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ORIGINAL PAPER

On the isomerization of a *trans*-dichloro to a *cis*-dichloro amide-chelated ruthenium benzylidene complex and the catalytic scope of these species in olefin metathesis

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Abstract Upon comparative NMR spectroscopy studies, the isomerization of newly disclosed dichloro [κ^2(C,O)-2-(*N*-propylaminocarbonyl)benzylidene][1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene]ruthenium from *trans*-dichloro configuration (*SPY*-5-31) to its thermodynamically more favored *cis*-dichloro derivative (with *SPY*-5-34 stereochemistry) was found to proceed via dissociation of one chloride ligand to form an intermediate cationic species. Furthermore, the performance of the *trans*- and the *cis*-dichloro derivatives as catalysts in ring-closing metathesis and as initiators in ring-opening metathesis polymerization was studied.

Keywords Organometallic compounds · Homogeneous catalysis · Structure–activity relationships · Polymerizations

Introduction

Olefin metathesis is a transition metal catalyzed carbon–carbon double bond forming reaction, which finds a vast number of applications in organic synthesis, polymer and material chemistry [1]. Amongst other metals ruthenium occupies a special rank, as its corresponding carbene complexes exhibit an extraordinary functional group tolerance [2]; hence, olefin metathesis is feasible even in water as the reaction medium [3]. Prominent ruthenium-based catalysts feature a *trans*-dichloro-based structure, i.e., ruthenium is coordinated in a square pyramidal fashion bearing the carbene carbon atom in the apical position. The base of the pyramid comprises two chlorides *trans* to each other and two neutral σ-donor ligands *trans* to each other. However, *cis*-dichloro species have also been described [4–14]. In these square pyramidal complexes the carbene carbon corresponds again to the apex of the pyramid, but the base is composed of two chloride ligands in mutual *cis* configuration, similar to the two neutral ligands. These *cis*-dichloro complexes are generally characterized by a latent behavior, meaning that they are catalytically inactive at ambient temperatures, but develop their activity at higher temperatures. This feature can be of particular interest in industrial processes where regulation of the initiation is crucial for the operational control [15, 16], e.g., in reactive injection molding (RIM) of strained cyclic olefins which are polymerized by ring-opening metathesis polymerization (ROMP) [17, 18]. Also, *cis*-dichloro catalysts outperform their *trans*-dichloro counterparts in several metathesis transformations which demand high temperature [14, 19, 20]. The latency is believed to be reasoned in the general inability of such *cis*-dichloro species to perform olefin metathesis; hence, an isomerization step to the respective *trans*-dichloro isomer has to precede olefin metathesis [21, 22]. Theoretical calculations confirm this hypothesis and suggest either a concerted mechanism or dissociation of a neutral ligand to start the isomerization process [23, 24]. However, only recently we have disclosed experimental evidence that the *cis*–*trans* isomerization of ruthenium complexes bearing a chelating ester substituted benzylidene ligand proceeds via dissociation of a chloride

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ligand, yielding a cationic species. In the course of that work we were able to isolate such cationic intermediates and we showed them to be more active in ROMP than the corresponding *cis*-dichloro species [25]. Herein we disclose the peculiarities of an analogous complex bearing a chelating carbene with an amide instead of an ester group as the second ligand.

Results and discussion

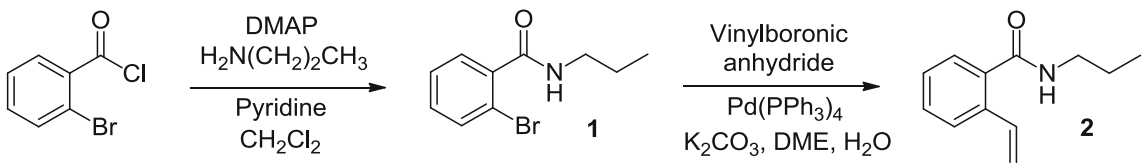
Complex preparation

The precursor for the chelating benzylidene ligand *N*-propyl-2-vinylbenzamide (**2**) was prepared in a two-step procedure starting with an amidation reaction of 2-bromobenzoic chloride with propylamine using nucleophilic catalysis by 4-(dimethylamino)pyridine (DMAP) [26]. 2-Bromo-*N*-propylbenzamide (**1**) was obtained in 72 % yield. The vinyl group was then attached via a Suzuki–Miyaura cross-coupling reaction with the 2,4,6-trivinylcyclotriboroxane–pyridine complex as the vinyl source, $Pd(PPh_3)_4$ as the catalyst, and K_2CO_3 as the base [27]. Ligand **2** was isolated in 84 % yield after purification via column chromatography (Scheme 1).

