

Carbynehydridoruthenium Complexes as Catalysts for the Selective, Ring-Opening Metathesis of Cyclopentene with Methyl Acrylate**

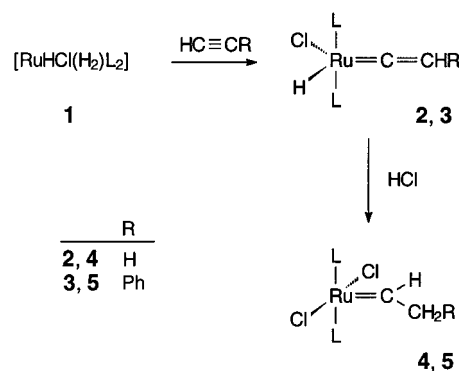
Wolfram Stüer, Justin Wolf, Helmut Werner,*
Peter Schwab, and Michael Schulz

*Dedicated to Professor Ernst-Otto Fischer
on the occasion of his 80th birthday*

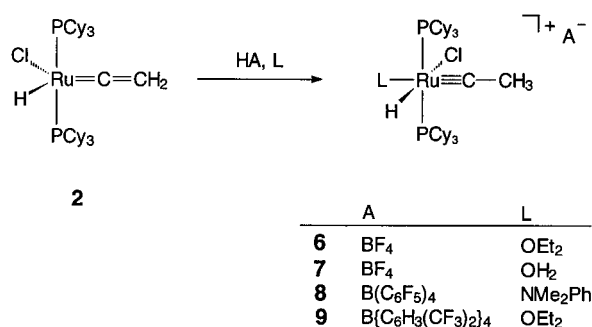
Carbeneruthenium complexes of the type $[\text{RuCl}_2(=\text{CHR})-(\text{PR}_3)_2]$, which were first prepared by Grubbs and co-workers, are not only highly efficient catalysts for olefin metathesis,^[1] but are also increasingly used in organic synthesis.^[2] In contrast to related catalytically active compounds of molybdenum and tungsten, the ruthenium complexes have the advantage of tolerating substrates containing polar functional groups.^[3] The disadvantage, however, is the low activity in the metathesis of electron-poor olefins such as acrylic acid and derivatives thereof. We are particularly interested in the selective ring-opening metathesis (ROM) of cyclopentene with various acyclic olefins as chain transfer reagents (CTA); the desired products are not telechelic polymers as in previous work,^[4] but linear functionalized olefins with a chain length of up to 20 carbon atoms. Owing to the work by Blechert, Crowe and co-workers it is known that the Grubbs-type catalysts are unsuitable for metathesis with electron-poor acyclic olefins as CTA, whereas the catalytically active carbene complexes of the Schrock-type can be applied to some extent.^[5] Here we describe the first catalysts based on ruthenium which are able to catalyze the selective ROM of cyclopentene with methyl acrylate as an electron-poor olefin, thereby leading to the formation of long-chain functionalized olefins as the main products.^[6]

Recently, we reported an efficient one-pot synthesis of the carbeneruthenium complexes $[\text{RuCl}_2(=\text{CHCH}_2\text{R})(\text{PCy}_3)_2]$ ($\text{R} = \text{H}$ (**4**), Ph (**5**); $\text{Cy} = \text{cyclohexyl}$) from RuCl_3 , Mg , PCy_3 , H_2 , $\text{HC}\equiv\text{CR}$, and H_2O .^[7] For establishing this synthesis it was important to recognize that upon treatment of **1**^[8] with 1-alkynes initially the hydridovinylidene compounds **2** and **3**^[9] are formed, which then react with HCl or a synthetic equivalent thereof to afford the desired carbene complexes **4** and **5**, respectively ($\text{L} = \text{PCy}_3$).

