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Peculiarities of the reaction of (*SPY*-5-34)-dichloro-(κ^2(*C*,*O*)-2-formylbenzylidene)(1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene)ruthenium with potassium hydridotris(pyrazolyl)borate

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Abstract

The reaction of (*SPY*-5-34)-dichloro-(κ^2(C,O)-2-formylbenzylidene)(H_2IMes)ruthenium (H_2IMes=1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene) with potassium hydridotris(pyrazolyl)borate (KTp) in dichloromethane yielded an unusual ruthenium complex chloro(κ^3(*N*,*N*,*N*)-chlorotris(pyrazolyl)borate)(κ^2(C,C)-1-(2,4,6-trimethylphenyl)-3-(4,6-dimethylphenyl-2-methylidene)-4,5-dihydroimidazol-2-ylidene)ruthenium (**2**). In **2**, a chlorotris(pyrazolyl)borate ligand, which had been created during this reaction, binds in κ^3(*N*,*N*,*N*)-mode to the central ruthenium atom. Additionally, a double C–H activation of a methyl group of the H_2IMes resulted in the formation of a chelating *N*-heterocyclic biscarbene ligand and liberation of the former 2-formylbenzylidene as 2-methylbenzaldehyde. Formally, a double hydrogen transfer from a methyl group of the H_2IMes to the initial carbene carbon occurred. **2** was characterized by NMR spectroscopy, elemental analysis and single crystal X-ray structure determination. The reaction of KTp with (*SPY*-5-34)-dichloro(κ^2(C,O)-2-ethoxycarbonylbenzylidene)(H_2IMes)ruthenium, on the other hand, gave the expected product chloro(κ^3(*N*,*N*,*N*)-hydridotris(pyrazolyl)borate)(H_2IMes)(2-ethoxycarbonylbenzylidene)ruthenium (**6**). Compound **6** was characterized by NMR spectroscopy, elemental analysis and single crystal X-ray structure determination. Investigations of the relative activities of these complexes in model ring opening metathesis polymerizations showed a pronounced thermal latency. Polymerizations proceeded at temperatures above 100 °C in case of **6** and 130 °C in case of **2**.

Keywords: Ruthenium; Hydridotris(pyrazolyl)borate; C–H activation; Metathesis

1. Introduction

Since first reports of olefin metathesis in the early sixties of the last century [1], tremendous progress was made in the field of this fundamentally novel reaction. Today olefin metathesis is a popular and widely applied reaction with many facets. Cross metathesis (CM), ring closing metathesis (RCM), ring opening cross metathesis (ROCM), ring rearrangement metathesis (RRM), ene-yne metathesis, ring-expansion metathesis, ring-closing alkyne metathesis (RCAM), ring opening metathesis polymerization (ROMP) and acyclic diene metathesis polymerization (ADMET) are the most prominent members of the olefin metathesis family. The virulent research area culminated in 2006 with the Nobel Prize award for Y. Chauvin, R.R. Schrock and R.H. Grubbs. Plenitudes of research articles, numerous reviews and books have been published on these or using these reaction types [2]. Most contributions stem from the field of organic synthesis. Especially RCM became a very versatile tool for organic chemists. Also industrial applications of olefin metathesis enjoyed increasing interest in recent years [2].

Less but considerable work has been done on polymerization. Commercialized applications in the field of

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polymer chemistry focus on 'simple' hydrocarbon polymers mainly for construction purposes and optical applications, while current research is more and more directed towards the production of often synthetically very complex functional materials of high value [3]. Besides the mentioned research lines, metathesis polymerization might also impact the fields of coatings and glues to name two important applications of heat or light durable compositions [4]. The processing methodology here is different. Monomers and initiators, sometimes also additives, fillers and solvents are mixed together and applied to the substrate by various techniques. Upon heating or irradiation the polymerization is then started. The question whether such a polymerization system is applicable is mainly connected to the availability of suitable initiators. Amongst other strategies [5,6], a deactivation of generally very active ruthenium based 1st and 2nd generation Grubbs initiators can be achieved by blocking vacant coordination sites with suitable ligands. Efforts along this strategy comprise work directed by Grubbs [7,8], Herrmann [9], Ozawa [10] and Verpoort [11]. Further promising examples are the hydridotris(pyrazolyl)borate (Tp) derivatives RuCl(κ^3-Tp)(PCy_3)(CHPh) (PCy_3=tricyclohexylphosphine) [12] and RuCl(κ^3-Tp)(H_2IMes)(CHPh) (**7**) (H_2IMes=1,3-bis(2,4,6-trimethylphenyl) 4,5-dihydroimidazol-2-ylidene) [13]. In these derivatives, the Tp ligand imposes a six-coordinate environment around ruthenium promoting substitution reactions to follow a dissociative pathway [14,15]. Therefore ligand dissociation is necessary before olefine coordination and subsequently metathesis can take place, rendering RuCl(κ^3-Tp)(PCy_3)(CHPh) inactive in RCM and ROMP at 70 °C in solution [12].