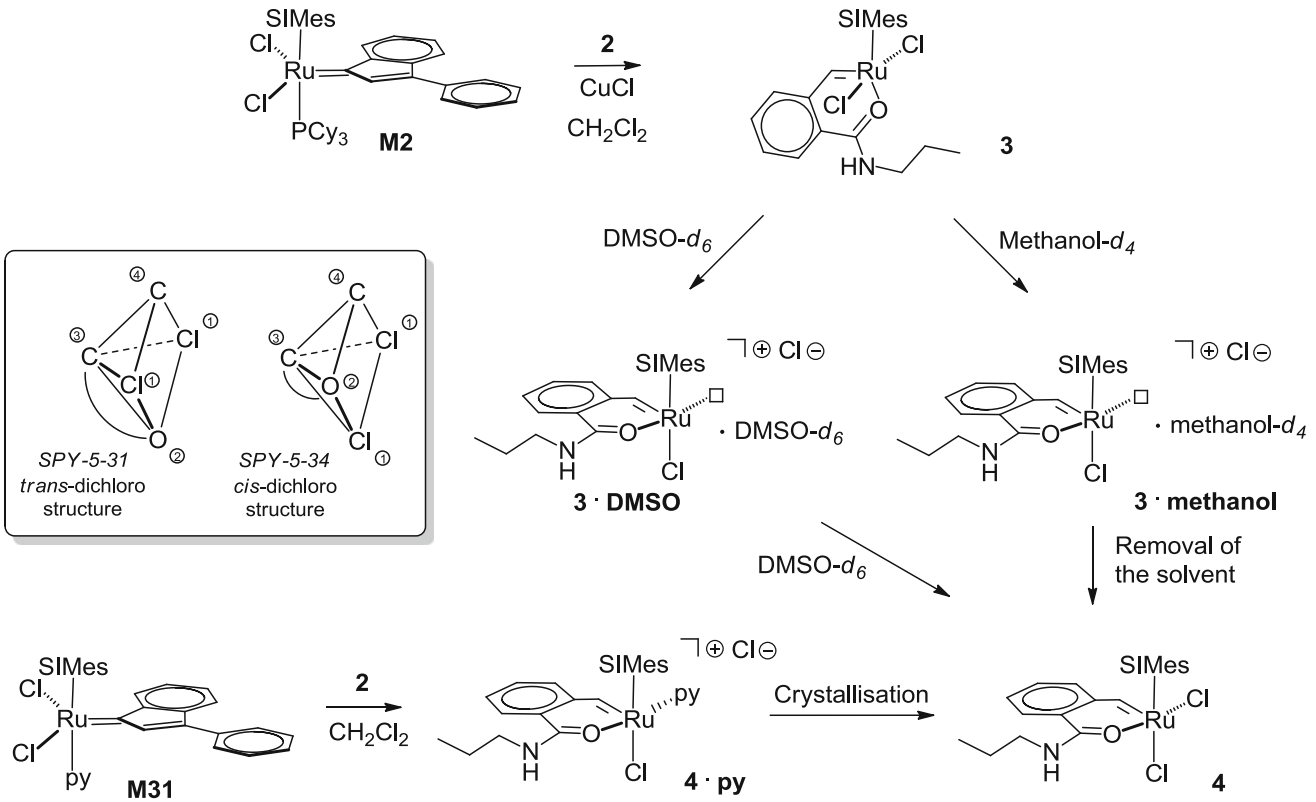
For the preparation of the complexes, two ruthenium indenylidene precursors were selected. First, dichloro(3-phenylindenylidene)[1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene](tricyclo-hexylphosphine) ruthenium (**M2**) (Scheme 2) was employed in a carbene exchange reaction with **2**. One equiv. of **M2** and 1.5 equiv. of **2** were dissolved in dry CH_2Cl_2 under an inert atmosphere of argon and 1.3 equiv. CuCl was added in order to capture the released phosphine [28]. The reaction mixture was then stirred for 4 days at room temperature whereupon a green microcrystalline precipitate formed which was collected and thoroughly washed with CH_2Cl_2. The copper–tricyclohexylphosphine adduct formed colorless insoluble spheres which were manually separated from the green powder. The green precipitate was obtained in 64 % yield and elemental analysis revealed the expected stoichiometry (Scheme 2).

The precipitate is insoluble in CH_2Cl_2, $CDCl_3$, Et_2O, H_2O, or pentane and only sparingly soluble in dimethyl sulfoxide (DMSO) and methanol. ^{1}H NMR spectroscopy in DMSO-d_6 and methanol-d_4 was used to elucidate the structure of the complex in solution. The ^{1}H NMR spectrum recorded in methanol-d_4 is shown in Fig. 1.

