Formation of Dinuclear Titanium and Zirconium Complexes by Olefin Metathesis—Catalytic Preparation of Organometallic Catalyst Systems

Jesus Cano Sierra, Doris Hüerländer, Michael Hill, Gerald Kehr, Gerhard Erker,* and Roland Fröhlich[+][a]

Abstract: The titanium complex [(C_5H_4–allyl)$TiCl_3$] (**2**) undergoes olefin metathesis coupling when treated with 3 mol% of [$Cl_2(L^1)(L^2)$Ru=CHPh] ($L^1 = L^2 = PCy_3$, **4a**; $L^1 = PCy_3$, $L^2 = (H_2IMes)$, **4b**) to yield the dimetallic complex [$Cl_3Ti(C_5H_4)$-CH_2CH=$CHCH_2$-(C_5H_4)$TiCl_3$] (**5**). The allyl-substituted titanocene complex [$Cp(C_5H_4$–allyl)$TiCl_2$] (**3**) analogously yields the dimetallic system **6** when treated with **4**. The ansa-zirconocene complex [$Me_2Si(C_5H_4)(C_5H_3$–allyl)$ZrCl_2$] (**7**) cleanly yields the analogous dimetallic coupling product **8** (>95% isomerically pure), when treated with catalytic amounts of **4b** in toluene. Complex **8** gives an active homogeneous ethene or propene polymerization catalyst, especially at elevated temperatures, when treated with excess methylalumoxane.

Keywords: catalysis · olefin metathesis · metallocenes · ruthenium · titanium · zirconium

Introduction

The Group 4 metallocenes and related compounds have become of great importance in view of their enormous potential as components in catalysis. Devising novel synthetic pathways for the selective preparation of specifically substituted and functionalized $CpML_n$ complexes of the Group 4 metals has become increasingly important because of the extensive use of such organometallic compounds in polymerization catalysis,[1] but also in catalytic organic synthesis.[2] In contrast to their late transition-metal analogues,[3] the use and transformation of functional groups at the Cp rings of these early transition-metal compounds has been rather limited.[4] Introduction of, for example, carbonyl functions usually must be carried out at the free ligand stage, that is before attachment to the oxophilic d-block metal.[5] We have investigated possible ways aimed at establishing specific functional group chemistry at the stage of the cyclopentadienyltitanium or -zirconium complexes.[4, 6] The many recent advances reported with regard to metal-catalyzed olefin metathesis reactions[7, 8] prompted us to search for potential applications of such methods for synthetic transformations in substituted-Cp Group 4 metal complex chemistry. First examples of intramolecular olefin metathesis coupling reactions leading to ansa-zirconocenes were independently disclosed recently by our group[9] and by Hayashi et al.[10] We have now applied this methodology for the intermolecular coupling reaction of [(allyl-Cp)$M^{IV}L_n$] precursors to yield novel dimetallic systems that may find some potential application in homogeneous Ziegler–Natta catalysis and related catalytic processes. Here we describe several examples in which organometallic catalyst precursors were prepared by metal-catalyzed pathways.

Results and Discussion

The titanium complexes used in this study were prepared by conventional methods. Treatment of allyl bromide with CpNa, followed by deprotonation with *n*-butyllithium gave **1**, which was then silylated and converted to the titanium complex **2** by the reaction with $TiCl_4$. Subsequent treatment of **2** with CpLi gave the substituted titanocene dichloride complex **3** (Scheme 1).[11]

Complex **3** was subjected to an intermolecular olefin metathesis reaction. For this purpose a solution of **3** (ca. 0.2 M) in toluene was treated with [$Cl_2(PCy_3)_2$Ru=CHPh][12] (**4a**, 3 mol%). The reaction mixture was kept at 80 °C for 5 h to give a 3:1 mixture of the organometallic metathesis products *trans*-**5** and *cis*-**5**, which were isolated in a combined yield of about 40% (Scheme 2). A similar result was obtained when the reaction was carried out in dichloromethane or benzene. We have also employed a "second-generation" metathesis catalyst[12c, 13] (**4b**). In this case the pure *trans*-**5**

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[+] X-ray crystal structure analyses.

