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Single component ruthenium(IV) catalysts for the ring-opening polymerization of norbornene

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Abstract

The neutral complexes $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})\{Sb(C_6H_5)_3\}Cl_2]$ **2a** and $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})\{P(OC_6H_5)_3\}Cl_2]$ **2b** were obtained by addition of neutral ligands $[Sb(C_6H_5)_3$ and $P(OC_6H_5)_3]$ to $[\{Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})(\mu\text{-}Cl)Cl\}_2]$ **1** and their structure was determined by both NMR spectroscopy and crystal structure analysis in case of **2a** (triclinic, space group $P\bar{1}$, $a = 10.556(6)$ Å, $b = 10.823(5)$ Å, $c = 13.156(7)$ Å, $\alpha = 93.34°$, $\beta = 108.47(3)°$, $\gamma = 112.64(3)°$, $V = 1288(1)$ Å^3, $Z = 2$, $D_{calc.} = 1.71$ g cm^{-3}, $R_w = 0.021$). The compounds **2a** and **2b** are very active single component catalysts for ring-opening polymerization of norbornene. Their catalytic activity depends on the displacement of the ligand L [$L = Sb(C_6H_5)_3$, $P(OC_6H_5)_3$] by the olefin. The polymers thus produced have high molecular weights M_n of $4.5 \cdot 10^5$ g mol^{-1} with a monomodal distribution and with polydispersities from 2.4 to 5.3. The *cis* selectivity of **2a** and **2b** (up to 30%) is higher than that of many other ruthenium-based catalysts for the polymerization of strained cyclo-olefins.

Keywords: Allylruthenium(IV); Norbornene; Polymerization; Ring opening

1. Introduction

Organometallic compounds in high oxidation states and their application in homogeneous catalysis are being intensively investigated at the present time [1,2]. Our interest has been focused on the synthesis and the catalytic properties of bis(allyl)ruthenium complexes in the +4 metal oxidation state.

In 1965 Porri et al. described the dimeric, chloro-bridged bis(allyl)ruthenium complex $[\{Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})(\mu\text{-}Cl)Cl\}_2]$ **1** [3]. The crystal structure of **1** shows that the complex has C_i symmetry [4]. In solution **1** exists as two diastereomers which, in non-coordinating solvents, are present in an approximate 1:1 ratio [5,6]. One isomer has C_i symmetry, while the authors propose the second isomer to have C_2 symmetry (Fig. 1).

1 reacts with neutral ligands to form monomeric complexes of type $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})LCl_2]$ (L = CO, pyridine, phosphines, $P(OMe)_3$, ^{t}BuNC and EtSH) [3,7–9]. The structure of these complexes is shown for the monomeric adduct $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})(PF_3)Cl_2]$ [10].

The catalytic properties of **1** and of the tertiary phosphine adduct **1** + 2 $P(C_6H_5)_3$ for norbornene polymerization were previously investigated [11,12]. Both systems catalyse the ring-opening polymerzation of norbornene with a slow activity (TON ≈ 30 mol PNB/(mol Ru · h) at 60°C [12]) and with a small *cis* selectivity (less than 10%) similar to the catalytic properties of ruthenium(III) chloride [13].

Recently, *Grubbs* et al. [14,15] reported vinylcarbene complexes of Ru(II) of the type $[Ph_2C{=}CHCH{=}RuCl_2(L)_2]$ for the ring-opening metathesis polymerization (ROMP) of norbornene. With $L = P(c\text{-}C_6H_{11})_3$ very high activities could be obtained [TON ≈ 8000 mol PNB/(mol Ru · h)] [15].

In this paper we describe the influence of neutral ligands in monomeric bis(allyl)ruthenium(IV) complexes $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})LCl_2]$ on the catalytic activity and *cis* selectivity in the polymerization of norbornene.