The carbene proton was observed as a singlet at 19.46 ppm. All protons from the (*N*-propylaminocarbonyl)benzylidene moiety gave nicely resolved signals exhibiting the expected coupling pattern. The signals for the mesityl groups in the aromatic region appeared as two broadened singlets at 7.07 and 6.6 ppm. This signal pattern is indicative of free rotation of an NHC ligand attached to a chiral ruthenium center, i.e., the appearance of the two signals for the aromatic mesityl protons can be deduced as a result of their diastereotopy. The rotation of one mesityl group around the N–C bond is slightly restricted, presumably due to steric hindrance caused by the benzylidene moiety. This assumption is corroborated by the upfield shift for two of the aromatic protons of a mesityl group, which is caused by anisotropic effects of the benzylidene ligand bonded such that π–π interactions of the two aromatic moieties are facilitated [29]. The signal pattern for the mesityl methyl groups (three different broad singlets each with the intensity of six protons) is in accordance with the aforementioned interpretation. The backbone of the NHC ligands gave a singlet with an intensity of 4 at 4.00 ppm, which indicates free rotation of the NHC ligand around the Ru–C(NHC) bond. Another peculiarity is the noticeable splitting of the signal for the methylene group next to the amide nitrogen into two signals. This phenomenon is best explained by the diastereotopic nature of the methylene group which is a clear indication that a chiral center is present in the compound. Summarizing these interpretations it is claimed that the solution structure of **3** in methanol-d_4 is consistent with a coplanar arrangement of a mesityl ring and the benzylidene moiety. Such a structure implies a chiral ruthenium center (Scheme 2). Similarly, DMSO-d_6 was used as solvent. The corresponding ^{1}H NMR spectrum is closely related to that in methanol-d_4; however, the peaks generally appear to be less sharp. The carbene signal is shifted to 18.99 ppm, and one of the mesityl group yields extremely broadened signals in the aromatic region (6.55 ppm) and also for the corresponding methyl groups (1.88 ppm). However, immediately after the dissolving process in DMSO-d_6, small signals from a second ruthenium species emerged and after 6 h at room temperature, **3** was fully converted into the new compound



Scheme 1



Scheme 2

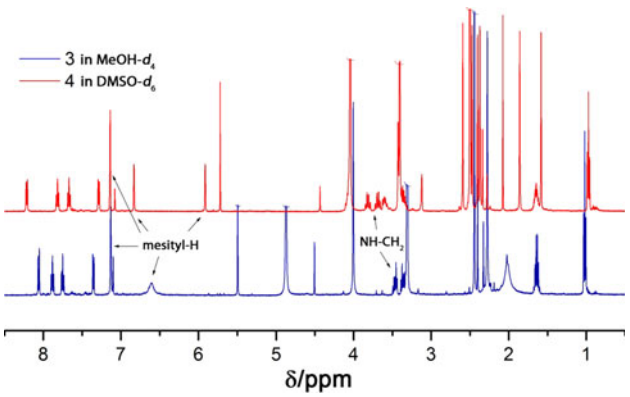


Fig. 1 ^{1}H NMR spectra of **3** in MeOH-d_4 (*bottom trace*) and **4** in DMSO-d_6 (*top trace*); carbene resonances (**3** 19.46 ppm and **4** 16.37 ppm) not shown; solvent peaks cut for clarity

4. Upon isomerization the carbene peak is shifted upfield to 16.37 ppm. The mesityl protons in the aromatic region appear as four sharp singlets at 7.17, 7.13, 6.87, and 5.95 ppm, indicating a hindered rotation around the Ru–C(NHC) bond (Fig. 1). The signal at 5.95 ppm is again a strong indication for a *cis*-dichloro arrangement of the complex and a coplanar arrangement of the mesityl group and the benzylidene moiety. Restricted rotation is also reflected by the signals for the ethylene group of the dihydroimidazol-2-ylidene moiety which give rise to four multiplets and the signals for the mesityl methyl groups, which appear as six distinct singlets. As in the spectra of **3** in methanol-d_4 and DMSO-d_6 mentioned before, the methylene group in α-position to the amide group is diastereotopic.

Compound **4** was prepared independently using dichloro(3-phenylindenylidene)[1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene](pyridine)ruthenium (**M31**) and **2** as the starting materials. The carbene exchange reaction was performed in CH_2Cl_2 under an inert atmosphere of argon. After stirring of the reactants for 24 h at room temperature, the solution had turned green. Upon precipitation with *n*-pentane, the product was isolated and identified as a pyridine-containing species by ^{1}H NMR investigations in $CDCl_3$. The spectrum of compound **4·py** (Scheme 2) exhibits a signal pattern which is strongly reminiscent of the cationic species described before. The carbene peak is located at 17.70 ppm, the pyridine signals appear at 8.41, 7.74, and 7.22 ppm. The mesityl signals can only roughly be determined due to their broadness and partly coalescence with adjacent peaks, in the aromatic region as well as for the methyl peaks. Furthermore, the spectrum resembles that of a related crystallographically characterized cationic complex [25]. From this analogy we deduced that **4·py** exhibits the structure as drawn in Scheme 2. Finally, **4** could be obtained as a green

microcrystalline powder upon slow crystallization of the sample **4·py** in 60 % yield. Complex **4** is only sparingly soluble in CH_2Cl_2, toluene, and $CHCl_3$ but exhibits reasonable solubility in DMSO. NMR spectroscopic investigation of **4** in DMSO-d_6 revealed exactly the same spectrum as in the case of **3** after the rearrangement.