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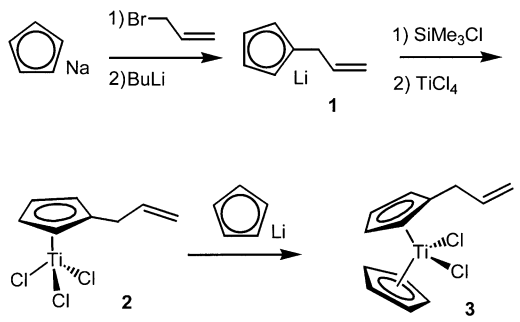
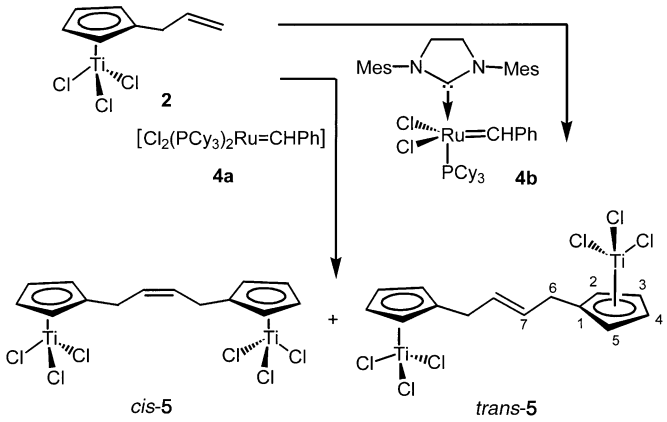


Scheme 1. Synthesis of **3**.



Scheme 2. Reaction of **2** with catalysts **4a** and **4b** to give *cis*-**5** and *trans*-**5**.

isomer was obtained from the reaction performed in benzene or toluene (Scheme 2).

Complex *trans*-**5** is characterized by two ^{1}H NMR multiplets of the two symmetry-equivalent C_5H_4 moieties at $\delta = 6.94$ and 6.84 ppm, a CH_2 multiplet at $\delta = 3.63$ ppm (6-H) and the olefin (7-H) resonance at $\delta = 5.79$ ppm. From the ^{13}C satellite signals in the ^{1}H NMR spectrum a $^{3}J(7\text{-}^{1}H, 7\text{-}^{1}H^{*})$ coupling constant of 16 Hz was obtained [GHSQC{selectively decoupled at 6-H}:[14] $^{1}J(^{13}C7, 7\text{-}^{1}H) = 157$ Hz]. The coproduct (*cis*-**5**) showed similar signals [$\delta^{1}H = 3.72$ (6-H), $\delta = 5.87$ ppm (7-H)] and a very characteristic set of coupling constants $^{3}J(7\text{-}^{1}H, 7\text{-}^{1}H^{*}) = 12$ Hz [$^{1}J(^{13}C7, 7\text{-}^{1}H) = 157$ Hz] that was used to assign the two obtained isomers as *trans*-**5** and *cis*-**5**, respectively.

From a concentrated solution of the mixture in benzene, single crystals of *trans*-**5** were obtained that were suitable for an X-ray crystal structure determination (Figure 1). The complex features a pseudotetrahedral coordination geometry around the titanium center: Ti–Cl1 2.2225(6), Ti–Cl3 2.2308(7), Ti–Cl2 2.2387(7) Å; Cl-Ti-Cl 101.55(3) – 104.47(3)°. The two $TiCl_3$ subunits and their adjacent organic ligand frameworks are symmetry equivalent (C_i symmetry). The monosubstituted R-C_5H_4 ring is η^5-coordinated to the titanium center; the Ti–C1 linkage (2.389(2) Å) is slightly longer than the proximal Ti–C2/C5 (2.333(2)/2.342(2) Å) and the distal Ti–C3/C4 (2.317(2)/2.311(2) Å) bonds. Inside the η^5-C_5H_4 ligand the C–C bonds range between 1.397(3) and 1.416(3) Å. The bond to the bridging butenediyl substituent is longer (C1–C6 1.500(3) Å), and almost identical to the C6–C7 bond length (1.498(3) Å; C1-C6-C7 114.2(2)°). The C7–C7* bond (1.311(4) Å) is in the expected range for a C–C double bond (C7*-C7-C6 124.2(2)°). The butenediyl unit is planar and *trans*-configurated. However, it is markedly rotated out of the C1–C6 plane with the C7=C7* double bond arranged away from the respective metal center (dihedral angles $\theta 1$: C5-C1-C6-C7 20.7(3)°, $\theta 2$: C1-C6-C7-C7* –118.3(3)°).

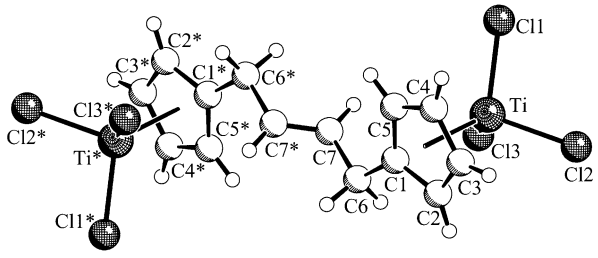
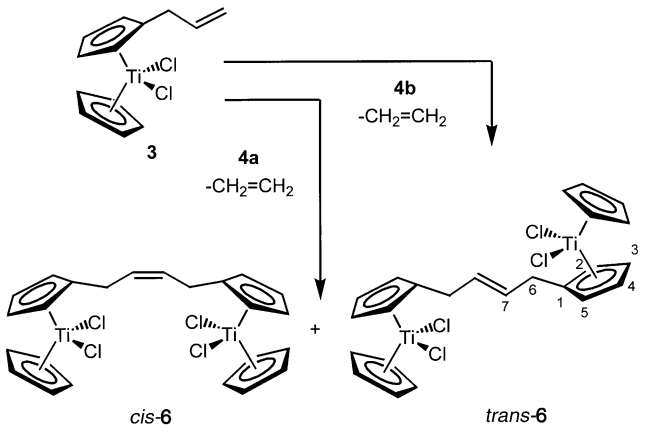


Figure 1. A view of the molecular structure of complex *trans*-**5**. For selected bond lengths and angles see the text.