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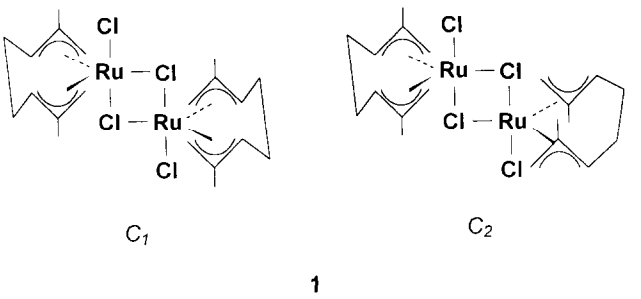
2. Results and discussion

Complexes **2a** and **2b** are obtained in quantitative yields by reaction of **1** with the neutral ligands $Sb(C_6H_5)_3$ and $P(OC_6H_5)_3$ in methylene chloride at room temperature (eqn. (1)).

$$\underset{\mathbf{1}}{\left[\{Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})(\mu\text{-}Cl)Cl\}_2\right]} + 2L \rightarrow 2\underset{\mathbf{2a,b}}{\left[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})LCl_2\right]} \quad (1)$$

(a) $L = Sb(C_6H_5)_3$; (b) $L = P(OC_6H_5)_3$

The orange complex **2a** is stable in air, but decomposes to a brown residue at 185–187°C under nitrogen. The point of decomposition of the yellow compound **2b** at 155°C (brown oil) is much lower, and the stability in air is limited to 3–4 d. After this time **2b** is decomposed to a black oil. **2a** and **2b** dissolve in protic solvents like methanol and ethanol (see Experimental details). They are also stable in a 0.1 molar etheric HCl for about 12 h. This is an indication of a high kinetic stability of the allylruthenium(IV) bound towards hydrolytic and protolytic attack.



C_1 C_2

1

Fig. 1. Schematic representation of the C_i and C_2 isomer of complex **1**.

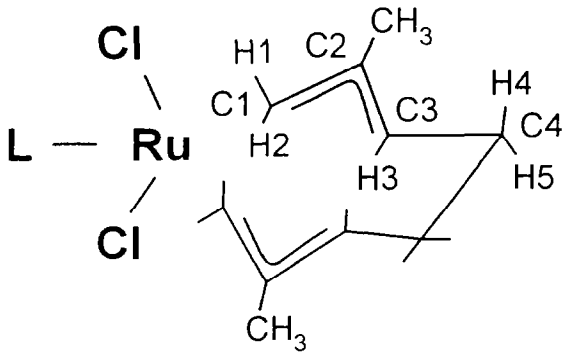
The mass spectra (EI) of **2a** and **2b** contain no molecular ion peak, however fragmentation peaks of the free ligands and of $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl_2]^+$ are present. This suggests relatively low thermal stability

Table 1
NMR data of **1**, **2a** and **2b** [a]

^{1}H-NMR Complex	H1	H2	H3	H4	H5	$-CH_3$	Others
1 [b]	6,08 (s, 2H) 5,36 (s, 2H) 5,06 (s, 2H) 4,71 (s, 2H)	5,70 (s, 2H) 5,20 (s, 2H) 4,85 (s, 2H) 4,46 (s, 2H)	4,70 (m, 2H) 4,63 (m, 2H) 4,49 (m, 2H) 4,43 (m, 2H)	2,60–2,48 (m, 16H)		2,46 (s, 6H) 2,36 (s, 6H) 2,27 (s, 6H) 2,22 (s, 6H)	
2a	4,59 (s, 2H)	3,14 (s, 2H)	4,86 (m, 2H)	3,36 (m, 2H)	2,73 (m, 2H)	2,20 (s, 6H)	7,66 (d, 6H, *o*-H, $^3J_{o\text{-H},m\text{-H}}$ = 6,7 Hz) 7,42–7,33 (m, 9H, *m*-H, *p*-H)
2b	4,72 (d, 2H, $^3J_{H1,P}$ = 9,2 Hz)	3,48 (d, 2H, $^3J_{H2,P}$ = 4,3 Hz)	5,35 (m, 2H)	3,59 (m, 2H)	2,71 (m, 2H)	2,20 (s, 6H)	6,99 (d, 6H, *o*-H, $^3J_{o\text{-H},m\text{-H}}$ = 8,5 Hz) 7,22 (t, 6H, *m*-H, $^3J_{m\text{-H},p\text{-H}}$ = 7,10 (t, 3H, *p*-H, $^3J_{p\text{-H},m\text{-H}}$ = 7,1 Hz)

^{13}C Complex	C1	C2	C3	C4	$-CH_3$	Ligand
2a	60,9	119,5	107,3	36,7	20,4	132,0 (*ipso*-C) 136,8 (*ortho*-C) 128,7 (*meta*-C) 129.8 (*para*-C)
2b	62,6 ($^2J_{C,P}$ = 7,1 Hz)	125,8	111,1 ($^2J_{C,P}$ = 14,8 Hz)	37,1	21,0	152,2 (*ipso*-C, $^2J_{i\text{-C,p}}$ = 15,2 Hz) 121,1 (*ortho*-C, $^3J_{o\text{-C,P}}$ = 3,8 Hz) 129,4 (*meta*-C) 124,7 (*para*-C, $^5J_{p\text{-C,P}}$ = 1,0 Hz)
^{31}P NMR						
2b [c]	118,4					

[a] All spectra were recorded in $CDCl_3$ at 25°C.
[b] ^{1}H NMR data are in agreement with the literature [5,6]
[c] $\delta(P(OC_6H_5)_3) = 128,5$ ppm in $CDCl_3$.