The structural identity of **4** was proven by single-crystal X-ray diffraction. Suitable crystals of **4**·CH_2Cl_2 were obtained by slow diffusion of diethyl ether into a concentrated solution of **4** in CH_2Cl_2 under an inert atmosphere of argon (Fig. 2).

The coordination geometry of Ru in **4**·CH_2Cl_2 turned out to be a distorted square pyramid with the two chloro ligands *cis* to each other. The carboxamido group is bonded via the oxygen atom. The amido-benzylidene is inclined by ca. 15° to the neighboring mesityl group and both show a partial π–π-stacking interaction with C21···C41 = 2.94 Å, C22···C42 = 3.38 Å, and C24···C43 = 3.49 Å as the shortest corresponding contacts [6]. The N–H group forms a hydrogen bond to a chlorine ligand of a neighboring complex, N50···Cl1 = 3.182(3) Å, thus linking two complexes to form a cyclically hydrogen-bonded centrosymmetric pair. The dichloromethane solvent molecule is integrated loosely into the crystal lattice by donated as well as accepted C–H···Cl interactions, of which the bifurcated C–H···Cl,Cl interaction to the Ru complex is one example (C1s···Cl1 = 3.41 Å, C1s···Cl2 = 3.59 Å).

From the results presented so far, the following conclusions can be drawn: reaction of **M2** with **2** gives the compound **3** bearing a *trans*-dichloro arrangement, which is extremely insoluble. This assumption is supported by work of Fürstner et al. [30] who obtained a related *trans*-dichloro species of the composition (*SPY*-5-31)-(IMes)[κ^2(C,O)-2-(isopropoxycarbonyl)benzylidene]Cl_2Ru (IMes = *N*,*N*-bis(mesityl)imidazol-2-ylidene) using similar reaction conditions. Upon formation of a cationic compound, **3** is sparingly soluble in methanol or DMSO, followed by rearrangement to **4** bearing a *cis*-dichloro stereochemistry. Complex **4** can be prepared by using **M31** and **2** as the starting materials. In that case, the formation of **4** proceeds via intermediacy of the cationic compound **4·py**.

Although the structures of the cationic compounds **3·DMSO** and **3·MeOH** are not fully established, corresponding NMR spectroscopic data and those of recently disclosed similar (and structurally fully characterized) complexes suggest cationic structures as drawn in Scheme 2 [25]. The chloride *trans* to the oxygen atom is dissociated and is acting as the counterion. The vacant coordination site is most probably occupied by a solvent molecule. Similarly to **4·py**, **3·DMSO** is an intermediate on the reaction pathway to **4**. In contrast to **3·DMSO** which transforms to **4** in a solution of DMSO, **3·MeOH** only forms **4** upon evaporation of the methanol. Hence in methanol the cationic species **3·MeOH** is stabilized in solution.