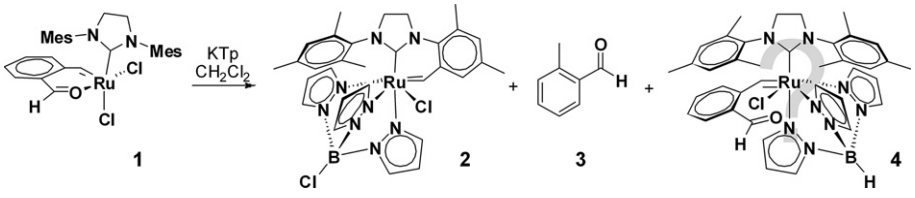
Herein we present our results on the difficulties which may arise when preparing RuTp-benzylidene complexes and report on the formation of an unusual by-product. Furthermore we demonstrate the capability of RuTp-benzylidene complexes to initiate ROMP at high temperatures and disclose data on their polymerization behavior.

2. Results and discussion

During our studies of the chemistry of **1** and related compounds featuring, instead of the formyl-group, ester functionalities in 2-position of the benzylidene ligand [16], we investigated the reaction of **1** with potassium hydridotris(pyrazolyl)borate (c.f. Scheme 1). We anticipated a simple decoordination of the formyl group and formation of compound **4**. Compound **4** is an analogue of RuCl(κ^3-Tp)(H_2IMes)(CHPh) (**7**) which was prepared by Grubbs et al. by reaction of $RuCl_2(H_2IMes)(pyridine)_2$(CHPh) with KTp [13]. We furthermore hoped to see an influence of the chelated benzylidene derivative in **1** on e.g. the reaction rate, when compared to the above mentioned transformation, or even to isolate a κ^2-Tp derivative conserving the initially chelated benzylidene moiety.

Reaction of **1** and KTp in CH_2Cl_2 for 16 h at room temperature gave, upon removal of insoluble residues, a mixture of several compounds as determined by NMR spectroscopy of the crude reaction mixture. As evidenced by two singlets at 19.20 and 18.88 ppm at least two complexes with an intact benzylidene moiety were formed (the starting material **1** is characterized by a carbene proton resonance of 18.86 ppm [16]). Additionally, a characteristic singlet at 10.28 ppm indicated the presence of an aldehyde bearing compound. The singlet at 10.03 ppm indicative for **1** is missing. By a combined purification with column chromatography on silica and subsequent crystallization we succeeded in obtaining one of the carbene containing complexes in pure form, while the other could not be isolated (crystallization and column chromatography on silica as well as on neutral or basic Al_2O_3 failed). The isolated compound could be identified by a combination of ^{1}H- and ^{13}C NMR spectroscopy, elemental analysis and, most important, single crystal X-ray structure determination. ^{1}H NMR spectroscopy revealed a carbene resonance at 19.20 ppm and characteristic signals for the Tp- and the H_2IMes-moiety. Signals for the 2-formyl-benzene group and for one methyl group of the H_2IMes-moiety were missing. Similarly, $^{13}C\{^1H\}$ NMR indicated the presence of a carbene (292.6 ppm), a H_2IMes-ligand (e.g. 224.8 ppm for the C^2) and the Tp ligand. Again, only five methyl groups corresponding to the H_2IMes-moiety were observed. From these NMR data, a double C–H activation of one methyl group of one of the mesityl CH_3 groups and concomitant loss of the 2-formylbenzylidene ligand appeared plausible.

To obtain a proof for this hypothesis, crystals were grown by vapor diffusion of Et_2O into a saturated solution of **2** in CH_2Cl_2. The obtained crystals were subjected to X-ray structure analysis and the result is shown in Fig. 1. As anticipated, the former H_2IMes ligand was activated at one of the *ortho*-methyl groups, forming a chelating biscarbene ligand. Furthermore the hydride originally present at the boron atom of the Tp unit was exchanged for a chloride. Thus, chlorotris(pyrazolyl)borate had formed and coordinates via a κ^3-coordination mode to the ruthenium center. The formation of this unusual chloro(trispyraz-



Scheme 1.

