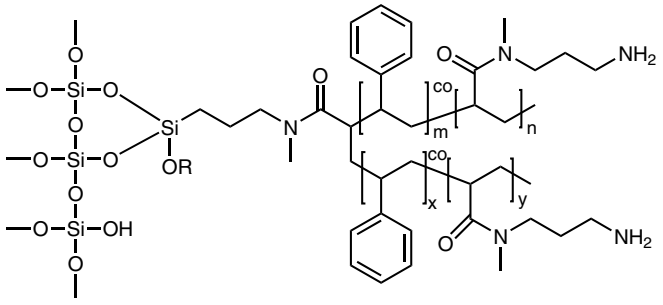


Fig. 2. Novel hybrid support: silica gel with a thin layer of a copolymer of styrene and acrylamide.

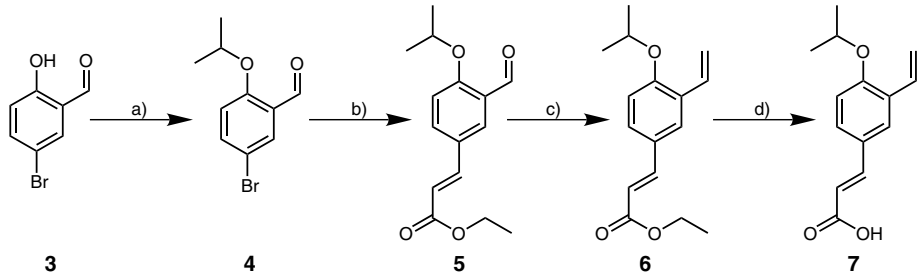
Besides this new, home-made material, commercially available solid phases were also applied. These materials were HypoGel 400, which is polystyrene bearing low molecular weight oligo(ethylene glycol) units, PEGA, a poly(acrylamide) interspaced with poly(ethylene glycol) units, and Trisoperl, an aminopropyl-modified silica gel. All these solid supports were tested side by side for their suitability to act as carriers for the catalyst.

The synthesis of the ligand is depicted in Scheme 1. 5-Bromosalicylaldehyde **3** was first reacted with 2-iodopropane to yield the isopropoxy ether **4**. In the following Heck reaction, the carboxyl group was introduced as ethyl ester. Then, the aldehyde **5** was transformed by Wittig reaction into the styrene derivative **6** and subsequent saponification led to ligand **7**. All steps proceeded with fair to high yields. The incorporated double bond should not hamper the olefin metathesis because terminal olefins are favored to internal ones. Additionally, the isopropoxy ether might act as a directing group for the catalytically active Ru-species.

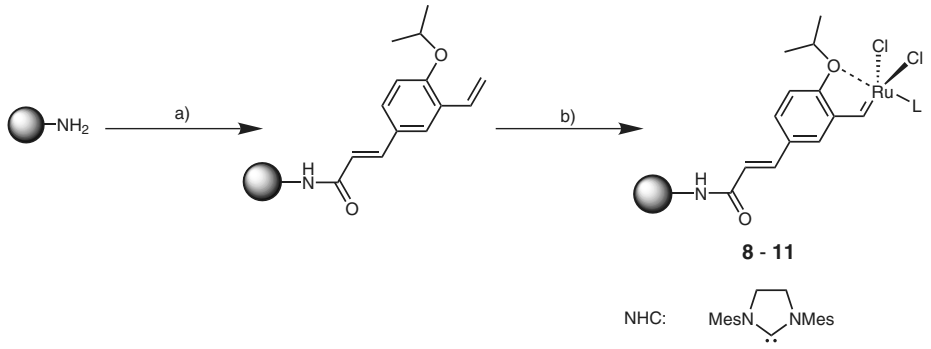
Ligand **7** was attached to the different solid supports using DCC, HOBt and Huenig's base for 24 h and no amino functions were detected afterwards. Nevertheless, this was followed by a masking step with acetic anhydride to ensure that possibly unreacted free amino groups were capped (Scheme 2). The immobilized catalysts were prepared in the presence of **1a** or **1b** and CuCl as activator (Scheme 2). For the removal of insoluble Cu-phosphine residues, we applied two different procedures. The silica-based materials (**8** and **11**) were filtered after the reaction and washed with DCM until the filtrates were colorless. The remaining Cu ions were then removed specifically by rendering them soluble as neocuproine complex, and their absence was confirmed by XPS-measurements [25]. In contrast, the catalysts on HypoGel 400 and on PEGA (**9** and **10**) were purified using a method described by Blechert et al., which exploited the different densities of the polymer-attached catalysts and the Cu-residues [26]. Finally, the Ru-loading of all immobilized catalysts was determined by atom absorption or inductively coupled plasma mass spectroscopy (ICP-MS) [27].

Although the support materials have different properties, the immobilized Ru-complexes should react according to the same principle. In the first turnover, the catalytically active Ru-species should be released from the support and catalyze the metathesis in a homogeneous fashion [28,29]. After depletion of the substrate, the Ru is recaptured by the solid phase bound ligands. In such a mechanism, the support should only play a minor role. In order to shed more light on this issue, we investigated the immobilized complexes in recycling experiments, using the ring closure of **12a** as a benchmark reaction (Scheme 3). Of each catalyst 1 mol% was placed under air in a reaction tube and the substrate was added from a stock solution. After 2 h, a sample was drawn to determine the conversion by HPLC, then the supernatant solution was separated and the solid support was washed with DCM. In this way, five consecutive runs were performed with each catalyst (Figs. 3 and 4).