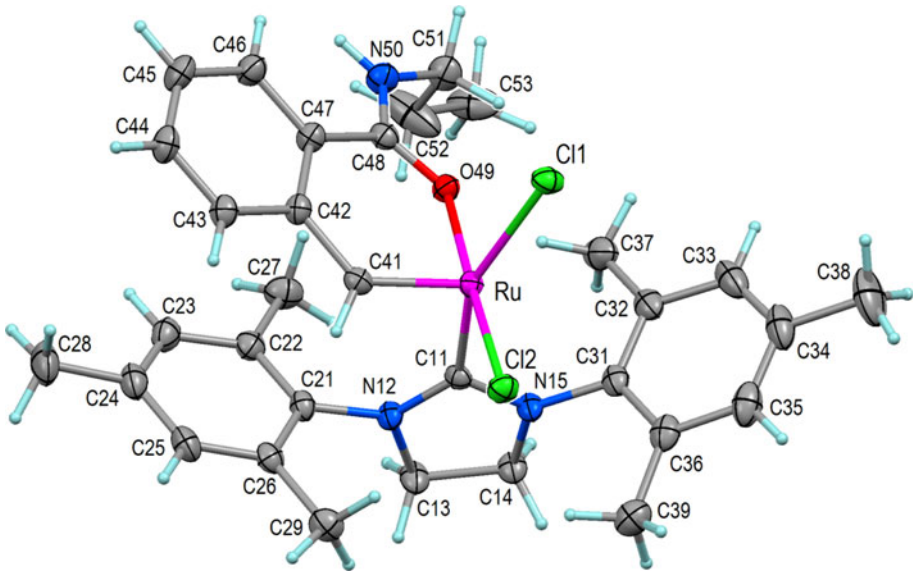


Fig. 2 Molecular structure of **4**·CH_2Cl_2 with displacement ellipsoids drawn at 50 % probability. Solvent molecule omitted for clarity. Selected bond lengths/Å and angles/° Ru–C41 = 1.815(3), Ru–C11 = 2.002(2), Ru–O49 = 2.080(2), Ru–Cl2 = 2.3693(7), Ru–Cl1 = 2.3947(6), C41–C42 = 1.463(4), C47–C48 = 1.493(4), C41–Ru–Cl1 = 96.55(10), C41–Ru–O49 = 89.19 (9), C41–Ru–Cl2 = 91.74(8), C41–Ru–Cl1 = 108.03(8), Cl1–Ru–O49 = 91.93(9), C11–Ru–Cl2 = 90.30(7), Cl1–Ru–Cl2 = 88.52(2), O49–C48–C47 = 122.7(2), O49–C48–N50 = 119.4(2)

Catalytic activity

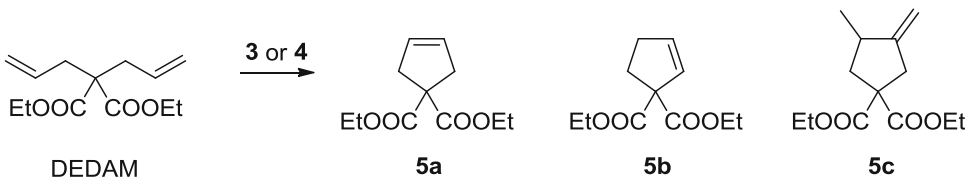
In order to test the catalytic performance of the complexes, **3** and **4** were subjected to ring-closing metathesis (RCM) and ring-opening metathesis polymerization (ROMP) experiments as follows. As the two isomers exhibit different solubilities, different solvents were used in the experiments. Other parameters to be varied were temperature and time. RCM experiments were carried out in dichloromethane, methanol, and toluene at 40, 65, and 110 °C. NMR spectra were recorded after 40 min, 3 h, 6 h, 20 h, and 3 days. Depending on catalyst and solvent (and temperature), three different products could be identified. Complex **3** is completely insoluble in CH_2Cl_2 and therefore showed no conversion at all, whereas **4** produced the classical RCM product **5a**, with a conversion of only 50 % within 3 days. No isomerization of the substrate or the product occurred. In contrast, the methanol setup yielded exclusively **5c** with both catalysts **3** and **4**. Full conversion occurred after 3 days in the case of **3**, whereas **4** gave only 50 % conversion towards **5c** in the same time. The toluene setup led to full conversion to **5a** after 40 min for both catalysts. After that, isomerization towards **5b** occurred stopping at a certain point (61 % **5b** in the case of **3**, 17 % in the case of **4** after 3 days). The isomerization processes can be related to Ru–H species that form during catalyst degradation [31]. It could be completely avoided by the addition of catalytic amounts of benzoquinone. Thus, **5a** is not converted to **5b** at any time and diethyl diallylmalonate is not converted to **5c** in methanol (Scheme 3).

Testing of **3** and **4** in RCM can be summarized as follows: both precatalysts require high temperatures for activation. In boiling toluene both exhibit an appealing activity. However, upon prolonged heating **3** and **4** cause a double bond migration of the ring-closed product, which is more prominent in the case of the *trans*-dichloro compound **3**, suggesting different decomposition pathways for **3** and **4**. This is most impressively revealed when the protic solvent methanol is used. Under those conditions, **3** and **4** are decomposed so fast that no olefin metathesis derived product can be obtained. Although no traceable decomposition products could be identified in both cases, it can be indirectly stated that the *trans*-dichloro compound **3** is more prone to form Ru–H species, which are held responsible for the formation of the cycloisomerization product **4c**.

As for ROMP, the monomer *endo*,*exo*-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid dimethyl ester (**6**) was dissolved in CH_2Cl_2 or toluene (0.2 mol/dm^3). Initiator **3** or **4** was added in a ratio of 300:1 (monomer/catalyst). The polymerization was monitored via TLC. After completion or 24 h at the latest, the reaction was quenched upon addition of ethyl vinyl ether. The resulting polymer was precipitated in methanol when possible. In the case of **3** no polymer could be obtained in CH_2Cl_2 at room temperature or 40 °C. This result can be explained by a combination of the insolubility of **3** in CH_2Cl_2 and low activity of **3** at that temperature. In contrast, using toluene and 110 °C, the polymerization was completed within 1 h. The corresponding polymer was obtained in 91 % yield and is characterized by an average number molecular weight (M_n) of 282,000 g/mol and a polydispersity index (PDI) of 2.1. Also, **4** did not show any activity at room temperature within 24 h. At 40 °C polymerization occurred but was far from completion after 24 h as evidenced by a poor yield of 20 %. In contrast, at 110 °C the reaction was finished again within 1 h and furnished the polymer in 92 % yield (M_n = 228,000 g/mol, PDI = 1.5). These results suggest that upon thermal treatment the same active species is formed irrespective of whether **3** or **4** is used as the precursor and that initiation rate is low (full conversion of **6** and complete initiation of the initiator would result in molecular weights of about 50,000 g/mol [32]). Switchability is more pronounced in the case of **3** because of its insolubility in apolar solvents at low temperature.