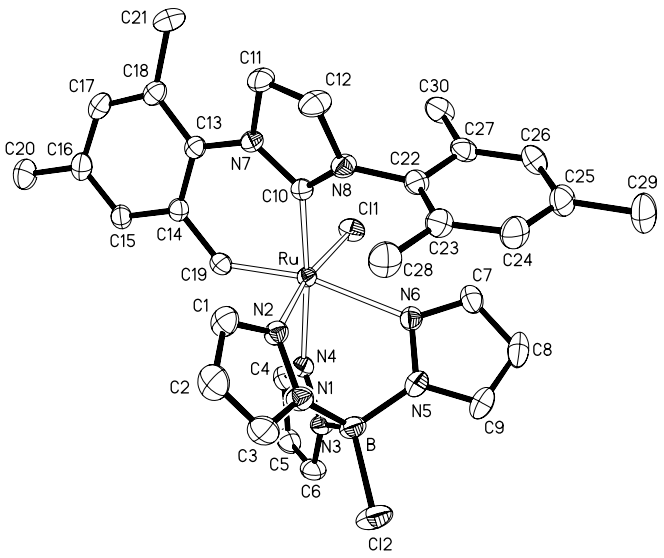


Fig. 1. ORTEP plot of **2** (displacement ellipsoids at 30% probability level, hydrogen atoms omitted). Selected bond lengths (Å) and angles (°): Ru–C(19) 1.857(2), Ru–C(10) 2.002(2), Ru–N(2) 2.076(2), Ru–N(4) 2.148(2), Ru–N(6) 2.303(2), Ru–Cl(1) 2.3861(5), Cl(2)–B 1.839(2), B–N(1) 1.538(2), B–N(3) 1.538(2), B–N(5) 1.533(2), C(10)–N(7) 1.385(2), C(10)–N(8) 1.356(2), C(11)–C(12) 1.490(3), C(14)–C(19) 1.419(3); C(10)–Ru–C(19) 87.4(1), Cl(1)–Ru–C(10) 93.2(1), Cl(1)–Ru–C(19) 96.7(1), Cl(1)–Ru–N(2) 171.2(1), C(10)–Ru–N(4) 175.0(1), C(19)–Ru–N(6) 166.8(1), Cl(2)–B–N(1) 109.5(1), Cl(2)–B–N(3) 110.0(1), Cl(2)–B–N(5) 110.3(1), N(7)–C(10)–N(8) 105.7(2), Ru–C(19)–C(14), 134.4(2).

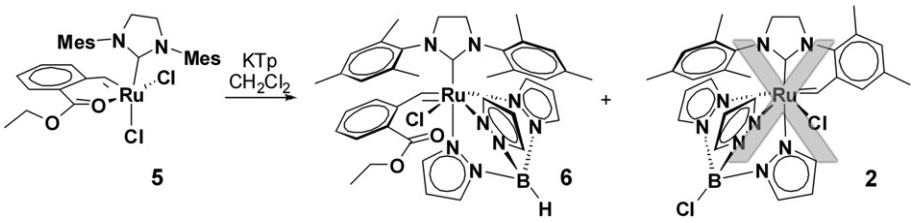
olyl)borate from common Tp during a halide abstraction reaction is without precedence in literature and no halo(trispyrazolyl)borate has been reported as yet [17]. The coordination geometry of Ru in **2** is a distorted octahedron. Important bond lengths and angles can be found in the caption of Fig. 1 Ru–N bond lengths increase from 2.076(2) Å for N(2) *trans* to Cl(1) to 2.303(2) Å for N(6) *trans* to C(19) (benzylidene carbon). The latter value reflects the strong *trans*-influence of the Schrock-carbene moiety and is even 0.1 Å longer than the corresponding Ru–N bond lengths in the related complex $[RuTp(H_2O)(PCy_3)(CHPh)]^+$ [18]. The carbene bond lengths Ru–C(19) is comparable to that of related Ru benzylidenes [18]. The same accounts for Ru–C(10) which is approximately 0.03 Å shorter than the corresponding bond in $RuCl_2(H_2IMes)(pyridine)_2(CHPh)$ [13].

The novel chloro(trispyrazolyl)borate ligand in **2** is surprisingly similar in bond lengths and angles with the classical Tp moiety (see also Fig. 3). The B–N bond lengths in **2** have a mean value of 1.536(3) Å which agrees with the mean value of 1.535(4) Å for a sample of 100 RuTp complexes taken from the Cambridge Crystallographic Data Base (version of 2005). The bond angles in the BN_3Cl tetrahedron are very close to the ideal value of 109.47° as they vary only from 108.2(2) to 110.4(2)° (mean value for N–B–N 109.0° and for N–B–Cl 109.9°). The three pyrazolyl rings in **2** show no special features. The mean ring bond lengths is 1.357(24) Å for all bonds (1.363(2) Å for the N–N bonds) [19].

When using the ethyl ester derivative **5** as starting material, again no clean reaction occurred (c.f. Scheme 2). ^1H NMR of the crude product indicated the presence of three different carbene containing species (signals at 18.63, 18.78 and 18.55 ppm), but no indication for **2** was found. Only **6** could be obtained in pure form and turned out to be an analogue to **7** with a dangling ethyl-ester group.

Compound **6** was characterized by a combination of ^1H- and ^{13}C NMR spectroscopy, elemental analysis and single crystal X-ray structure determination. ^1H and ^{13}C NMR spectroscopy data are in accordance with expected values [13] and are listed in the experimental section. Crystals of **6**, in the form of $\mathbf{6} \cdot 1/2C_5H_{12}$, were obtained by slow diffusion of pentane into a CH_2Cl_2 solution. The coordination geometry Ru in **6** is a distorted octahedron. Important bond lengths and angles can be found in the caption of Fig. 2. Ru–N bond lengths increase from 2.068(2) Å to 2.281(2) Å for Ru–N(31) (ligand in trans position: benzylidene). The latter value is somewhat shorter than the corresponding Ru–N bond lengths in **2**, while both carbene bonds of **6** are slightly longer. The close similarity of the Ru coordination figures in **2** and **6** and the mutual ligand dispositions are shown by a superposition plot in Fig. 3.

A working hypothesis for the mechanism of the formation of **2** is shown in Scheme 3. First, chloride abstraction by KTp takes place [20]. The Tp moiety binds in a $\kappa^2(N,H)$ coordination mode to the ruthenium, related compounds have been isolated and studied in the past [21]. At this stage, a hydride transfer to the ruthenium and formation of a ruthenium–boron bridging chloride is postulated. Related tetrahedral boron species are known from subphthalocyanines [19,22]. Furthermore, our findings are corroborated by some isolated reports describing a formal partial hydrolysis of the B–H or B–pz bonds to give the [B–O]-moiety [23]. Subsequently, the hydride undergoes a 1,2 H-shift from ruthenium to the carbene carbon and leaves an empty coordination sphere at ruthenium. Such 1,2 H shifts are well known especially for related iridium complexes [24].