As expected, the complexes **8b**–**11b** bearing the *N*-heterocyclic carbene ligand performed better than **8a**–**11a** carrying the phosphine ligand. When applying **8a**–**11a**, in the first recycling run itself, a drop in activity of almost all complexes took place (Fig. 3) and a dependency of the support material was indicated.



Scheme 1. Synthesis of the ligand **7**. a) *i*PrI, K_2CO_3, Cs_2CO_3, DMF, 24 h, r.t., 96%; b) Ethyl acrylate, $Pd(OAc)_2$, P(*o*-Tolyl)$_3$, Et_3N, DMF, 5 h, 100 °C, 89%; c) Ph_3PCH_3Br, *n*BuLi, THF, 24 h, 0 °C → r.t., 72%; d) KOH, water/dioxane, 24 h, r.t., 92%.

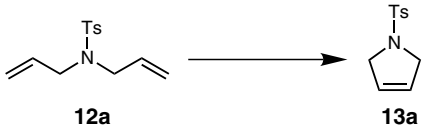


Support	Ligand	Solid Phase-bound Catalyst	Loading (μmol/g)
Hybrid Silica Gel	PCy_3	**8a**	32[a]
	NHC	**8b**	56[a]
HypoGel 400	PCy_3	**9a**	67[b]
	NHC	**9b**	217[b]
PEGA	PCy_3	**10a**	53[b]
	NHC	**10b**	41[b]
Trisoperl	PCy_3	**11a**	16[b]
	NHC	**11b**	5[b]

[a] Determined by ICP-MS [22].

[b] Determined by AAS [22].

Scheme 2. Synthesis of the supported olefin metathesis catalysts. a) (1) **7**, DCC, HOBt, Huenig's base, DMF, 24 h, r.t.; (2) Ac_2O, Et_3N, DMAP, CH_2Cl_2, 5 h, r.t., and b) **1a** or **1b**, CuCl, CH_2Cl_2, 4 h, rflx.



12a **13a**

Scheme 3. Benchmark RCM-reaction.

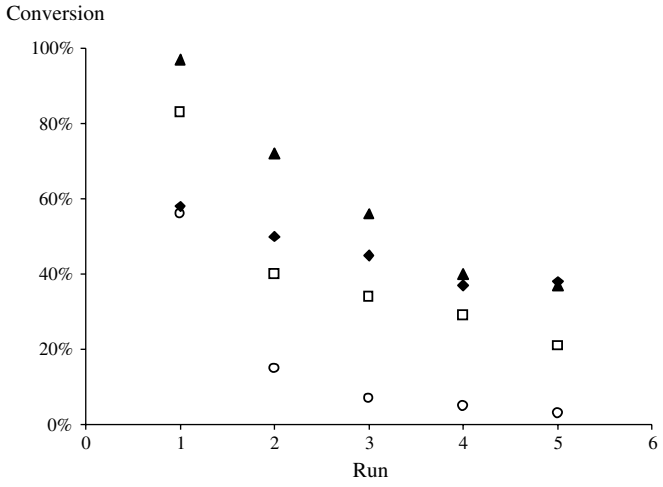


Fig. 3. RCM of **12a** catalyzed by (□) **8a**, (▲) **9a**, (○) **10a** and (◆) **11a**. Reaction conditions: 1 mol% Ru-complex, CH_2Cl_2, 2 h, rflx; conversion determined by HPLC.

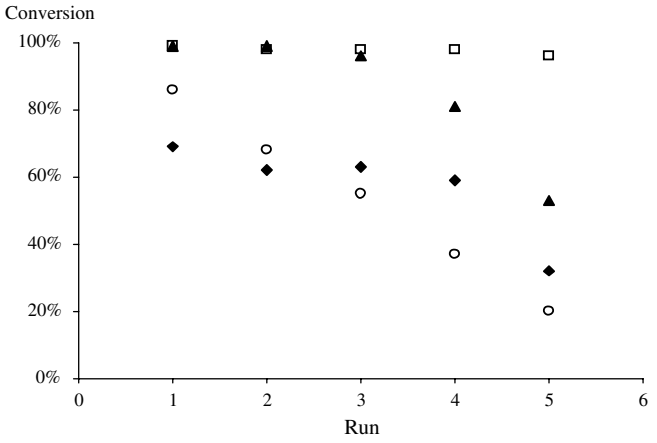
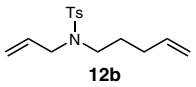
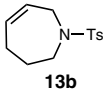
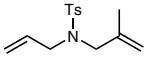
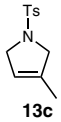
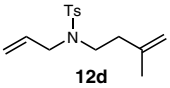
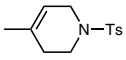
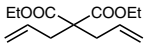
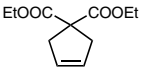
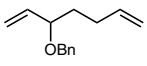
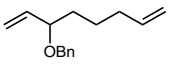
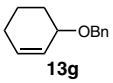
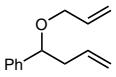


Fig. 4. RCM of **12a** catalyzed by (□) **8b**, (▲) **9b**, (○) **10b** and (◆) **11b**. Reaction conditions: 1 mol% Ru-complex, CH_2Cl_2, 2 h, rflx; Conversion determined by HPLC.