In conclusion, we have experimentally demonstrated for the first time that cationic species are involved in the isomerization of *trans*-dichloro ruthenium benzylidene complexes to their *cis*-dichloro counterparts. The key to this success is the very poor solubility of the *trans*-dichloro derivative under investigation. Dissolution in polar solvents was only observed upon formation of a cationic species through dissociation of a chloride ligand which acts as counterion. This ionic intermediate further rearranges to the corresponding *cis*-dichloro isomer. Although poor solubility of a complex is usually regarded as a drawback for potential application as catalyst or initiator, this property might be turned into an advantage whenever any activity at low temperature has to be prohibited.

Scheme 3



Experimental

Umicore **M2** and Umicore **M31** were received from Umicore AG [32, 33]. Propylamine, 2-bromobenzoyl chloride, 4-(dimethylamino)pyridine, 2,4,6-trivinylcyclotriboroxane–pyridine complex, and $Pd(PPh_3)_4$ were purchased from Aldrich and were used as received. *endo*,*exo*-Bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid dimethyl ester (**6**) was prepared according to literature methods [34]. The number average molecular weights (M_n) and polydispersity indices (PDI) were determined by gel permeation chromatography (GPC) using THF as solvent using the following arrangement: Merck Hitachi L6000 pump, separation columns from Polymer Standards Service, 8 × 300 mm STV 5 µm grade size (10^6, 10^4, and 10^3 Å), a refractive index detector from Wyatt Technology, and an Optilab DSP interferometric refractometer. Polystyrene standards purchased from Polymer Standard Service were used for calibration. NMR spectra were recorded on a Varian INOVA 500 MHz spectrometer.

2-Bromo-N-propylbenzamide (**1**, $C_{10}H_{12}BrNO$)
2-Bromobenzoyl chloride (500 mg, 2.2 mmol, 1 equiv.), 0.56 cm^3 pyridine (3 equiv.), and 14 mg DMAP (5 mol%) were dissolved in 10 cm^3 dry, degassed CH_2Cl_2 in a Schlenk flask, and stirred under argon atmosphere at 0 °C. *n*-Propylamine (0.21 cm^3, 1.1 equiv.) was added slowly. The mixture was brought to room temperature and stirred overnight. Progress of the reaction was monitored via TLC (silica, cyclohexane/ethyl acetate = 3:1, $R_f = 0.22$). For workup, the solution was washed with HCl and $NaHCO_3$. The organic extract was dried with Na_2SO_4. Removing the solvent in vacuo yielded a light yellow solid which was then purified by column chromatography (SiO_2, cyclohexane/ethyl acetate = 3:1). Yield 386 mg (72 %); $R_f = 0.22$ (cyclohexane/ethyl acetate = 3:1); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta =$ 7.56 (d, ph^6), 7.50 (d, ph^3), 7.34, 7.25 (2dd, $ph^{4,5}$), 6.03 (bs, N*H*), 3.41 (m, $NHCH_2$), 1.65 (m, CH_2CH_2), 0.99 (t, CH_3) ppm; $^{13}C\{^1H\}$-NMR (125 MHz, $CDCl_3$): $\delta =$ 170.1, 138.4, 133.0, 130.6, 128.1, 127.9, 119.2, 41.8, 23.0, 11.6 ppm.

N-Propyl-2-vinylbenzamide (**2**, $C_{12}H_{15}NO$)
2-Bromo-*N*-propylbenzamide (386 mg, 1.6 mmol, 1 equiv.), 462 mg vinylboronic anhydride–pyridine complex (1.2 equiv.), and 662 mg K_2CO_3 (3 equiv.) were dissolved in a mixture of 6 cm^3 degassed DME and 2 cm^3 H_2O in a Schlenk flask, heated to reflux (90 °C), and stirred under argon atmosphere. $Pd(PPh_3)_4$ (55 mg, 3 mol%) was added. The mixture was refluxed overnight. Water (10 cm^3) was added and the solution was then filtered and extracted with Et_2O. After drying with Na_2SO_4, the organic solvent was removed in vacuo. Purification via column chromatography (SiO_2, cyclohexane/ethyl acetate = 3:1) yielded a light yellow solid. Yield 323 mg (84 %); $R_f = 0.30$ (cyclohexane/ethyl acetate 3:1); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta =$ 7.50 (d, ph^6), 7.39 (d, ph^3), 7.33, 7.23 (2dd, $ph^{4,5}$), 6.98 (q, PhC*H*CH_2), 6.73 (bs, N*H*), 5.65 (d, $J_{HH} = 17.5$ Hz, CHCH^{trans}H), 5.28 (d, $J_{HH} = 6.5$ Hz, CHCHH^{cis}), 3.34 (m, $NHCH_2$), 1.56 (m, CH_2CH_2), 0.92 (t, CH_3) ppm; $^{13}C\{^1H\}$-NMR (125 MHz, $CDCl_3$): $\delta =$ 169.5, 135.9, 134.7, 130.2, 127.9, 127.5, 126.9, 126.4, 116.8, 41.9, 23.0, 11.6 ppm.

