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Synthesis, characterization, and catalytic activity of a ruthenium carbene complex coordinated with bidentate 2-pyridine-carboxylato ligands

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Abstract

The halide and phosphine free complex [(sIMes)(C_5H_4N-2-CO_2)$_2$Ru=CHPh] (**7**) (sIMes = 1,3-dimesitylimidazolidin-2-ylidene) bearing two bidentate 2-pyridinecarboxylato ligands was synthesized from the carbene complex [(sIMes)(PCy_3)Cl_2Ru=CHPh] (**4**) and the silver 2-pyridine-carboxylate (**8**). The molecular structure of the octahedral complex **7** reveals that the two carboxylato functions are coordinated in *cis* geometry to the ruthenium center. Catalyst **7** exhibits activity in ring-closing metathesis (RCM) reactions after addition of a cocatalyst (HCl) in dichloromethane as well as in methanol solution.

Keywords: *N*-heterocyclic carbene; Ruthenium; Olefin metathesis

1. Introduction

During the past decade catalytic olefin metathesis has become a versatile tool for the formation of C–C bonds [1]. The activity of the initially used ruthenium diphosphine complex **1** [2] was significantly increased by substitution of one phosphine ligand for an *N*-heterocyclic carbene. Particularly the ruthenium carbene complexes [(sIMes)(PCy_3)Cl_2Ru=CHPh] (sIMes = 1,3-dimesitylimidazolidin-2-ylidene) (**4**) [3] and [(sIMes)Cl_2-Ru(=CH-*o*-O*i*PrC_6H_4)] (**5**) [4] represent reagents of choice for a variety of applications in organic chemistry (Scheme 1). The imidazolidin-2-ylidene ligand in complexes **4** and **5** emerged as an ideal σ-donating ligand, and different procedures for the preparation of such ligands [5] and their Ru complexes including derivatives with unsymmetrically substituted carbene ligands [6] have been developed.

Complexes **2** and **3** represent examples of water soluble metathesis catalysts [7]. They have been employed successfully in ring-opening metathesis polymerizations (ROMP) [7a,7b]. However, they did not catalyze the ring-closing metathesis (RCM) of unsubstituted α,ω-dienes such as diethyl diallylmalonate [7c], a reaction readily catalyzed by complexes **1**, **4** and **5**. In an attempt to overcome some of the limitations of catalyst **1**, in particular its moderate O_2 and temperature stability in solution, Ru alkylidene complexes with a modified ligand sphere have also been studied. The octahedral 18 electron complex **6** (Scheme 1) is air-stable [8]. However, complex **6** is coordinatively saturated and ligand dissociation is necessary before olefin metathesis can take

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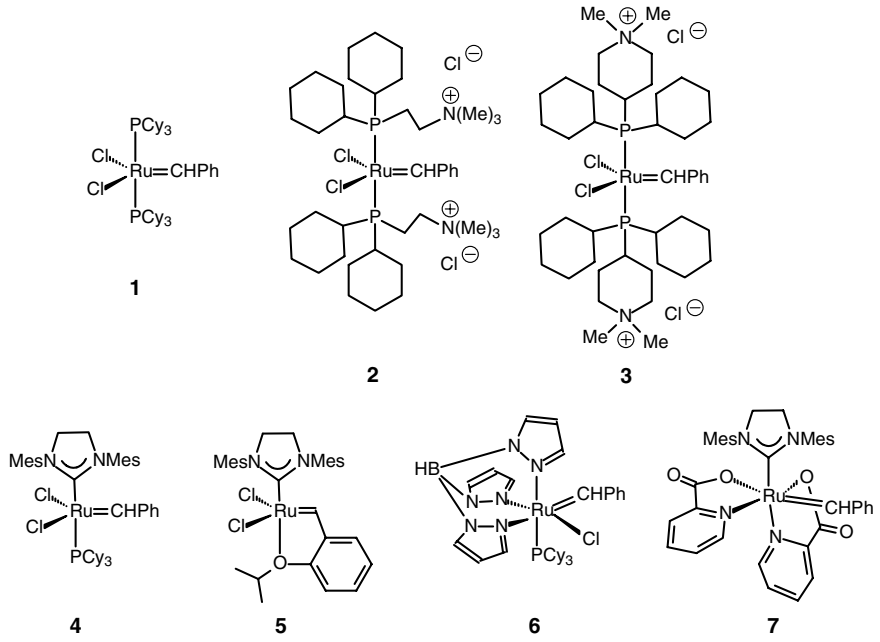