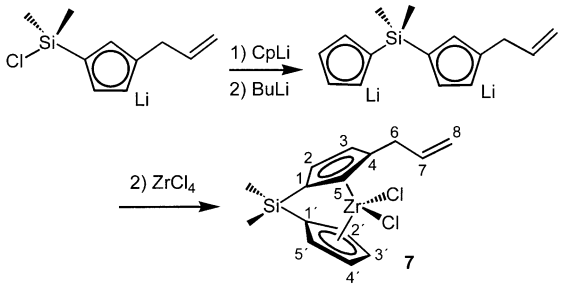
The allyl-Cp substituted titanocene dichloride complex **3** was similarly coupled by means of catalytic olefin metathesis. Treatment of **3** with 3 mol% of the ruthenium carbene complex **4a** in benzene, toluene, or dichloromethane furnished a mixture of *cis*-**6** and *trans*-**6** in a 1:1 ratio (ca. 40 – 50% isolated; Scheme 3). Similarly, treatment of **3** with the advanced catalyst system **4b** gave the pure *trans*-**6** isomer. Complex *trans*-**6** shows an olefinic 7-^{1}H NMR resonance signal at $\delta = 5.62$ ppm with a typical vicinal *trans*-coupling constant of $^{3}J(7\text{-}^{1}H, 7\text{-}^{1}H^{*}) = 16$ Hz (6-CH_2 signal at $\delta =$ 3.49 ppm, Cp resonance at $\delta = 6.53$ ppm), whereas the *cis*-**6** isomer is characterized by a 7-^{1}H resonance signal at $\delta = 5.65$ [$^{3}J(7\text{-}^{1}H, 7\text{-}^{1}H^{*}) = 12$ Hz].



Scheme 3. Reaction of **3** with catalysts **4a** and **4b** to give *cis*-**6** and *trans*-**6**.

We have applied the olefin metathesis reaction also for coupling of two ansa-zirconocene units. The dimethylsilanediyl-bridged ansa-metallocene complex **7** was prepared as depicted in Scheme 4 (57% yield).[15] Single crystals of **7** suitable for an X-ray structure determination (Figure 2) were obtained from a concentrated solution of the compound in chloroform with a few drops of benzene.

Complex **7** contains an element of planar chirality. Coupling of two such units by metathesis, therefore, should in principle lead to two diastereoisomers (*rac* and *meso*). Together with the possibility of the formation of *cis*- and



Scheme 4. Synthesis of **7**.

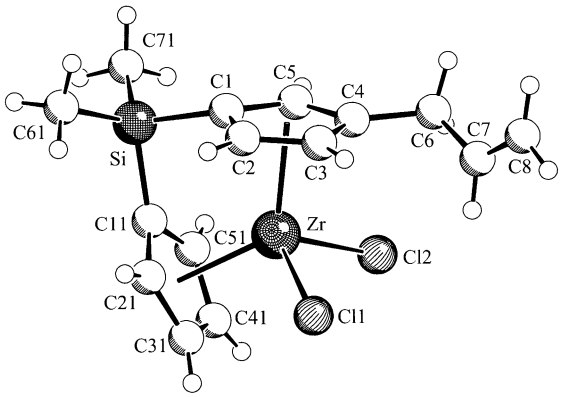


Figure 2. Molecular geometry of **7**. Selected bond lengths [Å] and angles [°]: Zr–Cl1 2.4294(7), Zr–Cl2 2.4286(6), Si–C1 1.866(2), Si–C11 1.860(2), Si–C61 1.847(2), Si–C71 1.845(2), C1–C2 1.424(3), C1–C5 1.420(3), C2–C3 1.410(3), C3–C4 1.389(3), C4–C5 1.414(3), C4–C6 1.508(3), C6–C7 1.493(4), C7–C8 1.304(4); Cl1-Zr-Cl2 98.74(3), C1-Si-C11 94.0(1), C1-Si-C61 110.1(1), C1-Si-C71 111.7(1), C11-Si-C61 112.7(1), C11-Si-C71 113.2(1), C61-Si-C71 113.7(1), C4-C6-C7 112.0(2), C6-C7-C8 125.9(3), C4-C5-C6-C7 -115.0(3).