Scheme 2.

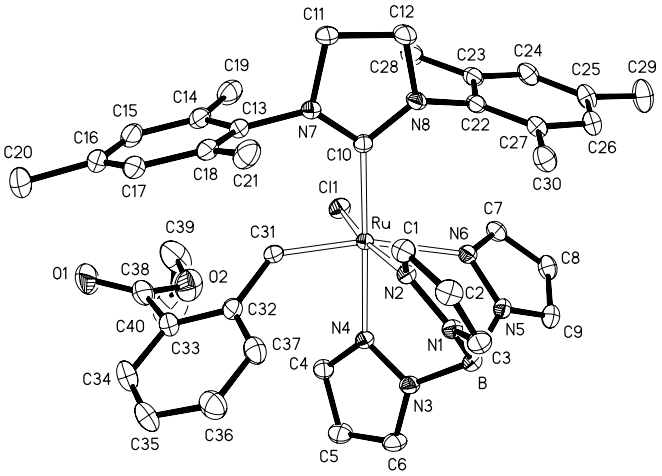


Fig. 2. ORTEP plot of $\mathbf{6} \cdot 1/2C_5H_{12}$ (displacement ellipsoids at 30 % probability level, hydrogen atoms and solvent molecule omitted for clarity). Selected bond lengths (Å) and angles (°): Ru–C(31) 1.871(2), Ru–C(10) 2.073(2), Ru–N(2) 2.068(2), Ru–N(4) 2.135(2), Ru–N(6) 2.281(2), Ru–Cl(1) 2.4255(5), B–N(1) 1.542(3), B–N(3) 1.534(3), B–N(5) 1.530(3), C(10)–N(7) 1.368(2), C(10)–N(8) 1.353(2), C(11)–C(12) 1.505(3), C(31)–C(32) 1.466(3); C(31)–Ru–C(10) 93.2(1), Cl(1)–Ru–C(31) 87.7(1), Cl(1)–Ru–C(10) 93.1(1), Cl(1)–Ru–N(2) 170.2(1), C(10)–Ru–N(4) 176.7(1), C(31)–Ru–N(6) 161.5(1), N(7)–C(10)–N(8) 105.7(2), Ru–C(31)–C(32) 133.2(2).

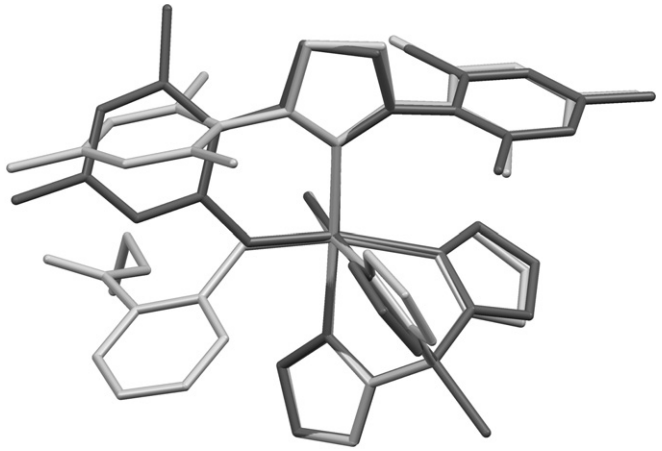
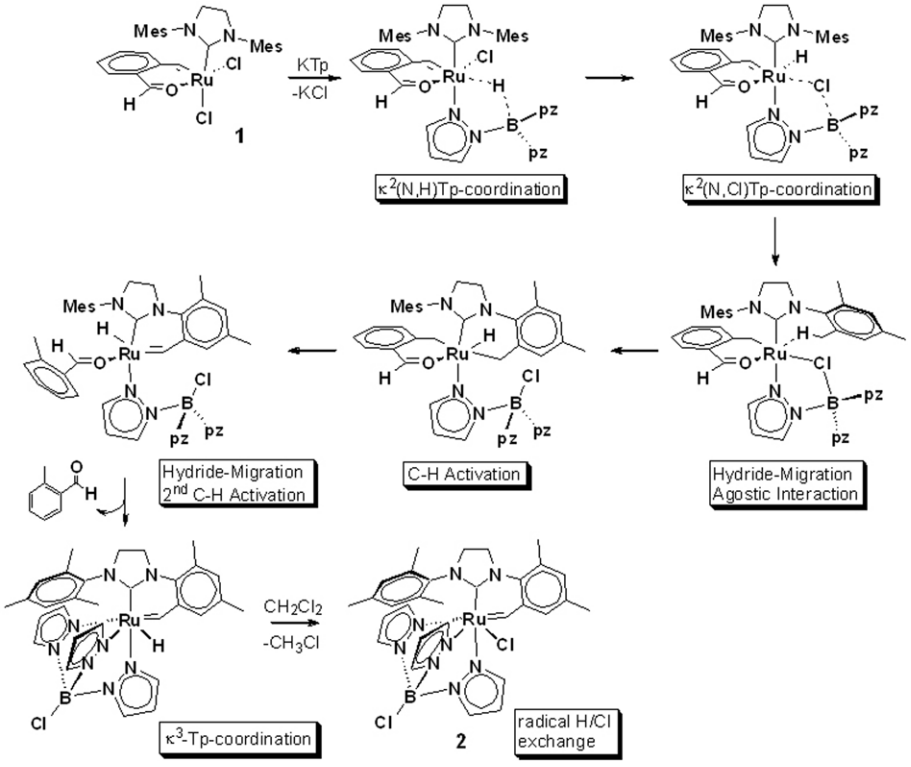


Fig. 3. Superposition plot of the Ru complexes **2** (dark grey) and $\mathbf{6} \cdot 1/2C_5H_{12}$ (light grey) with hydrogen atoms omitted. Disregarding the benzylidene carbon atoms (separation between C(19) of **2** and C(31) of **6** is 0.38 Å) the mutual r.m.s. deviation of the two $RuClC_2N_3$ coordination octahedra is 0.051 Å.