Following this observation, we were interested to find out whether the reaction of the hydridovinylidene compounds **2** and **3** with acids HA , containing an anion that does not coordinate to a metal center, would lead to the formation of



cationic carbene complexes of the general composition $[\text{RuCl}(=\text{CHCH}_2\text{R})(\text{PCy}_3)_2]^+$ (with A^- as anion). These 14-electron species could be the counterparts of the compound $[\text{Ru}(\text{Ph})(\text{CO})(\text{PtBu}_2\text{Me})_2]^+$, which was recently described by Caulton et al.^[10] Therefore, when a solution of complex **2** in $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ was treated with an excess of a solution of HBF_4 in Et_2O at -80°C and then worked-up in an appropriate way, a yellow solid was obtained. This compound is not the anticipated cationic ethylidene derivative $[\text{RuCl}(=\text{CHCH}_3)(\text{PCy}_3)_2]\text{BF}_4$ but, in agreement with the NMR spectra, the carbynehydrido complex **6**. The ^1H spectrum displays no signal in the low-field region, which would be expected for the α -hydrogen atom of an ethylidene ligand, but a triplet resonance at $\delta = -6.91$ ($^2J(\text{P},\text{H}) = 15$ Hz), assigned to a metal-bonded hydride. In the ^{13}C NMR spectrum of **6** the signal of the α -carbon atom of the carbyne ligand appears as a triplet at $\delta = 316.1$ ($^2J(\text{C},\text{P}) = 9$ Hz), and that of the β -carbon atom as a singlet at $\delta = 41.4$. Moreover, some resonances are observed which are assigned to an Et_2O ligand. This ligand is, however, only weakly coordinated and easily displaced by H_2O to give **7**. Analogous to the formation of **6**, compound **2** also reacts with $[\text{HNMe}_2\text{Ph}][\text{B}(\text{C}_6\text{F}_5)_4]$ and $[\text{H}(\text{OEt}_2)_2][\text{B}(\text{C}_6\text{H}_3(\text{CF}_3)_2)_4]$ ^[11] to afford the corresponding carbyne complexes **8** and **9**, which differ in the counterion and the donor ligand L . In addition to the spectroscopic data, the composition of **6–9** is supported by their reactivity towards soluble chloride sources. Instead of the neutral carbynehydrido complex $[\text{RuHCl}_2(=\text{CCH}_3)(\text{PCy}_3)_2]$ the isomeric carbene complex **4** is formed in quantitative yield.



To the best of our knowledge, compounds **6–9** are the first cationic carbynehydrido complexes of ruthenium. With respect to the characteristic ^1H and ^{13}C NMR spectroscopic data, they are related to the compound $[\text{OsHCl}(\equiv\text{CCH}_2\text{Ph})(\text{OH}_2)(\text{P}i\text{Pr}_3)_2]\text{BF}_4$, the only carbynehydridoosmium complex

[*] Prof. Dr. H. Werner, Dipl.-Chem. W. Stüer, Dr. J. Wolf
Institut für Anorganische Chemie der Universität
Am Hubland, D-97074 Würzburg (Germany)
Fax: (+49) 931-8884605
E-mail: helmut.werner@mail.uni-wuerzburg.de

Dr. P. Schwab, Dr. M. Schulz
BASF Aktiengesellschaft, Ammoniaklaboratorium
D-67056 Ludwigshafen (Germany)

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reported as yet.^[12a] Some uncharged compounds of the general composition $[\text{OsHCl}_2(\equiv\text{CCH}_2\text{R})(\text{PiPr}_3)_2]$ are also known.^[12b, c] Since for the corresponding osmium complex with $\text{R} = \text{Ph}$ the *cis* disposition of the hydrido and carbyne ligands has been confirmed by a single-crystal X-ray structure analysis,^[12b] we assume that for **6–9** a similar configuration exists. Density functional theory (DFT) calculations for **6** are in agreement with the proposed *cis* arrangement of the hydrido and carbyne ligands.^[13]

With regard to the mechanism of formation of compounds **6–9**, two possibilities are conceivable. The protonation of **2** either takes place at the β -carbon atom of the vinylidene ligand, or the attack of the proton is initially directed to the metal leading to the formation of the intermediate $[\text{RuH}_2\text{Cl}(\equiv\text{C}=\text{CH}_2)(\text{PCy}_3)_2]^+$, which subsequently isomerizes to the respective carbynehydrido complex by a 1,3-hydrogen shift. A labeling experiment, based on the reaction of **2** with $[\text{DNMe}_2\text{Ph}][\text{B}(\text{C}_6\text{F}_5)_4]$, clearly confirms that the protonation follows the first pathway. As the ^2H NMR spectrum reveals, the deuterated compound $[\text{RuHCl}(\equiv\text{CCH}_2\text{D})(\text{NMe}_2\text{Ph})(\text{PCy}_3)_2][\text{B}(\text{C}_6\text{F}_5)_4]$ (**D₁8**) is exclusively formed, while an isotopomer with the deuterium bonded to the metal center cannot be detected.