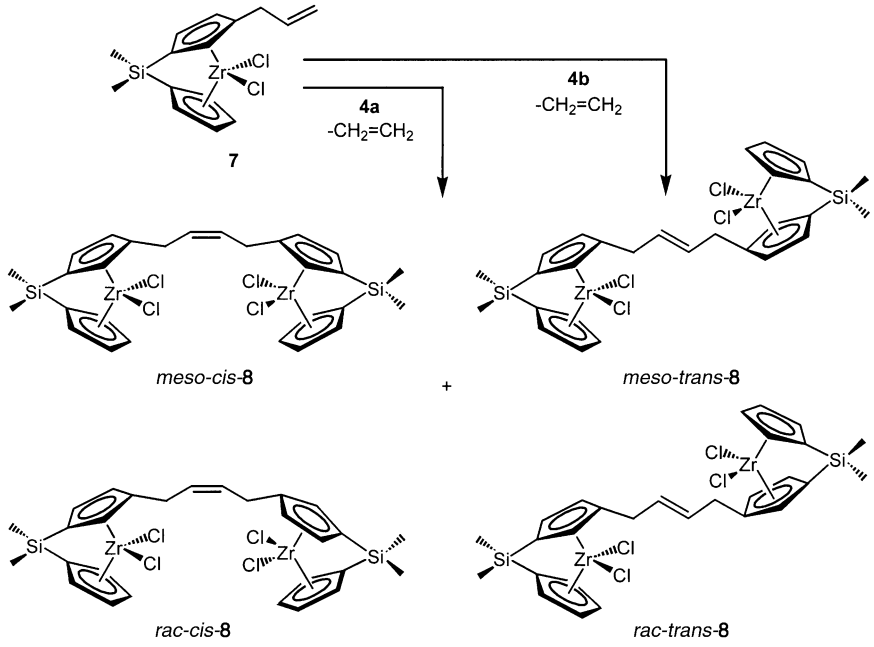
trans-1,2-disubstituted alkenes this makes a total of four possible stereoisomeric products that can be formed (see Scheme 5). Treatment of **7** with $[Cl_2(PCy_3)_2Ru{=}CHPh]$ (**4a**) in dichloromethane (2 h, reflux) gave a mixture of products, in which a single isomer predominates (ca. 80%) as judged from the $SiMe_2$ ^1H NMR pair of signals at $\delta = 0.74$ and 0.70 ppm. The reaction of **7** with catalytic amounts of **4a** or **4b** in benzene or toluene was more selective, yielding a single coupling product that was obtained >95% pure. We assume that it is one of the two *trans* isomers, but whether *rac*- or *meso*-**8** formation prevails is not clear at present.

We have briefly tested the catalytic features of the dimetallic ansa-metallocene system **8**. Accordingly, the isolated dizirconium complex was activated by treatment with a large excess of methylalumoxane in toluene. Only a rather low polymerization activity was displayed in ethene polymerization at room temperature, but the system **8**/MAO turned out to be a quite active ethene polymerization catalyst at 60 °C, yielding linear polyethylene (Table 1). Likewise, the **8**/MAO catalyst system polymerizes propene at both 25 °C and 60 °C with a reasonable catalyst activity to yield a typical rather low molecular weight polypropylene (Table 2).[16] Only slightly *isotactic* polypropylene was obtained at ambient temperature (36% *mmmm* intensity in the ^{13}C NMR methyl pentade analysis, the stereocontrol takes place by an enantiomorphic site control mechanism[17]). The polypropylene sample obtained at 60 °C was close to atactic (12% *mmmm*).

Table 1. Ethene polymerization with the **7**/MAO and **8**/MAO catalyst systems.[a]

Complex	T [°C]	Al/Zr	g PE	A[b]	M.p.
7	25	1200	3.6	360	126
8	25	1700	1.1	340	127
7	60	1200	49.4	9900	126
8	60	2000	23.0	7800	128

[a] Reaction in toluene, 10 min, 2 bar ethene. [b] Catalyst activities (A) in kg polyethylene/(mol Zr · h · bar(ethene)).



Scheme 5. Reaction of **7** with catalysts **4a** and **4b** to give *meso-cis*-**8** and *meso-trans*-**8**, *rac-cis*-**8**, and *rac-trans*-**8**.

The Ru–carbene complex catalyzed olefin metathesis reaction is increasingly being applied in organic synthesis. One reason for this development is its wide compatibility with functional groups present in substrates and products.[7] This, and the few other emerging studies[8–10] have shown that this C–C coupling methodology is even compatible with the very sensitive organometallic bent metallocene "functional group". We regard this as a major advantage in synthetic organometallic chemistry that will probably open up a variety of entries to novel active catalyst systems, especially of homo- and heterodi- and multimetallic nature. "Double catalysis", that is the catalytic preparation of organometallic catalysis systems, such as represented by the examples featured in this article seems to be an increasingly attractive and useful concept in synthetic homogeneous catalysis.