Regarding the complexes **8b**–**11b**, the recycling experiment showed again that the material had a major impact on the activity of the immobilized Ru-complexes (Fig. 4). The best results were obtained with **8b** and **9b**, where in the first three runs almost complete conversion was observed. Complexes **10b** (attached to PEGA) and **11b** (attached to Trisoperl) both showed a steady decrease in conversion, which was more pronounced for **10b** than for **11b**.

Table 1
Ring closing metathesis of several olefins[a]

Entry	Substrate	Product	Conversion run 1, run 2 (%)[b]	
			8a	**8b**
1	 **12b**	 **13b**	88, 46	>98, >98
2	 **12c**	 **13c**	14, 4	88, 76
3	 **12d**	 **13d**	25, 9	93, 84
4	 **12e**	 **13e**	47, 27	94, 91
5	 **12f**	 **13f**	84, 32	>98, 97
6	 **12g**	 **13g**	89, 51	>98, 97
7	 **12h**	 **13h**	85, 31	84, 50

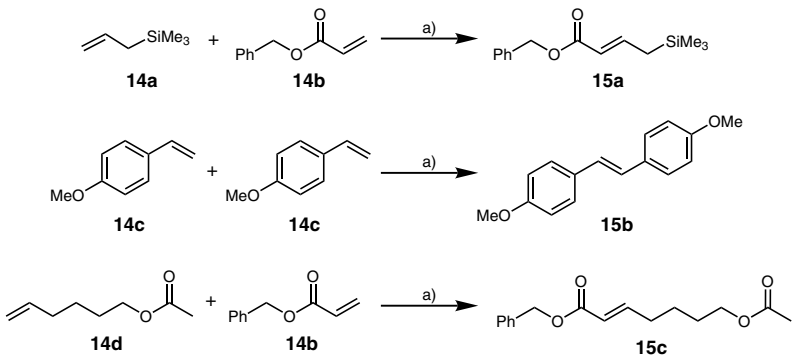
[a] Reaction conditions: 1 mol% **8a** or **8b**, CH_2Cl_2, 2 h, rflx.
[b] Determined by ^1H NMR.

We suppose that the high activities obtained with **8b** and **9b** are due to the good accessibility of the Ru centers at the surface of the materials. This is obviously not the case with **10b** and **11b**.

We further extended the applicability of the immobilized complexes on our new hybrid material **8a**,**b** to other ring closure reactions (Table 1). With every substrate, two runs were performed to demonstrate the recyclability. As in the previous experiments, 1 mol% of catalyst was used and the reactions were run simultaneously to guarantee identical conditions. Except for **13h** (entry 7), complex **8b** was always superior to **8a**. As already seen in the recycling experiments of the RCM of **12a** and also with the other substrates, a drop in activity was observed for the second run using **8a**. This was not the case with **8b**, where even the formation of the trisubstituted cyclic olefins **13c** and **d** ran smoothly (entry 2, 3).

Besides the RCM reaction, cross metathesis (CM) and ring-opening metathesis (ROM) also represent important applications of olefin metathesis. We tested both immobilized catalysts and compared them with both Grubbs catalysts in these reactions. The reaction conditions applied here were 2.5 mol% of catalyst and a reaction time of 24 h because CM reactions occur normally at a slower rate than RCM reactions. The catalysts of the first generation, **1a** and **8a**, hardly reacted. The second generation catalysts **1b** and **8b** showed different results. Both were highly active in the CM to **15b**, but the outcome of the CM to **15a** and **c** was unequal. With **1b**, the formation of **15a** worked better while the CM yielding **15c** showed higher conversion with **8b** (see Scheme 4).

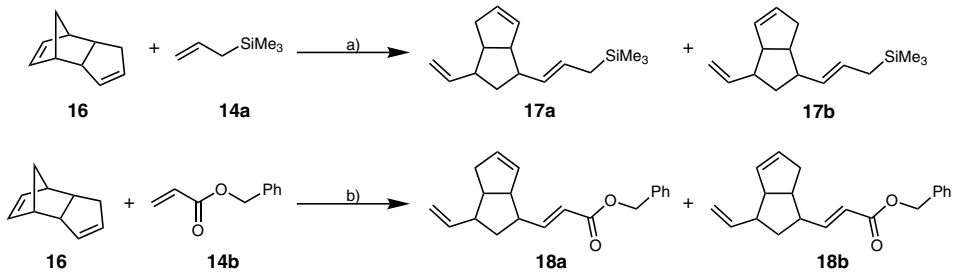
Finally, we investigated the ring opening metathesis of dicyclopentadiene **16** with **14a** and **14b** as partners (Scheme 5). The ROM of **16** with **14a** ran smoothly as



Entry	CM-Product	Conversion (%)[a]			
		1a	**8a**	**1b**	**8b**
1	**15a**	0	0	83	63
2	**15b**	46	11	>98	>98
3	**15c**	0	1	65	83

[a] Determined by ^{1}H NMR.