Scheme 1. Olefin metathesis catalysts.

place. It can be activated for RCM of diethyl diallylmalonate by cocatalysts such as HCl, CuCl or $AlCl_3$ but large amonts of **6** (20 mol%) are necessary to achieve complete ring closure.

Recently, improvement of catalyst design is centered around the substitution of the remaining phosphine in **4** [4] or of the halide ligands in **4** [9] and **5** [10]. Replacement of the chloride ligands in **4** by carboxylates represents a key step for the preparation of immobilized metathesis catalysts [9]. Highly active octahedral precatalysts of type $[(sIMes)L_2X_2Ru{=}CHR]$ (L = pyridine) were obtained by substitution of the phosphine in **4** by two pyridine ligands. These catalysts initiate metathesis by dissociating one L-type ligand [11]. Substitution of the bidentate alkylidene/ether ligand in **5** by a 2-pyridylethanyl carbene ligand gives the complex $[(sIMes)(Cl)_2Ru(CH(CH_2)_2C,N\text{-}2\text{-}C_5H_4N)]$ which exhibits a particularly slow initiation rate in ring-opening olefin metathesis polymerizations [12].

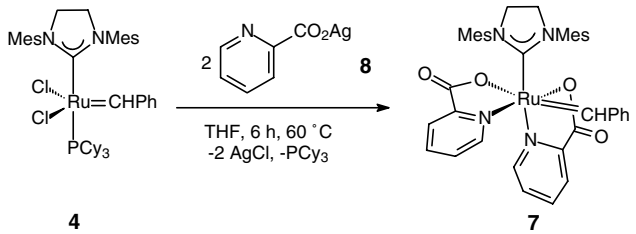
In an attempt to prepare new Ru alkylidene complexes with an improved stability, which maintain the favorable properties of the sIMes containing derivatives of type **4** but are halide free [13] we synthesized precatalyst **7** (Scheme 1). In complex **7** both the phosphine ligand and the two halide ligands of **4** are substituted by two 2-pyridinecarboxylato ligands coordinated in a chelating fashion [14]. In this contribution, we report on the preparation and molecular structure of precatalyst **7** and present the first results on its catalytic activity in ring-closing metathesis after activation with HCl in dichloromethane as well as in polar protic solvents such as methanol.

2. Results and discussion

2.1. Complex synthesis and characterization

The preparation of the ruthenium catalyst **7** is straightforward using readily available starting materials. Precatalyst **7** was obtained by heating a stoichiometric mixture of **4** and silver 2-pyridine-carboxylate **8** in THF at 60 °C for 6 h (Scheme 2). In the course of the reaction, the initial red color of the suspension turned to bright green. Complex **7** was isolated in about 80% yield after column chromatography in air. The silver salt **8** was synthesized by addition of sodium hydrogen carbonate and silver nitrate to an aqueous solution of pyridine 2-carboxylic acid. Some ruthenium complexes with pyridine 2-carboxylato ligands have been reported previously [14].

The ruthenium complex **7** can be stored in solutions of wet $CDCl_3$ or DMF under ambient conditions in air without noticeable decomposition for several weeks. The ^1H NMR spectroscopic characterization of **7** in



Scheme 2. Preparation of complex **7** from compounds **4** and **8**.