Table 2. Propene polymerization with the **7**/MAO and **8**/MAO catalyst systems.[a]

Complex	T [°C]	Al/Zr	g PP	A[b]	M_n[c]	PDI[c]	% mmmm[d]
7	25	1050	12.7	350	1300	2.0	33
8	25	1750	4.5	220	1650[e]	3.0[e]	36
7	60	1050	18.8	540	500	1.5	8
8	60	1750	7.1	340	675	2.1	12

[a] Reaction in toluene, 30 min, 2 bar propene. [b] Catalyst activities (A) in kg polypropylene/(mol Zr · h · bar(propene)). [c] Molecular weight [M_n] and polydispersities (PDI) were determined by GPC using a polystyrene standard. [d] Determined from a ^{13}C NMR methyl pentade analysis. [e] Bimodal distribution.

Experimental Section

General: All reactions were carried out under dry argon in Schlenk-type glassware or in a glove box. Solvents, including deuterated solvents used for NMR spectroscopy, were dried and distilled prior to use. For additional general conditions, including a list of instruments used for a physical characterization of the compounds, see ref. [9]. Most NMR assignments were secured by carrying out a variety of 2D NMR experiments.[18] The titanium complex **3** was prepared according to the literature procedure[11].

X-ray crystal structure analyses: Data sets were collected with a Nonius KappaCCD diffractometer, equipped with a rotating-anode generator Nonius FR591. Programs used: data collection COLLECT (Nonius B.V., 1998), data reduction Denzo-SMN (Z. Otwinowski, W. Minor, *Methods in Enzymology*, **1997**, *276*, 307–326), absorption correction SORTAV (R.H. Blessing, *Acta Crystallogr. Sect. A* **1995**, *51*, 33–37; R. H. Blessing, *J. Appl. Crystallogr.* **1997**, *30*, 421–426), structure solution SHELXS-97 (G. M. Sheldrick, *Acta Crystallogr. Sect. A* **1990**, *46*, 467–473), structure refinement SHELXL-97 (G. M. Sheldrick, Universität Göttingen, **1997**), graphics SCHAKAL (E. Keller, Universität Freiburg, **1997**).

CCDC-201229(**7**), CCDC-201230 (**5** · C_6H_6), and CCDC-201231(**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.can.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Center, 12 Union Road, Cambridge CB21EZ, UK; Fax: (+44) 1223-336033; or deposit@ccdc.cam.ac.uk).

[η^5-(2-Propen-1-yl)cyclopentadienyl]trichlorotitanium (2): A solution of [(2-propen-1-yl)cyclopentadienyl]trimethylsilane (2.12 g, 11.8 mmol) in toluene (20 mL) was added to a solution of $TiCl_4$ (2.25 g, 11.8 mmol) at 0 °C in the same solvent. After the resulting red solution had been stirred overnight at room temparature, the solvent was removed under reduced pressure. Extraction with pentane (2 × 50 mL) provided compound **2** as a yellow crystalline solid (2.76 g; 90 %). ^1H NMR ($CDCl_3$): $\delta = 6.94$ (m, 2H; 2,5-H), 6.93 (m, 2H; 3,4-H), 5.92 (m, 1H; 7-H), 5.20 (m, 2H; 8-H), 3.60 ppm (m, 2H; 6-H); $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 142.3$ (C7), 133.7 (C1), 123.6 (C2, C5), 123.0 (C3, C4), 118.6 (C8), 35.7 ppm (C6); elemental analysis calcd (%) for $C_8H_9Cl_3Ti$ ($M_r = 259.4$): C 37.04, H 3.50; found: C 37.38, H 3.50.

[η^5-(2-Propen-1-yl)cyclopentadienyl](η^5-cyclopentadienyl)dichlorotitanium (3)[11]: A suspension of cyclopentadienyllithium (0.50 g, 6.92 mmol) in toluene (20 mL) was added to a solution of [η^5-(2-propen-1-yl)cyclopentadienyl]trichlorotitanium (1.80 g, 6.92 mmol) at −20 °C in the same solvent. After the resulting red solution had been stirred for 3 h at 60 °C, the mixture was filtered and the solvent was removed under reduced pressure to provide compound **3** as a red solid (2.01 g; 92 %). ^1H NMR ($CDCl_3$): $\delta =$ 6.54 (s, 5H; C_5H_5), 6.42 (m, 2H; 2,5-H), 6.34 (m, 2H; 3,4-H), 5.95 (m, 1H; 7-H), 5.08 (m, 2H; 8-H), 3.49 ppm (m, 2H; 6-H); $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 136.9$ (C7), 135.6 (C1), 122.5, 116.1 (C2-C5), 119 (Cp), 117.0 (C8), 35.1 ppm (C6).