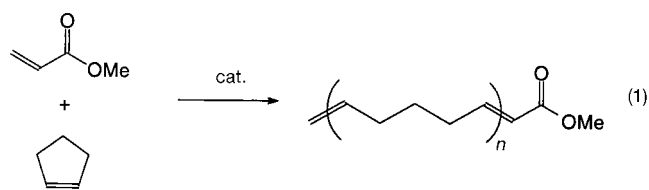
Compounds **6–9** are yellow air-sensitive solids which in solution at room temperature completely decompose within 20–30 min. The stability depends only slightly on the counterion A^- , but is strongly influenced by the donor ligand L . Thus, the analogue of **6** with $\text{L} = \text{THF}$ is significantly more labile in solution than the adduct with Et_2O . In this respect, it is important to note that the stability of the carbynehydrido derivatives increases considerably (up to several hours) upon addition of excess of L or HA to the solution. We therefore believe that the decomposition of **6–9** in solution is initiated both by the dissociation of L as well as by deprotonation.

The aforementioned lability of **6–9** possibly explains why these compounds are not accessible by halide abstraction from **4** with silver or thallium salts. At low temperature, no reaction between **4** and AgX or TiX occurs, and at room temperature unidentified mixtures of products are formed. However, if **4** is treated with a large excess (ca. 100-fold) of HBF_4 in Et_2O the carbynehydrido complex **6** is surprisingly generated in about 20% yield. As a by-product the phosphonium salt $[\text{HPCy}_3]\text{BF}_4$ (**10**) has been isolated.

Compounds **6–9** are highly efficient catalysts for olefin metathesis. We investigated in particular the catalytic activity of complex **6**, which catalyzes the ring opening metathesis polymerization (ROMP) of cyclic olefins such as cyclopentene, cyclooctene, cyclooctadiene, dicyclopentadiene, and oxanorbornene derivatives even more effectively than the Grubbs compound $[\text{RuCl}_2(\equiv\text{CHPh})(\text{PCy}_3)_2]$ (**11**).^[14] A comparison experiment reveals that ROMP of cyclooctene (room temperature, $c_{\text{cat.}} = 10^{-3}\text{ M}$, time: 3 min, yield 90%) with **6** as catalyst is about 20 times faster than with **11**. The molecular-weight distribution and the polydispersity index of the polymer (amount of *trans* olefin 76%) is presently under investigation. From some preliminary experiments it can be concluded that the activity of **7–9** is comparable to that of **6**.

However, the carbynehydrido complexes **6–9** also catalyze the cross-olefin metathesis of cyclopentene with methyl

acrylate [Eq. (1)]. Hereby a mixture of the first members of the homologous series of multiply unsaturated esters



$\text{C}_7\text{H}_{11}\text{CO}_2\text{CH}_3$, $\text{C}_{12}\text{H}_{19}\text{CO}_2\text{CH}_3$, and $\text{C}_{17}\text{C}_{27}\text{CO}_2\text{CH}_3$ are formed with a selectivity of 50, 40, and 10%. Compounds **4** and **11** are catalytically inactive in this process.

The cationic carbynehydrido complexes reported here are the first ruthenium compounds which are able to catalyze the metathesis of electron-poor olefins. Further applications of **6–9**, for example, for the cross-metathesis of alkynes,^[15] are now being studied in our laboratory. Weiss^[16a] as well as Fürstner^[16b] and co-workers have recently shown that the carbonyl complex $[\text{W}(\equiv\text{CCMe}_3)(\text{OCMe}_3)_3]$ is a highly active catalyst both for the metathesis of acyclic diynes (ADIMET) and for the ring-closing reaction of diynes to cycloalkynes. For the neutral carbyneruthenium compounds $[\text{RuCl}(\equiv\text{CR})(\text{CO})(\text{PPh}_3)_2]$, which have been prepared by Roper et al. from $[\text{RuCl}_2(\equiv\text{CCl}_2)(\text{CO})(\text{PPh}_3)_2]$ and LiR ,^[17] a similar catalytic activity is unknown. Besides **6–9**, most recently also *cationic* allyl- and allenylideneruthenium complexes were described which partly catalyze olefin metathesis upon activation with diazoalkanes.^[18]

Since the lifetime of the catalysts **6–9** is still lower than that of **4** or **11**, we are currently attempting to improve the stability by modifying the phosphane as well as the coordinated anionic ligand. The use of isocyanate or phenolate instead of chloride seems to be promising.