Scheme 4. CM-reactions using **1a**, **1b**, **8a**, **8b**. a) 2.5 mol% Ru-complex, CH_2Cl_2, 24 h, rflx.



Scheme 5. ROM/CM-reactions catalyzed by **8a** and **8b**. a) 0.5 mol% **8a** or **8b**, CH_2Cl_2, 2 h, rflx; **8a** > 98%, **8b** > 98%; b) 2.5 mol% **8b**, CH_2Cl_2, 6 h, rflx, 47% + ROMP-polymers from **16**.

reported earlier, using only 0.5 mol% of each immobilized catalyst [30]. However, it was not possible to determine the ratio of the regioisomers despite detailed 2D-NMR experiments. The ROM using **14b** instead gave disappointing results. With catalysts **1a** and **8a**, only ring opening metathesis polymerization (ROMP) of **16** was observed. Only with **1b** and **8b** the ROM-products were formed, although the ROMP of **16** also took place to a certain extent. The conversion of the ROM could be determined by proton NMR, but it was not possible to separate **18a**,**b** from the polymers. Probably, the olefin **14b** is not reactive enough to prevent the competing ROMP of **16**.

The major drawback of olefin metathesis is the high amount of Ru leaching into the product [12]. Several time-consuming or cost-intensive methods were developed to reduce the metal contamination after reaction [12–16]. Immobilization of the Ru-complexes is a strategy to avoid the contamination from the very start as can be seen in the literature [31–42].

The leaching of **8a**,**b** was determined by performing the RCM of **12a** on a larger scale. After the separation of the product by simple filtration, the Ru content was determined by atomic absorption spectroscopy (AAS). In the case of **8a**, 285 ppm of Ru were found in the product; with **8b**, the value was 684 ppm of Ru [43]. These results were not as low as the best systems reported so far [31–35] but were in the range observed for other supported Ru-complexes [36–42].

3. Conclusion

New Grubbs–Hoveyda-type catalysts were synthesized, which were attached via an amide bond to four different amino-functionalized solid supports. The activities of the immobilized catalysts were highly dependent on the nature of the support, which was demonstrated by recycling experiments using the ring closing metathesis of *N*,*N*-diallyl tosylamide. The best results were obtained applying a new home-made hybrid silica material and HypoGel 400 as supports. Furthermore, the catalysts on the hybrid silica

gel performed well in RCM, CM and ROM reactions of various substrates. The leaching of these catalysts into the product was 285 ppm Ru and 684 ppm Ru for **8a** and **8b**, respectively which is not as low as with the best systems reported so far but similar to other values reported for immobilized Ru complexes. Most importantly, our data indicate that although at least partly homogeneous, the catalysis was influenced by the nature of the applied support material.

4. Experimental

4.1. General procedure

All reagents were obtained from Aldrich, Fluka or Lancaster and were of highest purity available. CH_2Cl_2 was dried over CaH_2. The synthesis of **7** was described earlier [44].

Melting points were measured with the electrothermal digital melting device IA 9200 and are uncorrected. Column chromatography (CC) was performed using commercially available MN Silica gel 60 (0.063–0.2 mm/70–230 mesh) ASTM for CC from Baker. NMR Spectra were recorded on a 300 MHz (Varian), 400 and 500 MHz (Bruker) spectrometer for ^{1}H NMR, on a 100.6 and 125.7 MHz (Bruker) for ^{13}C NMR; chemical shifts δ in ppm rel. to Me_4Si (=0 ppm) for ^{1}H-NMR and rel. to $CHCl_3$ (=77.0 ppm) for ^{13}C-NMR respectively. J in Hz. MS: TSQ-700 (EI, CI, ESI) mass spectrometer; IR spectra were recorded on a SpectrumOne from Perkin Elmer. HPLC: Agilent 1100 system with binary pump, sample changer, column oven and diode array detector.

4.2. General procedure: (*E*)-3-(4-Isopropoxy-3-vinylphenyl)-acrylic acid (7) coupled to solid support

For the coupling, HOBt (0.27 g, 2.00 mmol) and **7** (0.46 g, 1.99 mmol) were dissolved in DMF (40 mL). To this solution DCC (0.41 g, 1.99 mmol) and Huenig's base (0.68 mL, 0.52 g, 4.03 mmol) were added. After 10 min, the coupling mixture was added to the solid phase (2.10 g, 0.13 mmol) suspended in fresh DMF and the flask was shaken at r.t. When the Kaiser-test for amino groups was negative, the solid phase was removed from the reaction and washed consecutively with DMF, water, DMF and CH_2Cl_2. Next, the solid phase was suspended in CH_2Cl_2. A solution of Et_3N (0.62 mL, 0.45 g, 4.45 mmol) and DMAP (48 mg, 390 μmol) in CH_2Cl_2 (4 mL) was added, followed by a solution of acetic anhydride (0.37 mL, 0.40 g, 3.92 mmol) in CH_2Cl_2 (2 mL), and the reaction mixture was shaken at r.t. for 4 h. Finally, the solid phase was washed with CH_2Cl_2, DMF, H_2O, DMF, CH_2Cl_2 and Et_2O and dried.