[Dimethylsilandiyl{η^5-(2-propen-1-yl)cyclopentadienyl}(η^5-cyclopentadienyl)]dichlorozirconium (7): Chilled toluene (250 mL, −78 °C) was added to a solid mixture of dilithio[(2-propen-1-yl)cyclopentadienyl](cyclopentadienyl)dimethylsilane (3.47 g, 14.5 mmol) and $ZrCl_4$ (3.37 g, 14.5 mmol). The suspension immediately became yellow and was allowed to warm to room temperature with stirring. After the mixture had been stirred overnight, the yellow suspension was filtered through celite. Removal of the volatiles in vacuo provided the product **7** as a yellow solid (3.23 g; 57 %). Suitable crystals for an X-ray crystal structure analysis were obtained from a concentrated solution in toluene at −30 °C. M.p. 104 °C. ^1H NMR ($CDCl_3$): $\delta = 7.03$ (m, 1H; 4-H′), 6.93 (m, 1H; 3-H′), 6.60 (m, 1H; 3-H), 5.98 (m, 1H; 2-H′), 5.92 (m, 2H; 2-H, 7-H), 5.82 (m, 1H; 5-H′), 5.54 (m, 1H; 5-H), 5.06, 5.04 (each m, each 1H; 8-H, 8-H′), 3.47, 3.38 (each m, each 1H; 6-H, 6-H′), 0.72, 0.69 (each s, each 3H; $Si(CH_3)_2$); $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 141.0$ (C4), 135.9 (C7), 128.0 (C3), 127.8 (C3′), 127.7 (C4′), 116.7 (C8), 115.3 (C2), 114.1 (C2′), 113.6 (C5′), 113.5 (C5), 107.9 (C1), 107.8 (C1′), 34.3 (C6), −5.1, −5.3 ppm ($Si(CH_3)_2$); elemental analysis calcd (%) for $C_{15}H_{18}SiCl_2Zr$ ($M_r = 388.5$): calcd C 46.37, H 4.67; found: C 46.26, H 4.70.

X-ray crystal structure analysis of **7**: $C_{15}H_{18}SiCl_2Zr$, $M_r = 388.5$, light yellow crystal, 0.20 × 0.15 × 0.05 mm, $a = 8.305(1)$, $b = 8.432(1)$, $c = 12.289(1)$ Å, $\alpha = 90.74(1)$, $\beta = 96.40(1)$, $\gamma = 108.70(1)°$, $V = 809.0(2)$ Å^3, $\rho_{calcd} = 1.595$ g cm^{-3}, $\mu = 10.68$ cm^{-1}, empirical absorption correction by SORTAV ($0.815 \le T \le 0.949$), $Z = 2$, triclinic, space group $P\bar{1}$ (no. 2), $\lambda = 0.71073$, $T =$ 198 K, ω and ϕ scans, 5175 reflections collected ($\pm h, \pm k, \pm l$), [$(\sin\theta)/\lambda$] = 0.65 Å^{-1}, 3669 independent ($R_{int} = 0.021$) and 3169 observed reflections [$I \ge 2\,\sigma(I)$], 174 refined parameters, $R = 0.030$, $wR^2 = 0.061$, max. (min.) residual electron density 0.31 (−0.44) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

Olefin metathesis reaction of 2 catalyzed by 4a: formation of *trans*-5 and *cis*-5: A solution of **2** (0.60 g, 2.30 mmol) in toluene (10 mL) was added to a solution of [$Cl_2(PCy_3)_2Ru{=}CHPh$] (**4a**) (57 mg, 3 mol %) in toluene (1 mL) and stirred for 5 h at 80 °C. The solvent was removed under reduced pressure and the resulting solid washed with pentane (2 × 25 mL) to obtain, after filtration, compound **5** in a ratio *trans*/*cis* (3/1) as an orange crystalline solid (0.22 g; 40 %). *trans*-**5**: ^1H NMR ($CDCl_3$): $\delta = 6.94$ (m, 2H; 2,5-H), 6.84 (m, 2H; 3,4-H), 5.79 (m, 1H; 7-H), 3.63 ppm (m, 2H; 6-H); $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 142.1$ (C1), 129.6 (C7), 123.6 (C2, C5), 122.9 (C3, C4), 34.4 ppm (C6); $^1H-^{13}C$ GHSQC{selectively decoupled at 6-H} ($CDCl_3$): $\delta^{13}C/\delta^1H = 129.6/5.79$ (C7/7-H dd $^1J(^{13}C\text{-}7, 7\text{-}^1H) = 157$ Hz, $^3J(7\text{-}^1H, 7\text{-}^1H^*) =$ 16 Hz). *cis*-**5**: ^1H NMR ($CDCl_3$): $\delta = 6.94$ (m, 2H; 2,5-H), 6.84 (m, 2H; 3,4-H), 5.87 (m, 1H; 7-H), 3.72 ppm (m, 2H; 6-H); $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta =$ 142.1 (C1), 127.8 (C7), 123.6 (C2, C5), 122.8 (C3, C4), 29.7 ppm (C6); $^1H-^{13}C$ GHSQC{selectively decoupled at 6-H} ($CDCl_3$): $\delta^{13}C/\delta^1H = 127.8/5.87$ (C7/7-H dd $^1J(^{13}C\text{-}7, 7\text{-}^1H) = 157$ Hz, $^3J(7\text{-}^1H, 7\text{-}^1H^*) = 12$ Hz); elemental analysis calcd (%) for $C_{14}H_{14}Cl_6Ti_2$ ($M_r = 490.7$): C 34.27, H 2.88; found: C 34.36, H 2.68.