(SPY-5-31) Dichloro[κ²(C,O)-2-(N-propylaminocarbonyl)-benzylidene][1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene]ruthenium (**3**, $C_{32}H_{39}Cl_2N_3ORu$)
M2 (280 mg, 0.3 mmol, 1 equiv.), 85 mg **2** (1.5 equiv.), and 37 mg CuCl (1.3 equiv.) were put into 15 cm^3 of degassed and dry CH_2Cl_2 in a glove box. The reaction mixture was allowed to stir for 4 days, whilst light green powder precipitated. The product was filtered and dried in vacuo. Yield 125 mg (64 %); ^{1}H NMR (500 MHz, DMSO-d_6): $\delta =$ 18.99 (s, Ru=C*H*), 8.07 (d, ph^6), 7.83 (dd, ph^4), 7.70 (dd, ph^5), 7.21 (d, ph^3), 7.07 (bs, 2H, mes), 6.76–6.54 (bs, 2H, mes), ca. 4.05 (overlapped, NCH_2CH_2N), 3.25 (m, $NHCH_2CH_2CH_3$), 2.36 (s, 6H, mes-CH_3), 2.21 (bs, 6H, mes-CH_3), 2.05–1.71 (bs, 6H, mes-CH_3), 1.53 (m, $NHCH_2CH_2CH_3$), 0.88 (t, $NHCH_2CH_2CH_3$) ppm; ^{1}H NMR (500 MHz, methanol-d_4): $\delta =$ 19.46 (s, Ru=C*H*), 8.06 (d, ph^6), 7.88 (dd, ph^4), 7.75 (dd, ph^5), 7.35 (d, ph^3), 7.13 (s, 2H, $mes^{3'}$), 7.10 (bs, NH), 6.61 (bs, 2H, $mes^{5'}$), 4.00 (bs, NCH_2CH_2N), 3.45, 3.37 (m, $NHCH_2CH_2CH_3$), 2.44 (s, 6H, mes-CH_3), 2.28 (s, 6H, mes-CH_3), 2.02 (bs, 6H, mes-CH_3), 1.63 (m, $NHCH_2CH_2CH_3$), 1.02 (t, $NHCH_2CH_2CH_3$) ppm.

(SPY-5-34) Dichloro[κ²(C,O)-2-(N-propylaminocarbonyl)-benzylidene][1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene]ruthenium (**4**, $C_{32}H_{39}Cl_2N_3ORu$)
M31 (100 mg, 0.13 mmol, 1 equiv.) and 38 mg **2** (1.5 equiv.) were dissolved in 4 cm^3 of degassed $CHCl_3$ in a Schlenk tube. The reaction mixture was allowed to stir at room temperature for 18 h. During this time the color turned from brownish red to deep green. The solvent was removed by evacuation. The residual solid was washed with *n*-pentane. At this stage an NMR of the residue in $CDCl_3$ was performed and allowed the observation of **4**·**py**. Ether diffusion into a concentrated CH_2Cl_2 solution of **4**·**py**, carried out under argon atmosphere, furnished emerald green crystals of **4**. Yield 53 mg (60 %). TLC: greenish trace up to $R_f = 0.51$ (silica, CH_2Cl_2/MeOH = 20:1).

4·**py**: ^{1}H NMR (500 MHz, $CDCl_3$): $\delta =$ 17.73 (s, Ru=C*H*), 8.91 (bs, 1H, ph), 8.41 (d, 2H, $py^{2,6}$), 8.27 (bs, 1H, ph), 7.78 (bs, 1H, mes), 7.74 (dd, py^4), 7.52 (dd, 1H, ph), 7.22 (dd, 2H, $py^{3,5}$), 7.40 (d, 1H, ph), ca. 7.05 (overlapped, bs, 1H mes), ca. 6.45 (bs, 2H, mes), ca. 4.03 (bs, NCH_2CH_2N), 3.57–3.51 (m, NHC*HH*), ca. 2.60–1.61

(overlapped, 18H, mes-CH_3), 1.89–1.81 (m, CH_2CH$_3$), 1.04 (t, CH$_2$CH_3) ppm; N*H* not observed.