4.2.1. Ligand (7) on hybrid silica gel

IR (neat): 3652, 3331, 3085, 3065, 3028, 2979, 2927, 1991, 1878, 1717, 1626, 1601, 1544, 1535, 1493, 1453, 1417, 1386, 1374, 1052, 801, 699 cm^{-1}.

4.2.2. Ligand (7) on HypoGel 400

IR (neat): 3509, 3329, 3083, 3059, 3027, 2935, 2603, 2504, 2338, 2260, 1946, 1874, 1806, 1748, 1668, 1623, 1601, 1539, 1495, 1448, 1420, 1348, 1304, 1243, 1088, 1046, 1030, 991, 956, 907, 843, 817, 802, 760, 702, 655, 642, 543 cm^{-1}.

4.2.3. Ligand (7) on PEGA

IR (neat): 3497, 3302, 3063, 2917, 2124, 1964, 1737, 1648, 1536, 1492, 1454, 1399, 1350, 1300, 1252, 1091, 1043, 952, 852, 555 cm^{-1}.

4.2.4. Ligand (7) on Trisoperl

IR (neat): 3606, 3428, 2982, 2938, 1979, 1871, 1652, 1621, 1393, 1066, 917, 803, 673 cm^{-1}.

4.3. General procedure: Solid phase-bound catalyst for metathesis reactions (*8*–*11*)

The solid phase was suspended in dry CH_2Cl_2 under argon. Grubbs catalyst **1a** or **1b** (1.3 equiv) and CuCl (1.3 equiv) were added and the reaction was heated to reflux for 4 h. After cooling to r.t., the solid phase was removed from the reaction mixture, washed with CH_2Cl_2, and dried in a desiccator.

The loading of Ru was determined by ICP-MS or AAS.

4.3.1. (*8a*) (32 μmol/g Ru)

IR (neat): 3642, 3367, 3085, 3066, 3029, 2930, 2856, 1991, 1878, 1743, 1623, 1494, 1453, 1413, 1373, 1123, 802, 699 cm^{-1}.

4.3.2. (*8b*) (56 μmol/g Ru)

IR (neat): 3657, 3639, 3363, 3066, 3028, 2926, 1996, 1874, 1619, 1493, 1453, 1420, 1376, 1072, 801, 699 cm^{-1}.

4.3.3. (*9a*) (67 μmol/g Ru)

IR (neat): 3517, 3428, 3334, 3082, 3059, 3027, 3001, 2916, 2338, 2305, 1944, 1870, 1803, 1743, 1669, 1627, 1602, 1590, 1537, 1512, 1493, 1452, 1413, 1386, 1375, 1348, 1329, 1266, 1248, 1206, 1103, 1030, 1003, 983, 951, 928, 850, 819, 799, 760, 737, 705, 623, 562, 540, 519, 480 cm^{-1}.

4.3.4. (*9b*) (217 μmol/g Ru)

IR (neat): 3942, 3513, 3332, 3082, 3059, 3027, 3002, 2918, 2307, 2711, 2524, 2413, 1947, 1876, 1807, 1740, 1667, 1626, 1602, 1540, 1512, 1493, 1453, 1422, 1399, 1375, 1348, 1329, 1266, 1103, 1031, 982, 952, 909, 854, 797, 733, 702, 646, 621, 579, 542 cm^{-1}.

4.3.5. (*10a*) (53 μmol/g Ru)

IR (neat): 3487, 3317, 3060, 2865, 2127, 1943, 1720, 1643, 1536, 1492, 1452, 1399, 1350, 1297, 1254, 1100, 1046, 1000, 949, 849, 731, 698, 559 cm^{-1}.

*4.3.6. (**10b**) (41 μmol/g Ru)*

IR (neat): 3500, 3312, 3059, 2873, 2128, 1943, 1711, 1643, 1539, 1489, 1455, 1400, 1350, 1297, 1255, 1119, 1042, 997, 950, 851, 769, 731, 698, 580 cm^{-1}.

*4.3.7. (**11a**) (16 μmol/g Ru)*

IR (neat): 3606, 3431, 2982, 2935, 2857, 1979, 1872, 1652, 1622, 1385, 1076, 916, 803, 673 cm^{-1}.

*4.3.8. (**11b**) (5 μmol/g Ru)*

IR (neat): 3601, 3425, 2983, 2936, 1977, 1869, 1740, 1653, 1623, 1384, 1080, 916, 804, 673 cm^{-1}.

*4.4. General procedure: Recycling experiments with **12a***

The supported catalysts **8**–**11** were placed in a reaction tube under air and **12a** was added from a stock solution (1 mL, 50 μmol, 0.05 M in CH_2Cl_2). The reaction mixture was shaken for 2 h at 60 °C (oil bath). Then, a sample of the reaction mixture was taken to determine the conversion by HPLC. After this, the supernatant solution was removed and the solid phases were washed with CH_2Cl_2 (3 × 1.5 mL). Then, fresh substrate was added and the next run was started. In total, five consecutive runs were performed like this.