Olefin metathesis reaction of 2 catalyzed by 4b: formation of *trans*-5: Analogously to the procedure described above: Compound **2** (0.10 g, 0.34 mmol) was metathesized at room temperature by treatment with [$(H_2IMes)(PCy_3)Cl_2Ru{=}CHPh$] (**4b**) (9 mg, 3 mol %). After filtration, *trans*-**5** was obtained as an orange crystalline solid (54 mg; 58 %). Crystals suitable for an X-ray crystal structure analysis were obtained from a concentrated solution in benzene.

X-ray crystal structure analysis of (*trans*-**5** · C_6H_6): $C_{14}H_{14}Cl_6Ti_2 \cdot C_6H_6$ $M_r =$ 568.8, orange crystal, 0.35 × 0.20 × 0.10 mm, $a = 7.053(1)$, $b = 9.418(1)$, $c =$ 9.542(1) Å, $\alpha = 71.38(1)$, $\beta = 76.38(1)$, $\gamma = 83.38(1)°$, $V = 583.7(1)$ Å^3, $\rho_{calcd} = 1.618$ g cm^{-3}, $\mu = 13.76$ cm^{-1}, $Z = 1$, triclinic, space group $P\bar{1}$ (no. 2), $\lambda = 0.71073$, $T = 198$ K, ω and ϕ scans, 3967 reflections collected ($\pm h$, $\pm k$, $\pm l$), [$(\sin\theta)/\lambda$] = 0.66 Å^{-1}, 2788 independent ($R_{int} = 0.018$) and 2340 observed reflections [$I \ge 2\sigma(I)$], 127 refined parameters, $R = 0.032$, $wR^2 =$ 0.071, max. (min.) residual electron density 0.35 (−0.37) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

A second set of single crystals of *trans*-**5** were obtained from a concentrated solution in chloroform with a few drops of benzene. The X-ray crystal structure analysis gave analogous results, only that in this case no solvent was included in the crystal. X-ray crystal structure analysis of solvent-free *trans*-**5a**: $C_{14}H_{14}Cl_6Ti_2$, $M_r = 490.75$, red crystal 0.15 × 0.10 × 0.05 mm, $a =$ 6.478(1), $b = 11.844(1)$, $c = 12.430(1)$ Å, $\beta = 96.13(1)°$, $V = 948.2(2)$ Å^3, $\rho_{calcd} = 1.719$ g cm^{-3}, $\mu = 16.78$ cm^{-1}, empirical absorption correction ($0.787 \le T \le 0.921$), $Z = 2$, monoclinic, space group $P2_1/n$ (no. 14), $\lambda =$ 0.71073 Å, $T = 198$ K, ω and ϕ scans, 3787 reflections collected ($\pm h$, $\pm k$, $\pm l$), [$(\sin\theta)/\lambda$] = 0.67 Å^{-1}, 2272 independent ($R_{int} = 0.036$) and 1595 observed reflections [$I \ge 2\,\sigma(I)$], 100 refined parameters, $R = 0.057$, $wR^2 =$ 0.136, max. residual electron density 0.74 (−0.53) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

Olefin metathesis reaction of 3 catalyzed by 4a: formation of *trans*-6 and *cis*-6: Analogously to the procedure described above: Compound **3** (0.50 g,