Possibly an agostic interaction of a methyl hydrogen of a mesityl group precedents a C–H activation reaction [25], which then results in formation of a ruthenium(IV) species featuring two alkyl ligands and a hydride. Similar insertions of the ruthenium center into the C–H bond of one of the mesityl CH_3 groups had been observed in the past [26,27]. A further 1,2 H shift of the hydride from ruthenium to the former carbene carbon and a subsequent second C–H activation reaction releases 2-methylbenzaldehyde from the coordination sphere and a $\kappa^3(N,N,N)$-ClTp ruthenium hydride species is formed. Finally, the hydride is exchanged for chlorine, presumably stemming from CH_2Cl_2. This reaction might be due to a radical process [20,24], or due to an intermediate chlorocarbene species [28]. In the latter case, the reaction should occur before the κ^3-Tp coordination is formed.

Although the proposed mechanism is speculative, some findings corroborate the hypothesis. Most importantly, 2-methylbezaldehyde was isolated and subsequently characterized by NMR spectroscopy and GC–MS. When non chlorinated solvents (toluene, benzene) were used, **2** was not obtained. Instead, mainly decomposition of the educts occurred and small amounts of a carbene containing product with a characteristic resonance of 18.87 ppm was detected. It was not possible to isolate or identify neither any of the decomposition products nor the unknown carbene complex. It is worth to mention, that no Ru-hydride signals were observed in ^{1}H NMR spectra during this study which somewhat favors the chlorocarbene mechanism for the final H/Cl exchange. Following the reaction in the NMR tube using $CDCl_3$ as solvent led to almost the same crude product mixture as obtained from the CH_2Cl_2 solutions. No evidence for intermediate products was retrieved. Equally interesting, the reaction of **5** did not yield **2** but **6**. This can be rationalized by the earlier observation that **1** is more reluctant in ROMP of norbornene derivatives than **5** [16], meaning that the formyl benzylidene moiety in **1** is less hemilabile than the ethoxycarbonyl benzylidene moiety **5**. It seems to be crucial for the formation of **2**, that the formyl benzylidene moiety stays in the κ^2-(C,O) coordination mode until the C–H activation reactions have occurred. Furthermore, **6** could not be converted into **2**. Even prolonged heating (3 days) in $CHCl_3$ resulted in complete recovery of the starting material, revealing that such κ^3-Tp species are not intermediates in the formation of **2**.

To gain information on the latency of compounds **2** and **6** in ROMP we conducted model polymerizations utilizing (±)-*endo*,*exo*-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid diethyl ester (**8**) as monomer. The polymerizations were monitored by means of DSC. Initiator (1 equiv.) and monomer (300 equiv.) were placed in DSC-pans, which were then transferred into the apparatus. A heating ramp of 3 °C/min was commenced and the reaction exotherm was read out as a function of temperature [5]. A 'switching temperature' for the initiators (i.e. the temperature at which, under certain conditions, the polymerization is detectable), can be given as the onset of the exothermic heat-flow. By means of this method a very easy and convenient way for benchmarking the thermal latency of the two complexes is available. Fig. 4 shows the corresponding data. For comparison, also **7** was used as initiator in the same model polymerization. Initiators **2**, **6** and **7** 'started' the polymerization at 109 °C, 128 °C and 138 °C respectively. Since the propagating species is the same in case of **6** and **7**, the lower temperature necessary for the polymerization initiated with **6** is due to the dangling ethoxycarbonyl in 2-position of the benzylidene ligand. Possibly, the additional substituent favors the initiation because of



Scheme 3.

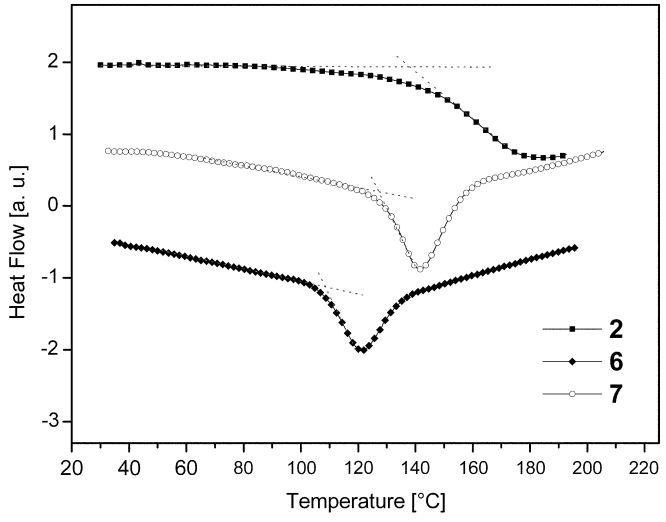


Fig. 4. Course of the polymerization of **8** initiated by **2**, **6** and **7** (heating rate: 3 °C/min; initiator:8 = 1:300).