$CDCl_3$ reveals the characteristic resonance signal for the alkylidene proton at $\delta = 18.13$ ppm. Compared to the corresponding resonance of this proton in the phosphine containing complex **4** ($\delta = 19.16$ ppm [3a]) and the hexacoordinate pyridine complex [(sIMes)(py)$_2$(Cl)$_2$-Ru=CHPh] ($\delta = 19.67$ ppm [11a]) a slight high field shift is observed. In addition, a broad multiplet resonance signal of the methylene protons of the *N*-heterocyclic ring of the carbene ligand is observed in the range of $\delta = 3.79$–3.92 ppm. We attribute this observation to the hindered rotation of the carbene ligand around the ruthenium carbene carbon axis at ambient temperature. The coalescence temperature for this process is too high to be reached with conventional NMR solvents and was therefore not determined.

Crystals of **2** · 2DMF suitable for an X-ray crystal structure determination were grown by vapor diffusion of diethyl ether into a saturated DMF solution of **7** at room temperature. The molecular structure of **7** complex is depicted in Fig. 1.

The carboxylato groups as well as the pyridine donors are coordinated in *cis* fashion in **7**. To our knowledge, this kind of coordination environment and geometry has not been reported for ruthenium carbene complexes previously. Coordination of two pyridine ligands in *cis* fashion has been described for octahedral ruthenium carbene complexes of type [(sIMes)(py)$_2$X$_2$-Ru=CHPh] [11a]. The anionic ligands in these complexes, however, are normally coordinated in *trans* positions. Octahedral complexes *cis*-[Ru(PPh$_3$)$_2$L$_2$] (L = 2-pyridinecarboxylate or 2-pyrazinecarboxylate) show a *cis* arrangement for the phosphine and pyridine donors and a *trans* orientation for the carboxylato groups [14]. NOE experiments confirm that only one pair of enantiomers of **7** exists in solution.

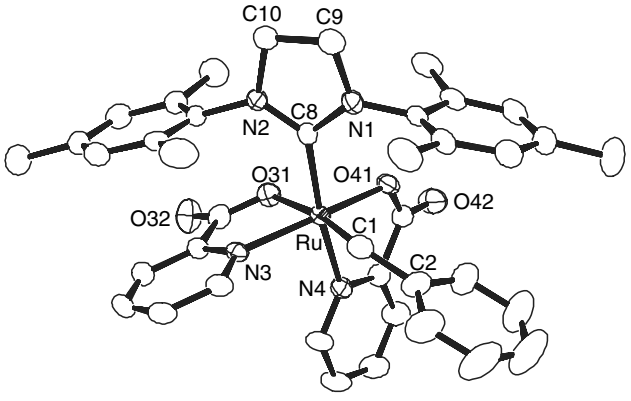


Fig. 1. Molecular structure of **7** in **7** · 2DMF (hydrogen atoms and DMF molecules have been omitted for clarity). Selected bond lengths (Å) and bond angles (°): Ru–O31 2.173(3), Ru–O41 2.062(3), Ru–N3 2.078(3), Ru–N4 2.107(3), Ru–C1 1.876(5), Ru–C8 2.088(4), N1–C8 1.353(5), N2–C8 1.348(5); O31–Ru–O41 84.55(12), O31–Ru–N3 77.69(12), O31–Ru–N4 82.49(12), O31–Ru–C1 170.43(15), O31–Ru–C8 96.94(14), O41–Ru–N3 160.57(12), O41–Ru–N4 78.73(12), O41–Ru–C1 102.0(2), O41–Ru–C8 93.41(13), N3–Ru–N4 91.10(13), N3–Ru–C1 94.8(2), N3–Ru–C8 96.45(14), N4–Ru–C1 91.8(2), N4–Ru–C8 172.14(14), C1–Ru–C8 89.7(2), N1–C8–N2 106.1(4).