4.5. General procedure: RCM reactions

The supported catalysts **8**–**11** were placed in a reaction tube under air and the α,ω-olefin was added from a stock solution (1 mL, 50 μmol, 0.05 M in CH_2Cl_2). The reaction mixture was shaken for 2 h at 60 °C (oil bath). After cooling to r.t., the supernatant solution was removed and the solid phases were washed with CH_2Cl_2 (3 × 1.5 mL). Then, fresh substrate was added and the next run was started. The conversions were determined by ^{1}H-NMR.

*4.5.1. 1-(Toluene-4-sulfonyl)-2,5-dihydro-1H-pyrrole (**13a**) [45]*

^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 2.42$ (s, 3H, Ar-CH_3), 4.12 (s, 4H, CH_2CH=CHCH_2), 5.65 (s, 2H, CH_2CH=$CHCH_2$), 7.32 ($m_{AA'BB'}$, $J_{app} = 8.1$ Hz, 2H, arom.), 7.72 ($m_{AA'BB'}$, $J_{app} = 8.1$ Hz, 2H, arom.); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 21.6$, 54.9, 125.5, 127.5, 129.8, 134.4, 143.5; MS–EI (70 eV): *m/z* (%) = 223 (50) [M^+], 155 (52), 91 (92), 86 (13), 84 (20), 68 (100), 65 (24), 41 (24).

*4.5.2. 1-(Toluene-4-sulfonyl)-2,3,4,7-tetrahydro-1H-azepine(**13b**) [46]*

^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.80$ (m_c, 2H), 2.18 (m_c, 2H), 2.41 (s, 3H, CH_3—Ar), 3.39 (t, $J = 6.1$ Hz, 2H, N—CH_2—CH_2—), 3.83 (d, $J = 4.5$ Hz, 2 H, NCH_2CH=CH—), 5.64 (dt, $J = 5.1$, 10.6 Hz, 1H, H-2/H-3), 5.77 (dt, $J =$ Hz, 5.3, 10.9 Hz, 1H, H-2/H-3), 7.28 ($m_{AA'BB'}$, $J_{app} = 8.2$ Hz, 2H, arom.), 7.68 ($m_{AA'BB'}$, $J_{app} = 8.1$ Hz, 2H, arom.); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 21.5$, 26.9, 31.0, 46.4, 49.7, 126.7, 127.3, 129.6, 133.0, 136.5, 143.1; MS–EI (70 eV): *m/z* (%) = 251 (100) [M^+], 236 (7), 184 (85), 155 (40), 96 (87), 91 (37), 69 (35), 67 (30), 41 (24).

*4.5.3. 3-Methyl-1-[(4-methylphenyl)sulfonyl]-2,5-dihydro-1H- pyrrole (**13c**) [23]*

^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.66$ (m_c, 3H, CH=C(CH_3)CH_2), 2.43 (s, 3H, SO_2PhCH_3), 3.95–3.98 (m, 2H), 4.05–4.09 (m, 2H), 5.25 (m_c, 1H, CH_2CH=C(CH_3)CH_2), 7.32 (m, 2H, arom.), 7.72 (m, 2H, arom.); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 14.1$, 21.5, 55.1, 57.7, 119.1, 127.5, 129.7, 134.4, 135.1, 143.3; GC/MS–EI (70 eV); *m/z* (%) = 237 (22) [M^+], 236 (16), 222 (23) [$C_{11}H_{12}NO_2S^+$], 172 (5), 155 (92) [$C_7H_7O_2S^+$], 91 (67) [$C_7H_7^+$], 82 (100) [$C_5H_8N^+$], 80 (10), 67 (7), 65 (17), 55 (10).

*4.5.4. 5-Methyl-1-[(4-methylphenyl)sulfonyl]-1,2,3,6-tetrahydropyridine (**13d**) [23]*

^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.64$–1.66 (m, 3H, CH_2C(CH_3)=CHR), 2.08–2.13 (m, 2H, NCH_2CH_2), 2.42 (s, 3H, SO_2PhCH_3), 3.16 (t, $J = 5.8$ Hz, 2H, NCH_2CH_2), 3.52 (ddq, $J = 5.5$, 2.3, 2.3 Hz, 2H, NCH_2CH=C(CH_3)-CH_2), 5.30 (ddq, $J = 6.5$, 3.2, 1.6 Hz, 1H, CH_2CH=C(CH_3)CH_2), 7.31 ($m_{AA'BB'}$, $J_{app} = 8.2$ Hz, 2H, arom.), 7.67 ($m_{AA'BB'}$, $J_{app} = 8.2$ Hz, 2H, arom.); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 21.5$, 22.9, 30.0, 42.9, 44.8, 116.6, 127.7, 129.6, 132.8, 133.4, 143.4; GC/MS–EI (70 eV); *m/z* (%) = 252 (14), 251 (100) [M^+], 237 (14), 236 (92) [$C_{12}H_{14}NO_2S^+$], 155 (61) [$C_7H_7O_2S^+$], 147 (6), 96 (70) [$C_6H_{10}N^+$], 94 (29), 91 (47) [$C_7H_7^+$], 69 (55), 68 (15), 67 (12), 65 (14), 53 (6), 41 (25).