Experimental Section

6: Compound **2** (102 mg, 0.14 mmol) was dissolved in a mixture of CH_2Cl_2 (5 mL) and Et_2O (5 mL). The red-brown solution was then treated at -80°C with an excess of HBF_4 in Et_2O (ca. 0.1 mL of a 1.6 M solution of HBF_4 in Et_2O). The reaction mixture was slowly warmed to 0°C , the solvent was removed in vacuo, and Et_2O (5 mL) was added to the brown residue. After a few minutes a yellow solid precipitated, which was filtered and washed with Et_2O (5 mL). Yield: 90 mg (72%). Equivalent conductivity in CH_2Cl_2 : $47\text{ cm}^2\text{ }\Omega^{-1}\text{ mol}^{-1}$. The NMR spectra were measured in the presence of a small amount of Et_2O and $[\text{HPCy}_3]\text{BF}_4$ at room temperature (see text). ^1H NMR (400 MHz, CD_2Cl_2): $\delta = 4.77$ (q, $^3J(\text{H,H}) = 7.0$ Hz, 4H, $\text{RuOCH}_2\text{CH}_3$), 2.52–2.46 and 2.01–1.30 (both m, 75H, PCy_3 , $\text{RuOCH}_2\text{CH}_3$ and RuCCH_3), -6.91 (t, $^2J(\text{P,H}) = 15$ Hz, 1H, RuH); ^{31}P NMR (162 MHz, CD_2Cl_2): $\delta = 55.5$ (s); ^{19}F NMR (376.4 MHz, CD_2Cl_2): $\delta = -151.1$ (s); ^{13}C NMR (100.6 MHz, CD_2Cl_2): $\delta = 316.1$ (t, $^2J(\text{C,P}) = 9$ Hz, RuCCH_3), 84.6 (s, $\text{RuOCH}_2\text{CH}_3$), 41.4 (s, RuCCH_3), 35.7 (vt, $N = 22$ Hz, C_1 of PCy_3), 31.6, 30.4 (both s, PCy_3), 27.6, 27.3 (both vt, $N = 10$ Hz, C_2 of PCy_3), 26.2 (s, PCy_3), 12.7 (s, $\text{RuOCH}_2\text{CH}_3$).

7: A solution of **6** (80 mg, 0.09 mmol) in CH_2Cl_2 (5 mL) was shaken with degassed H_2O (3 mL) for 1 min. The organic phase was separated, and the solvent was removed in vacuo to provide a yellow solid. Yield: 61 mg (81%). ^1H NMR (400 MHz, CD_2Cl_2 , -60°C): $\delta = 2.49$ –2.39 and 2.00–1.09 (both m, 71H, PCy_3 , OH_2 , CH_3), -6.48 (brt, $^2J(\text{P,H}) = 12$ Hz, 1H, RuH); ^{31}P NMR (162 MHz, CD_2Cl_2 , -60°C): $\delta = 56.2$ (s); ^{13}C NMR (100.6 MHz, CD_2Cl_2 , -60°C): $\delta = 314$ (brs, RuCCH_3), 40.8 (s, RuCCH_3), 34.1 (vt, $N = 22$ Hz, C_1 of PCy_3), 30.6, 29.0, 26.8, 26.5, and 25.4 (all s, PCy_3).