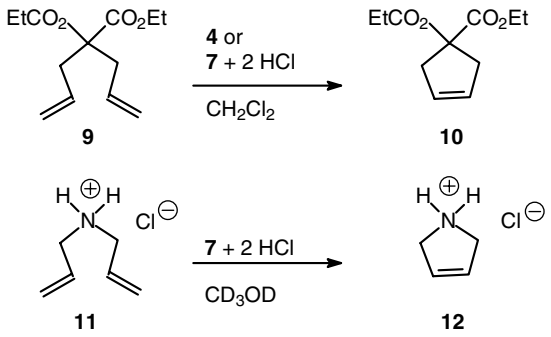
The Ru–alkylidene bond length in **7** (Ru=C1 1.876(5) Å) is slightly longer than the corresponding distances in five-coordinate Ru–carbene catalysts like **4** (Ru=C 1.835(2) Å [11d]) and **5** (Ru=C 1.828(5) Å [4a]) which is a result of the enlarged coordination number in **7**. Similar observations were made for other octahedral ruthenium alkylidenes [8]. The Ru–N separations are different with the bond distance Ru–N4 longer than Ru–N3 owing to the larger *trans* effect of the carbene ligand. Similar arguments hold for the Ru–O distances.

2.2. Catalysis experiments

The catalytic activity of **7** was initially tested in the ring-closing metathesis reaction of diethyl diallylmalonate **9** to give the cyclopentene **10** (Scheme 3). In contrast to catalyst **4** complex **7** alone does not promote the conversion of **9** to **10**. The ring-closing metathesis reaction is initiated upon addition of two equivalents of HCl to the mixture of **9** and **7** (5 mol%) in CH_2Cl_2. The addition of the cocatalyst and the generation of the catalytically active species is accompanied by a color change from green to brown. We propose that the addition of HCl to **7** leads to protonation of at least one of the pyridine-2-carboxylato ligands. Pyridine 2-carboxylic acid and the 2-pyridinecarboxylato complex [(sIMes)(C_5H_4N-2-CO_2)(Cl)Ru=CHPh] were identified in the reaction mixture after addition of HCl by mass spectroscopy.

After the addition of the cocatalyst complex **7** cyclizes diethyl diallylmalonate to give **10**. After 90 min at room temperature a conversion of 94% and after 120 min complete conversion was achieved (Table 1). However, catalyst **7** is even after activation with HCl less active then catalyst **4** which at a concentration of only 1 mol% is capable to convert 99% of **9** within 90 min into **10** (Table 1, entry 6) [15].

The advantages of precatalyst **7** become apparent when protic solvents are needed for the metathesis reaction. The diallylamine hydrochloride **11** is soluble in



Scheme 3. RCM experiments carried out with complexes **4** and **7**.

Table 1
Ring-closing metathesis with catalysts **4** and **7**

Entry	Catalyst	Substrate	Product	Time (min)	Yield (%)
1[a]	**7**	**9**	**10**	20	11
2[a]	**7**	**9**	**10**	40	38
3[a]	**7**	**9**	**10**	60	68
4[a]	**7**	**9**	**10**	90	94
5[a]	**7**	**9**	**10**	120	100
6[b]	**4**	**9**	**10**	90	99
7[c]	**7**	**11**	**12**	300	43
8[c]	**7**	**11**	**12**	720	70

[a] 5 mol% **7**, cocatalyst 2 eq. HCl, CH_2Cl_2 20 °C.
[b] 1 mol% **4**, CH_2Cl_2, 20 °C, data from [15].
[c] 5 mol% **7**, cocatalyst 2 eq. HCl, CD_3OD, 40 °C.

methanol, a solvent where catalyst **4** exhibits only a limited stability. Precatalyst **7**, however, is stable in methanol for weeks and can be activated in this solvent with two equivalents of HCl. Under these conditions a moderate activity (70% conversion after 12 h at 40 °C) in ring-closing metathesis to give **12** was observed (Table 1, entries 7–8).