*4.5.5. Cyclopent-3-ene-1,1-dicarboxylic acid diethyl ester (**13e**) [47]*

^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.25$ (t, $J = 7.1$, 6 H, —CH_2CH_3), 3.01 (s, 4H, —CH_2—CH=CH—CH_2—), 4.20 (q, $J = 7.1$, 4H, —CH_2CH_3), 5.61 (s, 2H, —CH_2—CH=CH—CH_2—); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 14.0$, 40.9, 58.9, 61.2, 127.8, 172.3; MS–EI (70 eV): *m/z* (%) = 212 (63) [M^+], 166 (60), 138 (100), 111 (38), 93 (32), 79 (40), 66 (54).

*4.5.6. (Cyclopent-2-enyloxymethyl)-benzene (**13f**) [48]*

^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.82$–1.89 (m, 1H, H_A-4′/H_B-4′), 2.12–2.19 (m, 1H, H_A-4′/H_B-4′), 2.23–2.30 (m, 1H, H_A-5′/H_B-5′), 2.47–2.55 (m, 1H, H_A-5′/H_B-5′), 4.51 (d, $J_{AB} = 11.7$ Hz, 1H, HCH—Ar), 4.55 (d, $J_{AB} = 11.7$ Hz, 1H, HCH—Ar), 4.67 (m_c, 1H, >CHOR), 5.88–5.91 (m, 1H, H-3′), 6.01–6.04 (m, 1H, H-2′), 7.24–7.37 (m, 5H, arom.); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 29.8$, 31.1, 70.6, 84.5, 127.4, 127.8, 128.3, 130.8, 135.7, 138.9; MS–CI (NH_3, 130 eV): *m/z* (%) = 192 (12) [$(M + NH_4)^+$], 175 (4) [$(M + H)^+$], 157 (10), 126 (21), 108 (17), 91 (36), 84 (100), 67 (7).

*4.5.7. (Cyclohex-2-enyloxymethyl)-benzene (**13g**) [49]*

^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.51$–1.59 (m, 1H), 1.71–1.89 (m, 3H), 1.91–1.99 (m, 1H), 2.02–2.10 (m, 1H),

3.93–3.98 (br m, 1H, H-1), 4.55 ($d_{AA'}$, $J = 12.0$ Hz, 1H, C*H*HO), 4.61 ($d_{AA'}$, $J = 12.0$ Hz, 1 H, CH*H*O), 5.79–5.89 (m, 2H, H-2/H-3), 7.24–7.37 (m, 5H, arom.); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 19.3$, 25.3, 28.4, 70.0, 72.2, 127.4, 127.6, 127.8, 128.3, 130.9, 139.1; MS–EI (70 eV): m/z (%) = 188 (5) [M^+], 130 (9), 97 (48), 91 (100), 84 (8), 81 (13), 79 (13), 77 (7), 69 (22), 65 (11), 55 (10), 41 (15).

*4.5.8. 2-Phenyl-3,6-dihydro-2H-pyran (**13h**) [50]*

^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.20$–2.44 (m, 2H), 4.33–4.39 (m, 2H), 4.56 (dd, $J = 3.8$, 10.0 Hz, 1H, O–CH—Ar), 5.77–5.85 (m, 1H), 5.88–5.96 (m, 1H), 7.25–7.41 (m, 5H, arom.); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 32.9$, 66.6, 75.7, 124.5, 125.9, 126.4, 127.5, 128.4, 142.6; MS–EI (70 eV): m/z (%) = 160 (16) [M^+], 105 (100), 77 (18), 54 (75).

4.6. General procedure CM-reactions

Both terminal olefins (each 1 equiv.) were placed in a reaction tube under air (0.2 mL CH_2Cl_2, 0.25 M). The reaction was started by adding the catalyst. The reaction mixture was shaken for 2 h at 60 °C (oil bath). After cooling to r.t., the supernatant solution was removed and the solid phases were washed with CH_2Cl_2 (3×1.5 mL). Then, fresh substrate was added and the next run was started. The conversions were determined by ^{1}H NMR.

*4.6.1. (2E)-4-Trimethylsilanyl-but-2-enoic-acid-benzylester (**14a**)*

^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.04$ (s, 9H, —Si(C*H*$_3$)$_3$), 1.72 (d, $J = 8.9$ Hz, 2H, —C*H*$_2$Si), 5.15 (s, 2H, PhC*H*$_2$), 5.70 (d, $J = 15.4$ Hz, ROOCC*H*=), 7.08 (dt, $J = 15.4$, 8.9 Hz, =C*H*CH$_2$), 7.29–7.35 (m, 5H, arom.); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 0.0$, 26.9, 67.6, 120.5, 129.86, 129.92, 130.3, 138.3, 150.6, 168.5; MS–CI (NH_3, 130 eV); m/z (%) = 268 (7), 267 (21), 266 (100), 249 (25), 194 (15), 108 (9), 90 (6); Anal. Calc. for $C_{14}H_{20}O_2Si$: C 67.70, H 8.12; found: C 67.83, H 8.00%.