1.73 mmol) was metathesized by treatment with $[Cl_2(PCy_3)_2Ru{=}CHPh]$ (**4a**) (44 mg, 3 mol %). After filtration, compound **6** in a ratio *trans*/*cis* (1/1) was obtained as a red crystalline solid (0.22 g; 46 %). *trans*-**6**: ^{1}H NMR ($CDCl_3$): $\delta = 6.53$ (s, 5H; C_5H_5), 6.42 (m, 2H; 2,5-H), 6.33 (m, 2H; 3,4-H), 5.62 (m, 1H; 7-H), 3.49 ppm (m, 2H; 6-H); ^{13}C{^{1}H} NMR ($CDCl_3$): $\delta =$ 137.7 (C1), 129.7 (C7), 122.2 (C2, C5), 116.0 (C3, C4), 119.7 (Cp), 33.8 ppm (C6); ^{1}H – ^{13}C GHSQC{selectively decoupled at 6-H} ($CDCl_3$): δ^{13}C/δ^1H = 129.7/5.62 (C7/7-H dd ^1J(^{13}C-7, 7-^{1}H) = 157 Hz, ^3J(7-^{1}H, 7-^{1}H*) = 16 Hz); *cis*-**6**: ^{1}H NMR ($CDCl_3$): $\delta = 6.54$ (s, 5H; C_5H_5), 6.42 (m, 2H; 2,5-H), 6.37 (m, 2H; 3,4-H), 5.65 (m, 1H; 7-H), 3.57 ppm (m, 2H; 6-H); ^{13}C{^{1}H} NMR ($CDCl_3$): $\delta = 137.6$ (C1), 128.3 (C7), 122.2 (C2, C5), 115.9 (C3, C4), 119.7 (Cp), 28.9 ppm (C6); ^{1}H – ^{13}C GHSQC{selectively decoupled at 6-H} ($CDCl_3$): δ^{13}C/δ^1H = 128.3/5.65 (C7/7-H dd ^1J(^{13}C-7, 7-^{1}H) = 157 Hz, ^3J(7-^{1}H, 7-^{1}H*) = 12 Hz); elemental analysis calcd (%) for $C_{24}H_{24}Cl_4Ti_2$ ($M_r =$ 549.9): C 52.41, H 4.40; found: C 52.90, H 4.30.

Olefin metathesis reaction of 3 catalyzed by 4b: formation of *trans*-6: Analogously to he procedure described above: **3** (0.12 g, 0.41 mmol) was metathesized by treatment with $[(H_2IMes)(PCy_3)Cl_2Ru{=}CHPh]$ (**4b**) (10 mg, 3 mol %) at room temperature. After filtration, *trans*-**6** was obtained as a red crystalline solid (69 mg; 61 %).

Olefin metathesis reaction of 7 catalyzed by 4a: formation of *trans*-8 and *cis*-8: A solution of **7** (0.70 g, 1.81 mmol) in dichloromethane (100 mL) was brought to reflux temperature. Over a period of 2 h a solution of $[Cl_2(PCy_3)_2Ru{=}CHPh]$ (**4a**) (44 mg, 3 mol %) in dichloromethene (100 mL) was added by syringe pump and the mixture was stirred for an additional 2 h. The solvent was removed under reduced pressure and the resulting solid washed with pentane (2 × 25 mL) to obtain compound **8** as a yellow crystalline solid (0.5 g; 42 %). Major product 80 % (*trans*-**8**): ^{1}H NMR (CD_2Cl_2): $\delta = 7.01$ (m, 1H; 4-H′), 6.91 (m, 1H; 3-H′), 6.56 (m, 1H; 4-H), 6.01 (m, 1H; 2-H′), 5.93 (m, 2H; 2-H), 5.86 (m, 1H; 5-H′), 5.64 (m, 1H; 7-H), 5.58 (m, 1H; 5-H), 5.56 (m, 1H; 4-H) 3.40 (m, 4H; 6-H), 0.74, 0.70 ppm (each s, each 3H; $Si(CH_3)_2$); ^{13}C{^{1}H} NMR (CD_2Cl_2): $\delta =$ 142.0 (C; C-3), 130.0 (CH; C-7), 128.1 (CH; C-4′), 127.9 (CH; C3′), 127.8 (CH; C4), 115.9 (CH; C-2), 114.7 (CH; C2′), 114.0 (CH; C5′), 113.9 (CH; C5), 108.7 (C; C1), 108.6 (C1′), 33.3 (CH_2; C6), – 4.9, – 5.2 ppm ($Si(CH_3)_2$); ^{1}H – ^{13}C GHSQC{selectively decoupled at 6-H} ($CDCl_3$): δ^{13}C/δ^1H = 128.3/5.65 (C7/7-H dd ^1J(^{13}C-7, 7-^{1}H) = 155 Hz, ^3J(7-^{1}H, 7-^{1}H*) = 16 Hz); elemental analysis calcd (%) for $C_{28}H_{32}Cl_4Si_2Zr_2$ ($M_r = 657.7$): C 51.13, H 4.90; found: C 51.03, H 4.80.

Olefin metathesis reaction of 7 catalyzed by 4a: formation of *trans*-8: Analogously to the procedure described above: **7** (0.59 g, 1.51 mmol) was metathesized by treatment in toluene or benzene with $[Cl_2(PCy_3)_2Ru{=}CHPh]$ (**4a**) (38 mg, 3 mol %) at room temperature. After filtration, *trans*-**8** was obtained as a yellow solid (0.24 g; 48 %).

Olefin metathesis reaction of 7 catalyzed by 4b: formation of *trans*-8: Analogously to the procedure described above: **7** (0.59 g, 1.51 mmol) was metathesized by treatment in toluene or benzene with $[(H_2IMes)(PCy_3)Cl_2Ru{=}CHPh]$ (**4b**) (38 mg, 3 mol %) at room temperature. After filtration, *trans*-**8** was obtained as a yellow solid (0.29 g; 55 %).

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