4: ^{1}H NMR (500 MHz, DMSO-d_6): $\delta = 16.37$ (s, Ru=C*H*), 8.25 (d, ph^6), 7.86 (dd, ph^4), 7.70 (dd, ph^5), 7.32 (d, ph^3), 7.17, 7.13, 6.87, 5.95 (s, 4H, mes), 5.76 (s, NH), 3.86 (m, 1H, NCH_2CH_2N), 3.77 (m, 1H, NCH_2CH_2N), 3.65 (m, 1H, NHCH*H*), 3.45–3.35 (m, 3H, NCH_2CH_2N + NHCH*H*), 2.63 (s, 3H, mes-CH_3), 2.52 (s, 3H, mes-CH_3), 2.43 (s, 3H, mes-CH_3), 2.41 (s, 3H, mes-CH_3), 1.90 (s, 3H, mes-CH_3), 1.68 (m, CH_2CH$_3$), 1.62 (s, 3H, mes-CH_3), 1.01 (t, CH$_2$CH_3) ppm; ^{13}C{^{1}H}-NMR (125 MHz, DMSO-d_6): $\delta = 204.4$ (C=O), 171.3 (NCCN), 143.0, 138.3, 137.7, 137.6, 137.2, 136.9, 136.7, 136.1, 135.6, 135.4, 132.9, 131.3, 130.3, 129.7, 129.5, 129.4, 128.7, 128.0, 125.5 (18 ph + 1 n.d.), 52.8, 50.3 (NCCN), 42.6 (NH*C*CH$_2$), 21.8 (CH$_2$*C*H$_2$CH$_3$), 20.8, 20.5, 18.5, 18.2, 17.5, 17.2, 16.6 (6 × CH$_3^{mes}$), 11.5 (CH$_2$*C*H$_3$) ppm; carbene carbon not observed.

X-ray structure determination

X-ray data of **4**·CH$_2$Cl$_2$ were collected on a Bruker Kappa APEX-2 CCD diffractometer using graphite-monochromated Mo–Kα radiation ($\lambda = 0.71073$ Å) and 0.5° φ- and ω-scan frames. Corrections for absorption and $\lambda/2$ effects were applied [35]. After structure solution with SHELXS97 and direct methods, refinement on F^2 was carried out with SHELXL97 [36]. Non-hydrogen atoms were refined anisotropically. H atoms were placed in calculated positions and thereafter treated as riding. An orientation disorder of the CH$_2$Cl$_2$ was taken into account. Crystallographic data are **4**·CH$_2$Cl$_2$, C$_{32}$H$_{39}$Cl$_2$N$_3$ORu·CH$_2$Cl$_2$, $M_r = 738.56$, green prism, $0.30 \times 0.26 \times 0.22$ mm^3, monoclinic, space group $P2_1/n$ (no. 14), $a = 11.8369(6)$ Å, $b = 15.0041(8)$ Å, $c = 19.3544(11)$ Å, $\beta = 105.054(3)°$, $V = 3319.4(3)$ Å^3, $Z = 4$, $\mu = 0.825$ mm^{-1}, $d_x = 1.478$ g/cm^3, $T = 100$ K. 77,347 reflections collected ($\theta_{max} = 30.0°$) and merged to 9,629 independent data ($R_{int} = 0.049$); final R indices (all data) $R_1 = 0.0603$, $wR_2 = 0.1096$, 396 parameters. CCDC 857672 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre viahttp://www.ccdc.cam.ac.uk/data_request/cif.

RCM experiments

All experiments were carried out using standard Schlenk technique with Ar gas. Catalyst **3** or **4** (3.4 mg, 0.0052 mmol, 1 equiv.) was dissolved in 5.2 cm^3 of the corresponding solvent (CH$_2$Cl$_2$, MeOH, toluene) and brought to reflux temperature (40, 65, or 110 °C). Diethyl diallylmalonate (DEDAM, 0.125 cm^3, 0.52 mmol, 100 equiv.) was added resulting in a concentration of 0.2 mol/dm^3. For reaction control, 0.300 cm^3 of the mixture was taken, dried, and submitted to ^{1}H NMR (20 °C, CDCl$_3$, 300 MHz) after 40 min, 3 h, 16 h, 24 h, and 3 day. The resulting distributions of substrate DEDAM and the products **5a**, **5b**, and **5c** were compared. NMR spectroscopic data of the products are identical to those published previously [37].

ROMP experiments

The monomer *endo*,*exo*-dimethyl bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate (**6**, 0.45 mmol, 300 equiv.) was dissolved in the solvent (DCM or toluene, 2.3 cm^3), leading to a 0.2 mol/dm^3 solution, and heated to the corresponding boiling point of the solvent. Initiator **3** or **4** was added (1 mg, 0.0015 mmol, 1 equiv.). The polymerization was monitored via TLC and quenched with an excess of ethyl vinyl ether after completion of the polymerization or at the latest after 24 h. The resulting polymer was precipitated in vigorously stirred methanol, dried in vacuo, and submitted to GPC. NMR spectroscopic data of the polymers are identical to those published previously [38, 39].

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