steric reasons. The corresponding curve for **2** is smoother than the curves for **6** and **7**, indicating a distinctly lower polymerization rate compared to **6** and **7**. To assure that ROMP and not e.g. radical polymerization occurred, bulk polymerizations were performed and the polymers were investigated by NMR and IR spectroscopy. **8** was polymerized with **6** or **7** as the initiator in a ratio of 300:1 at 140 °C. No solvent was used. Determination of the weight average molecular weight (M_W) using gel permeation chromatography in THF revealed high M_Ws of about 1000 ± 300 kg/mol for the polymers prepared with either **6** or **7**. No significant influence of the choice of initiator on the M_W values was found. The polydispersity of all polymers was in the range of 2.5–3.5. NMR and IR spectra of the polymers are very similar to polymers obtained from the same monomer and $RuCl_2(H_2IMes)(PCy_3)(CHPh)$ as the initiator [29], thus indeed ROM polymers were obtained.

3. Conclusion

In summary, this report describes two unprecedented reaction-pathways. The first is the formation of chlorotris(pyrazolyl)borate from hydridotris(pyrazolyl)borate. The second is a formal double hydrogen transfer from a methyl group of the H_2IMes ligand to a carbene carbon, transforming the H_2IMes into a chelating biscarbene ligand. Knowledge of both transformations might help in future to identify by-products in either Tp-chemistry or in Schrock-carbene chemistry. Furthermore, it was demonstrated, that $RuCl(\kappa^3\text{-Tp})(H_2IMes)(CHPh)$ and its derivatives **2** and **6** are active ROMP initiators at elevated temperatures above 100 °C.

4. Experimental

4.1. Materials and measurements

Manipulations were performed under an inert atmosphere of purified nitrogen or argon using Schlenk techniques and/or a glovebox. All chemicals were standard

reagent grade and used without further purification. The solvents were purified according to standard procedures.[30] The deuterated solvents were purchased from Aldrich.

(*SPY*-5-34)-Dichloro(κ^2(C,O)-2-formylbenzylidene)(H_2IMes)ruthenium (**1**) [16], (*SPY*-5-34)-dichloro(κ^2(C,O)-2-ethoxycarbonylbenzylidene)(H_2IMes)ruthenium (**5**) [16], potassium hydridotris(pyrazolyl)borate (KTp) [31], chloro(κ^3(*N*,*N*,*N*)-Tp)(H_2IMes)(benzylidene)ruthenium (**7**) [13] and the mixture of *endo*- and *exo*-bicyclo[2.2.1]hept-5-ene-2-carboxylic acid ethyl ester (**8**) [32] were prepared according to literature. The weight-average molecular weights (M_W) and polydispersity indices (*PDI*) were determined by gel permeation chromatography using THF as solvent in the following arrangement: Merck Hitachi L6000 pump, separation columns of Polymer Standards Service, 8×300 mm STV 5 μm grade size (10^6 Å, 10^4 Å, and 10^3 Å), refractive index detector from Wyatt Technology, model Optilab DSP Interferometric Refractometer. Polystyrene standards purchased from Polymer Standard Service were used for calibration. ^{1}H NMR spectra were recorded on a Varian INOVA 500 MHz spectrometer operating at 499.803 MHz and were referenced to $SiMe_4$, the relaxation delay was set to 5 s. $^{13}C\{^1H\}$ NMR spectra were recorded on a Varian INOVA 500 MHz spectrometer operating at 125.687 MHz and were referenced to $SiMe_4$. Differential scanning calorimetry (DSC) was performed on a Pyris Diamond DSC calibrated by using an indium standard.

4.2. Synthesis of Chloro(κ^3(*N*,*N*,*N*)-chlorotris(pyrazolyl)borate)(κ^2-1-(2,4,6-trimethylphenyl)-3-(4,6-dimethylphenyl-2-methylidene)-4,5-dihydroimidazol-2-ylidene)ruthenium (**2**)