8: A solid sample of **2** (72 mg, 0.10 mmol) was mixed with $[\text{HNMe}_2\text{Ph}][\text{B}(\text{C}_6\text{F}_5)_4]$ (80 mg, 0.10 mmol) and treated at -80°C with of CD_2Cl_2 (2 mL). According to the NMR spectra, the generated yellow solution contained exclusively complex **8**. ^1H NMR (200 MHz, CD_2Cl_2 , -60°C): $\delta = 7.32\text{--}6.97$ (m, 5H, Ph-H), 3.0 (brs, 6H, NCH_3), 2.39–1.24 (m, 69H, PCy_3 and RuCCH_3), -6.33 (t, $^2J(\text{P,H}) = 15$ Hz, 1H, RuH); ^{31}P NMR (162 MHz, CD_2Cl_2 , -70°C): $\delta = 56.6$ (s); ^{13}C NMR (100.6 MHz, CD_2Cl_2 , -70°C): $\delta = 311.9$ (brs, RuCCH_3), 147.4 (d, $^1J(\text{C,F}) = 239$ Hz, C_6F_5), 137.7 (d, $^1J(\text{C,F}) = 245$ Hz, C_6F_5), 135.7 (d, $^1J(\text{C,F}) = 247$ Hz, C_6F_5), 129.0 (s, NPh), 123.2, 118.1 and 113.4 (all brs, NPh), 41.5 (brs, NCH_3), 40.2 (s, RuCCH_3), 34.0 (vt, $N = 23$ Hz, C_1 of PCy_3), 30.6, 28.9, 26.7, 26.4, and 25.3 (all s, PCy_3).

9: Analogous to the synthesis of **8**, compound **9** was prepared in quantitative yield from **2** (20 mg, 0.028 mmol) and $[\text{H}(\text{OEt})_2]\text{B}[\text{C}_6\text{H}_3(\text{CF}_3)_2]_4$ (28 mg, 0.028 mmol) in CD_2Cl_2 and characterized spectroscopically at room temperature. ^1H NMR (200 MHz, CD_2Cl_2): $\delta = 7.75$, 7.59 (both m, 12H, $\text{B}[\text{C}_6\text{H}_3(\text{CF}_3)_2]_4$), 3.36 (q, $^3J(\text{H,H}) = 6.6$ Hz, 8H, OCH_2CH_3), 2.7–1.2 (m, 69H, PCy_3 and RuCCH_3), 1.19 (t, $^3J(\text{H,H}) = 6.6$ Hz, 12H, OCH_2CH_3), -6.57 (t, $^2J(\text{P,H}) = 15$ Hz, 1H, RuH); ^{31}P NMR (81 MHz, CD_2Cl_2): $\delta = 57.2$ (s).

Selective ROM of cyclopentene with methyl acrylate: A solution of **2** (56 mg, 0.077 mmol) in a mixture of CH_2Cl_2 (2 mL), Et_2O (2 mL), and 0.5 mL of a 1.6 M solution of HBF_4 in Et_2O was added to a mixture of methyl acrylate (50 mL, 0.552 mol) and cyclopentene (4 mL, 0.045 mol) at room temperature. After the solution was stirred for 2 h at room temperature, the solvent and excess of substrate were distilled off at normal pressure, the remaining residue was treated with pentane (10 mL), and upon addition of Et_2O (60 mL) the solution was filtered through aluminum oxide (neutral, activity grade III). After removal of the solvent, a colorless liquid (2.5 g) was obtained, the composition of which was investigated by GC/MS. The liquid contained the first members of a homologous series of long-chain multiply unsaturated esters $\text{C}_7\text{H}_{11}\text{CO}_2\text{CH}_3$, $\text{C}_{12}\text{H}_{19}\text{CO}_2\text{CH}_3$, and $\text{C}_{17}\text{H}_{27}\text{CO}_2\text{CH}_3$ in ratios of 50, 40, and 10%.

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Rapid Assembly of Oligosaccharides: Total Synthesis of a Glycosylphosphatidylinositol Anchor of *Trypanosoma brucei***

Daniel K. Baeschlin, André R. Chaperon, Virginie Charbonneau, Luke G. Green, Steven V. Ley,* Ulrich Lücking, and Eric Walther

Glycoproteins and glycolipids are major components of the outer surface of eukaryotic cells and play a vital role in fundamental biological processes such as viral, bacterial, and parasitic infections, immune defence, and inflammation.^[1] Intensive research into the biological role of carbohydrates has led to an increased need for the synthesis of natural and modified glycoconjugates. Although remarkable progress has been made in the field of oligosaccharide synthesis,^[2] further innovations are still required since the synthesis of complex oligosaccharides remains a highly specialized and time con-

[*] Prof. Dr. S. V. Ley, D. K. Baeschlin, Dr. A. R. Chaperon, V. Charbonneau, Dr. L. G. Green, U. Lücking, Dr. E. Walther
Department of Chemistry, University of Cambridge
Lensfield Road, Cambridge CB2 1EW (UK)
Fax: (+44) 1223-336442
E-mail: svl1000@cam.ac.uk

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