*4.6.2. 1,1′-(E)-Ethene-1,2-diylbis(4-methoxybenzene) (**14b**)*

Mp.: 214–216 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 3.81$ (s, 6H, OC*H*$_3$), 6.87 ($m_{AA'BB'}$, $J_{app} = 8.6$ Hz, 2H, arom.), 6.91 (s, 2H, C*H*=C*H*), 7.41 ($m_{AA'BB'}$, $J_{app} = 8.6$ Hz, 2H, arom.); ^{13}C NMR (100.6 MHz, CD_2Cl_2): $\delta = 55.6$, 114.4, 126.4, 127.7, 130.8, 159.5; GC/MS–EI (70 eV); m/z (%) = 241 (17), 240 (100) [M^+], 226 (8), 225 (48) [$M^+ - CH_3$], 182 (13), 181 (8), 166 (12), 165 (33), 154 (8), 153 (20), 152 (14), 120 (13); Anal. Calc. for $C_{16}H_{16}O_2$: C 79.97, H 6.71; found: C 79.99, H 6.67%.

*4.6.3. Benzyl-(2E)-7-(acetyloxy)hept-2-enoate (**14c**)*

^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.49$–1.57 (m, 2H), 1.61–1.69 (m, 2H), 2.04 (s, 3H, OC(O)C*H*$_3$), 2.24 (dtd, $J = 7.2$, 7.2, 1.5 Hz, 2H, CH=CHC*H*$_2$), 4.06 (t, $J = 6.4$ Hz, 2H, C*H*$_2$OAc), 5.17 (s, 2H, PhC*H*$_2$O), 5.88 (dt, $J = 15.6$, 1.5 Hz, 1H, C*H*=CHCH$_2$), 7.00 (dt, $J = 15.6$, 6.9 Hz, 1H, CH=C*H*CH$_2$), 7.33–7.38 (m, 5H, arom.); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 21.0$, 24.4, 28.1, 31.7, 64.0, 66.1, 121.5, 128.2, 128.2, 18.6, 136.1, 149.1, 166.4, 171.1; MS–EI (70 eV): m/z (%) = 276 (1) [M+], 216 (6) [$C_{14}H_{17}O_2^+$], 169 (15), 156 (18), 127 (97), 110 (32), 107 (30) [$C_7H_7O^+$], 91 (100) [$C_7H_7^+$], 81 (50), 68 (13), 43 (10) [$C_2H_3O^+$].

4.7. General procedure ROM-reactions

Dicyclopentadiene and the terminal olefin (each 1 equiv.) were placed in a reaction tube under air (CH_2Cl_2, 1 mL, 0.07 M). The reaction was started by adding the catalyst. The reaction mixture was shaken for 2 h at 60 °C (oil bath). After cooling to r.t., the supernatant solution was removed and the solid phases were washed with CH_2Cl_2 (3×1.5 mL). Then, fresh substrate was added and the next run was started. The conversions were determined by ^{1}H-NMR.

*4.7.1. Mixture of (2E)-3-(3-Vinyl-1,2,3,3a,4,6a-hexahydropentalene-1-yl)-prop-2-ene-1- trimethylsilane (**17a**) and (2E)-3-(3-Vinyl-1,2,3,3a,6,6a-hexahydropentalene-1-yl)-prop-2-ene-1- trimethylsilane (**17b**)*

^{1}H NMR (500 MHz, $CDCl_3$): $\delta = -0.01$ (s, 6H), 0.015 (s, 1H), 0.018 (s, 2H), 1.20–1.30 (m, 1H, CH*H*), 1.41–1.45 (m, 2H, C*H*$_2$SiMe$_3$), 1.54–1.61 (m, 1H, C*H*H), 2.23–2.29 (m, 2H, C*H*$_2$), 2.53–2.69 (m, 2H, $2 \times$ C*H*), 2.76–2.89 (m, 1H, C*H*), 3.18–3.29 (m, 1H, C*H*), 4.92–5.04 (m, 2H, =C*H*$_2$), 5.12–5.32 (m, 1H, =C*H*), 5.34–5.45 (m, 1H, C*H*=CH$_2$Si), 5.47–5.55 (m, 1H, =C*H*), 5.64–5.72 (m, 1H, =C*H*), 5.74–5.92 (m, 1H, C*H*=CH$_2$); ^{13}C NMR (125.7 MHz, $CDCl_3$): $\delta = -1.9$, −1.7, 22.8, 35.0, 35.3, 43.9, 47.0, 47.4, 55.3, 114.3, 125.8, 130.3, 131.1, 131.4, 140.4; GC/MS–CI (NH_3, 130 eV); m/z (%) = 248 (21), 247 (100), 246 (6) [M^+], 245 (10), 173 (4), 172 (4), 90 (56), 73 (3).

Acknowledgements

We thank Fluka for AAS-measurements and Novabiochem, Rapp-Polymers and VitraBio GmbH for samples of solid supports. Also, we would like to thank Dr. M. Keller, Mrs. M. Schonhard and Mr. F. Reinbold for recording NMR spectra, Mr. C. Warth and Dr. J. Wörth for recording MS spectra, Mr. E. Hickl for performing elemental analyses and Mrs. S. Hirth-Walter for performing AAS.

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