To a solution of **1** (100 mg, 0.168 mmol) in CH_2Cl_2 (4 mL) solid KTp (50 mg, 0.198 mmol) was added. The reaction mixture was stirred for 16 h at room temperature. Volatiles were removed in vacuo and the residue was redissolved in 2 mL CH_2Cl_2. Removal of insoluble parts by filtration over Celite and evaporation of the filtrate to dryness gave a yellow to brown powder (approx. 105 mg). The residue was partly dissolved in Et_2O (1 mL) and both, the remaining solid and the Et_2O solution were subjected to column chromatography (SiO_2, 10 g). The column was eluated with Et_2O (50 mL), CH_2Cl_2 (100 mL, at least until the yellow band was eluated). The CH_2Cl_2 fraction was concentrated to about 1 mL and transferred to a 6 mL vial. This vial was placed without closing it in a 150 mL vial, which was filled with 20 mL Et_2O. The big vial was then closed with a screw cap and placed in a dark, vibration free place. Upon slow diffusion of the Et_2O into the CH_2Cl_2 solution, greenish crystals were obtained after 2 days. The crystals were separated from the mother liquor and dried in vacuo. Yield: 15 mg (13 %). Anal. Calcd for $C_{30}H_{33}BCl_2N_8Ru$ (MW: 688.42): C, 52.34; H, 4.83. Found: C, 52.56; H, 5.09. ^{1}H NMR (δ, 20 °C, $CDCl_3$, 500 MHz): 19.20 (s, 1 H, Ru=C*H*), 8.03 (d, 1H, Tp), 7.87 (d, 1H, Tp), 7.86 (d, 1H, Tp), 7.73 (d, 1H, Tp), 7.40 (b, 1H, $Mes^{3,5}$), 7.30 (bs, 1H, $Mes^{3,5}$), 7.00 (d, 1H, Tp), 6.89 (bs, 1H, $Mes^{3,5}$), 6,34 (bs, 1H, $Mes^{3,5}$), 6.33 (d, 1H, Tp), 6.15 (vt, 1H, Tp^4), 5.92 (vt, 1H, Tp^4), 5.83 (vt, 1H, Tp^4), 4.73 (m, 1H, $Im^{3,4}$), 4.24 (m, 1H, $Im^{3,4}$), 3.81 (m, 2H, $Im^{3,4}$), 2,77 (s, 3H, Me), 2.59 (s, 3H, Me), 2.47 (s, 3H, Me), 2.18 (s, 3H, Me), 1.09 (s, 3H, Me). $^{13}C\{^1H\}$ NMR (δ, 20 °C, $CDCl_3$, 125 MHz): 292.6 (1C, Ru=CH), 224.8 (1C, NCN), 145.3, 145.2, 143.4, 142.9, 138.8, 138.48, 138.38, 137.2, 136.9, 134.2, 133.6, 130.5, 129.6, 129.0, 123.9 (18C, Mes^{1-6}, $Tp^{3,5}$), 106.3, 106.0, 105.3 (3C, Tp^4), 53.8, 51.0 (2C, NCH_2CH_2N), 23.2, 21.4, 21.0, 20.2, 17.2 (5C, Me).

The Et_2O fraction was concentrated and dried in vacuo. Several compounds and a main product (2-methylbenzaldehyde) were present. Yield: 2 mg. ^{1}H NMR (δ, 20 °C, $CDCl_3$, 500 MHz): 10.28 (s, 1H, CHO), 7.82 (d, 1H, Ph^6), 7.49, 7.37 (m, 2H, $Ph^{4,5}$), 7.27 (d, 1H, Ph^3), 2.68 (s, 3H, Me). $^{13}C\{^1H\}$ NMR (δ, 20 °C, $CDCl_3$, 125 MHz): 192.7 (1C, CHO), 140.5, 134.0, 133.6, 131.9, 131.8, 126.2, 19.5 (1C, Me). (only the signals for the main product are given). GC–MS: main fraction showed a molecular peak of $[M]^+ = 120.06$.

4.3. Synthesis of Chloro(κ^3(*N*,*N*,*N*)-hydridotris(pyrazolyl)borate)(1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene)(2-ethoxycarbonylbenzylidene)ruthenium (**6**)

To a solution of **5** (100 mg, 0.156 mmol) in CH_2Cl_2 (4 mL) solid KTp (50 mg, 0.198 mmol) was added. The reaction mixture was stirred for 16 h at room temperature. Volatiles were removed in vacuo and the residue was redissolved in 2 mL CH_2Cl_2. Removal of insoluble parts by filtration over Celite and evaporation of the filtrate to dryness gave a yellow to brown powder (approx. 105 mg). The residue was partly dissolved in Et_2O (1 mL) and both, the remaining solid and the Et_2O solution were subjected to column chromatography (SiO_2, 10 g). The column was purged with CH_2Cl_2 (30 mL), acetone (30 mL) and finally MeOH (60 mL). The MeOH fraction was evaporated to dryness and redissolved in CH_2Cl_2 (1 mL). The same crystallization procedure as described above gave green micro crystals. Yield: 32 mg (25 %).

Anal. Calcd for $C_{40}H_{46}BClN_8O_2Ru$ (MW: 818.18): C, 58.72; H, 5.67. Found: C, 58.95; H, 5.81. ^{1}H NMR (δ, 20 °C, $CDCl_3$, 500 MHz): 18.55 (s, 1H, Ru=C*H*), 8.35 (d, 1H, Tp), 8.29 (d, 1H, Ph), 7.95 (dd, 1H, Ph), 7.82 (dd, 1H, Ph), 7.73 (d, 1H, Tp), 7.50 (d, 1H, Tp), 7.42 (d, 1H, Tp), 7.27 (d, 1H, Ph), 7.10 (d, 1H, Tp), 6.80 (s, 2H, $Mes^{3,5}$), 6.48 (vt, 1H, Tp^4), 6.24 (bs, 2H, $Mes^{3,5}$), 5.96 (vt, 1H, Tp^4), 5.61 (d, 1H, Tp), 5.50 (vt, 1H, Tp^4), 4.50 (m, 2H, OCH_2CH_3), 3.87 (m, 4H, $Im^{3,4}$), 2.50 (bs, 6H, Me), 2.03 (bs, 6H, Me), 2 Me not observed, 1.25 (t, 3H, OCH_2CH_3). $^{13}C\{^1H\}$ NMR (δ, 20 °C, $CDCl_3$, 125 MHz): 258.2 (1C, Ru=CH), 213.1 (1C, NCN), 177.2 (1C, *C*OOEt),145.2, 143.5, 142.6, 138.9, 137.5, 137.3, 137.0,

136.45, 136.40, 134.6, 131.9, 130.5, 130.4, 130.3, 130.2, 121.3 (24C, Mes^{1-6}, Ph^{1-6}, $Tp^{3,5}$), 108.0, 106.7, 104.9 (3C, Tp^4), 65.2, 64.1 (3C, $COOCH_2CH_3$, NCH_2CH_2N), 29.9, 21.1, 19.7, 14.2 (7C, Me, $COOCH_2CH_3$).