In this contribution, we have describe the preparation of an air-stable 18 valence-electron ruthenium alkylidene-carbene-2-pyridinecarboxylato complex **7**, which is soluble and stable in CH_2Cl_2 and methanol. Complex **7** was fully characterized including an X-ray diffraction analysis of the air-stable solvate **7** · 2DMF. Complex **7** acts as a precatalyst for the ring-closing olefin metathesis after activation by the cocatalyst HCl. The catalytically active species is most likely formed by protonation of a 2-pyridinecarboxylato ligand. Ring-closing olefin metathesis was observed in CH_2Cl_2 and, with moderate activity, in methanol. Attempts to further optimize the RCM in polar and protic solvents using precatalyst **7** are underway.

3. Experimental

3.1. General procedures

All manipulations were performed in an atmosphere of dry argon by standard Schlenk techniques. Silver 2-pyridinecarboxylate [14] and [(sIMes)(PCy_3)$(Cl)_2$Ru=CHPh] (sIMes = 1,3-dimesitylimidazolidin-2-ylidene) **4** [3a] were prepared according to the literature procedures. Other reagents and solvents were used as purchased. Silica gel used for column chromatography was obtained from Merck (Kieselgel 60, 230–400 mesh). ^1H and ^{13}C NMR spectra were recorded on a Bruker AMX 400 (400 MHz) or a Varian Unity Plus (600 MHz) spectrometer using Me_4Si as internal standard. Mass spectral analyses were performed on Varian MAT 212 (EI), Bruker Reflex IV (MALDI) or Finnigan MAT IDT 800 (GC–MS) spectrometers. Elemental analyses were obtained with a Vario EL III CHNS Elemental Analyzer at the Institut für Anorganische und Analytische Chemie, Westfälische Wilhelms-Universität Münster.

3.2. Synthesis of di(2-pyridinecarboxy-lato)-benzylidene(1,3-dimesitylimidazolidin-2-ylidene)-ruthenium(II) (7)

Silver 2-pyridinecarboxylate **8** (172 mg, 0.75 mmol) was added to a solution of [(sIMes)(PCy_3)$(Cl)_2$-Ru=CHPh] **4** (255 mg, 0.3 mmol) in THF (20 mL). The resulting mixture was heated at 60 °C for 6 h, during which time the suspension became greenish. After cooling, all further operations were carried out in air. The suspension was filtered and the solvent was removed under vacuum. Column chromatography (silica gel, diethyl ether/methanol 10:1, v:v) of the crude product gave **7** as a green solid. Alternatively, purification could be achieved by repeated recrystallization from methanol/diethyl or DMF/diethyl ether. In the latter case the solvate **7** · 2DMF was obtained. Yield 178 mg (0.24 mmol, 80%). Anal. Calc. for **7** · 2DMF: $C_{46}H_{54}N_6O_6Ru$: C, 62.22; H, 6.13; N, 9.46%. Found: C, 62.01; H, 5.98; N, 9.79%. ^1H NMR (400.1 MHz, $CDCl_3$): δ1.96, 2.02, 2.46 (3 × s, 18H, mesityl-CH_3), 3.79–3.92 (m, br, 4H, NCH_2CH_2N), 5.54 (d, 1H, py-H), 6.40, 6.79 (2 × s, 4H, mesityl-H), 6.50 (br s, 1H, py-CH), 6.87 (dd, ^3J(H,H) = 7.5 Hz, 7.5 Hz, 2H, Ph–H_{meta}), 7.01 (d, ^3J(H,H) = 7.5 Hz, 2H, Ph–H_{ortho}), 7.15 (t, ^3J(H,H) = 7.5 Hz, 1H, Ph–H_{para}), 7.22 (m, 1H, py-H), 7.44 (m, 1H, py-H), 7.64 (t, 1H, py-H), 7.70 (d, 1H, py-H), 8.02 (d, 1H, py-H), 8.67 (d, 1H, py-H), 18.13 (s, 1H, Ru=C*H*Ph). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 17.8, 18.4, 20.8 (mesityl-CH_3), 51.6 (NCH_2), 124.6, 125.9, 126.3, 127.1, 127.2, 127.8, 128.5, 129.0, 136.3, 136.5, 136.8, 136.9, 137.9, 145.0, 147.9, 151.7, 154.3, 157.8 (py-C, mesityl-C, Ph–C), 165.6, 174.0 (C=O), 207.0 (NCN), 310.7 (Ru=CH–Ph). MS (MALDI): *m/z*: 741 $[M]^+$, 651 $[M - C_7H_6]^+$, 619 $[M - C_5H_4NCO_2]^+$.