4.4. Polymerization procedure in bulk

Complexes **6** or **7** (1 mg; 1.0 equiv.) were dissolved in 50 μL of CH_2Cl_2 and added to monomer **8** (300 equiv.) placed in a Schlenk-tube. The reaction vessel was put into a preheated (140 °C) oil-bath for 8 h. Within 1 h a gelation of the reaction mixture occurred. After cooling the reaction mixture to room-temperature, the residue was dissolved in CH_2Cl_2 and 50 μL of ethylvinylether was added. Absence of **8** was confirmed by TLC. Afterwards, the solution was added slowly to vigorously stirred methanol. The resulting white precipitate was sampled and dried in vacuum. Yields ranged from 86–97%. ^{1}H NMR (500 MHz, $CDCl_3$, 20 °C): δ 5.5–5.2 (2H, m, CH_2=), 4.08 (4H, q, OCH_2CH_3), 3.20–2.55 (4H, m, CH), 1.99–1.44 (2H, m, CH_2), 1.20 (6H, t, OCH_2CH_3). IR (NaCl, cm^{-1}): 2984 (m), 1731 (s), 1447 (w), 1382 (m), 1258 (m), 1180 (s), 1097 (w), 1031 (m), 972 (w), 862 (w).

4.5. Polymerization procedure in DSC pans

Defined solutions of **2**, **6** and **7** (0.002 mmol/mL, 1.0 equiv.) and monomer **8** (1.000 mmol/mL, 300 equiv.) in CH_2Cl_2 were prepared. Equal amounts of initiator and monomer were mixed on a watch glass and the solvent was evaporated at room temperature within 5–7 minutes. The resulting mixture was transferred into a DSC pan. The polymerization was then followed by monitoring the heat-flow when employing a heating rate of 3 °C/min.

4.6. Crystal structure determinations of compound 2 and 6

X-ray data of **2** and **6** (in the form of the pentane solvate $\mathbf{6}\cdot 1/2C_5H_{12}$) were collected on a Bruker Smart APEX CCD area detector diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) and 0.3° ω-scan frames. Corrections for absorption, λ/2 effects, and crystal decay were applied. [33] The structures were solved by direct methods using the program SHELXS97. [34] Structure refinement on F^2 was carried out with the program SHELXL97. [39] Non-hydrogen atoms were refined anisotropically. All H atoms were placed in calculated positions and thereafter treated as riding. A torsional parameter was refined for each methyl group. The constraints $U_{iso}(H) = 1.2U_{eq}(C_{alkyl,aryl}, B)$ and $U_{iso}(H) = 1.5U_{eq}(C_{methyl})$ were used. Salient crystallographic data are:

2: $C_{30}H_{33}BCl_2N_8Ru$, $M_r = 688.42$, green prism, $0.59 \times 0.06 \times 0.02$ mm, triclinic, space group $P-1$ (no. 2), $a = 8.6727(6)$ Å, $b = 12.5790(8)$ Å, $c = 14.5951(10)$ Å, $\alpha = 95.521(1)°$, $\beta = 102.513(1)°$, $\gamma = 102.035(1)°$, $V = 1503.5(2)$ Å^3, $Z = 2$, $\mu = 0.735$ mm^{-1}, $T = 297$ K. 26044 reflections were collected up to $\theta_{max} = 30.1°$ and, after applying absorption corrections, merged to 8712 independent data ($R_{int} = 0.027$); final R indices: $R_1 = 0.0320$ (7117 reflections with $I > 2\sigma(I)$), $wR_1 = 0.0780$ (all data), 384 parameters.

$\mathbf{6}\cdot 1/2C_5H_{12}$: $C_{40}H_{46}BClN_8O_2Ru \cdot 1/2C_5H_{12}$, $M_r = 854.25$, green prism, $0.52 \times 0.22 \times 0.18$ mm, monoclinic, space group $C2/c$ (no. 15), $a = 31.7233(17)$ Å, $b = 16.7259(9)$ Å, $c = 21.2705(11)$ Å, $\beta = 131.613(1)°$, $V = 8438.0(8)$ Å^3, $Z = 8$, $\mu = 0.480$ mm^{-1}, $T = 173$ K. 61873 reflections were collected up to $\theta_{max} = 30.0°$ and, after applying absorption corrections, merged to 12255 independent data ($R_{int} = 0.033$); final R indices: $R_1 = 0.0345$ (9888 reflections with $I > 2\sigma(I)$), $wR_1 = 0.0949$ (all data), 515 parameters. The COOEt group of this compound showed orientation disorder for the ethyl group which was taken into account with split positions and distance restraints.

Views of the molecular structures of **2** and $\mathbf{6}\cdot 1/2C_5H_{12}$ are shown in Figs. 1 and 2. CCDC 613067 and 613068 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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