3.3. Olefin metathesis experiments

3.3.1. Ring-closing metathesis of diethyl diallylmalonate

Diethyl diallylmalonate (130 mg, 0.54 mmol) and catalyst **7** (20 mg, 0.027 mmol) were dissolved in degassed dichloromethane (20 mL). The catalytic reaction was started by addition of hydrochloric acid (1 M in diethyl ether, 0.054 mL, 0.054 mmol). Samples of the reaction mixture (3 mL) were taken after 20, 40, 60, 90, and 120 min. They were washed twice with an aqueous solution of sodium hydrogen carbonate (1 mL). The organic phase was separated, dried over magnesium sulphate and finally subjected to GC–MS analysis. The yield of cyclized product was determined by integration of the

peaks for the starting material and the product in the GC–MS chromatogram.

3.3.2. Ring-closing metathesis of diallylamine hydrochloride

Diallylamine hydrochloride (79 mg, 0.59 mmol), which was prepared from diallylamine and an etheral solution of hydrogen chloride, and catalyst **7** (22 mg, 0.029 mmol) were dissolved in degassed methanol (0.6 mL). The reaction mixture was stirred at 40 °C. The catalytic reaction was initiated by addition of hydrochloric acid (2 M in diethyl ether, 0.03 mL, 0.06 mmol). Samples of the reaction mixture (0.2 mL) were taken after 5 h and after 12 h. The solvent was removed under vacuum, the samples were redissolved in CD_3OD and immediately subjected to an ^1H NMR spectroscopic investigation. An estimate of the conversion rate was obtained by integration of the signal for the methylene protons in α-position to the double bond in the cyclized product ($\delta = 4.10$ ppm, s) relative to the methylene protons of the uncyclized diallylamine hydrochloride ($\delta = 3.66$ ppm, d).

3.4. Selected crystallographic details for 7 · 2DMF

Bright green crystals of **7** · 2DMF were obtained by diffusion of diethyl ether into a saturated solution of **7** in DMF. Selected crystallographic details: size of data crystal $0.25 \times 0.05 \times 0.03$ mm^3, formula $C_{44}H_{54}N_6O_4Ru$, $M = 888.02$ a.m.u., triclinic, space group $P\bar{1}$ (No. 2), $a = 8.183(1)$ Å, $b = 16.087(1)$ Å, $c = 18.514(1)$ Å, $\alpha = 66.30(1)°$, $\beta = 78.69(1)°$, $\gamma = 79.29(1)°$, $V = 2172.7(3)$ Å^3, $Z = 2$, $\rho_{calc} = 1.357$ g cm^{-3}, Mo Kα radiation, μ(Mo Kα) $= 0.416$ mm^{-1}. 18 541 intensity data were collected at 198(2) K in the 2Θ-range 4.3–51.6°. 8800 symmetry independent ($R_{int} = 0.0664$), absorption corrected ($0.988 \leqslant T \leqslant 0.90$) intensities. Structure solution with Patterson and refinement with Fourier methods, refinement (on F^2) of positional parameters of all non-hydrogen atoms with anisotropic thermal parameters. $R^1 = 0.0624$, $wR^2 = 0.1276$ for 6825 structure factors $I \geqslant 2\sigma(I)$ and 542 refined parameters, max. residual electron density 0.83 (−0.65) e Å^{-3}. Hydrogen atoms reside on calculated positions and were refined as riding atoms. All calculations were carried out with the SHELX program package [16,17].

4. Supplementary material available

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 256804 for compound **7** 2DMF. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1ZE, UK, fax. (int code) +44 1223 336 033 or e-mail: deposit@ccdc.cam.ac.uk.

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