2a, b

a: L=$Sb(C_6H_5)_3$

b: L=$P(OC_6H_5)_3$

Fig. 2. Schematic representation of $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})LCl_2]$ with atom numbers.

and a weak metal–ligand bond which can be attributed to the steric and electronic influence of the ligands. These properties are generally important in homogeneous catalysis [16].

2.1. NMR spectroscopical characterization

The proton NMR spectrum of **1** in $CDCl_3$ (Table 1) is in agreement with the literature [5,6]. The presence of eight distinct resonances for the terminal allyl protons H1 and H2, four resonances for the internal allyl protons H3, and four resonances for the methyl protons supports the existence of two diasteriomeric forms of **1** which, in non-coordinating solvents, are present in an approximate 1:1 ratio, see Fig. 1.

The proton NMR spectra of complexes **2a** and **2b** exhibit resonances of relative intensity 3 for the methyl groups and five equally intense resonances attributable to the five types of protons of the 2.7-dimethylocta-2.6-diene-1.8-diyl ligand. This implies that there is C_2 symmetry, see Fig. 2.

The resonances of the H1 and H2 protons for the phosphite complex **2b** appear as 1/1 doublets, clearly arising from spin-coupling with the phosphorus nucleus. Besides these, both complexes show additional lines in the ^1H NMR spectra for protons present on the ligands L.

In the ^{13}C NMR spectra of complex **2a** the resonances of the allyl group coordinating at the ruthenium are shifted to high field compared with **2b** (Table 1). This suggests that $Sb(C_6H_5)_3$ is a stronger donor than $P(OC_6H_5)_3$, assuming a relationship between the chemical shift of the allyl group and the effective donor strength of the ligand L in which increasing electron transfer to ruthenium produce a high field shift of $\delta C1$, $\delta C2$ and $\delta C3$. Both ligands show similar cone angles [$Sb(C_6H_5)_3$ 130° and $P(OC_6H_5)_3$ 128°] [16] so that steric effects do not come into question.

Complex **2b** shows a spin-coupling with the phosphorus nucleus by appearance of C1 and C2 as doublets. The ^{13}C NMR spectra of **2a** and **2b** are not significantly affected by either temperature change or addition of five equivalents of free ligand.

In the ^{31}P NMR spectrum of **2b** the phosphorus resonance at 118.4 ppm is shifted 10 ppm to high field in comparison with free $P(OC_6H_5)_3$ (128.5 ppm). The increase of electron density at phosphorus can be attributed to the good acceptor ability of the phosphite ligand. Similar effects have been observed at cationic allylnickel(II) bis(triphenylphosphite) complexes [17].

Further details about structure and coordination of **2a** and **2b** have been obtained by crystal structure analysis of **2a**.

2.2. Crystal structure analysis

The molecular structure of complex **2a** shows distorted trigonal bipyramidal geometry about the ruthenium atom. Both allyl groups and the triphenylstibine ligand reside in equatorial positions, while the chlorides are bonded in axial positions. The arrangement of the octadienyl group is similar to that found in the crystal structures of the dimeric chloro-bridged complex **1** [4] and its PF_3 adduct [10]. Selected bond distances and angles are listed in Table 2.

The allyl groups are anti-periplanar to each other. Thus, each of the methyl groups is *syn*-periplanar along with one of the chloro-ligands. The ethylene bridge between the allyl groups is disordered (C51, C61, C52, C62).

The Ru 1–Sb 1 bond length of 2.6594(3) Å agrees favourably with the sum of the covalence radii (2.66 Å). However comparable structures [19–21], where a triphenylstibine ligand or a trimethylstibine ligand is coordinated on a low valent ruthenium atom clearly show shorter Ru–Sb distances of 2.583 Å to 2.624 Å. There-

Table 2
Selected bond distances (Å) and angles (°) for **2a**

SB(1)–RU(1)	2.6594(3)	CL(1)–RU(1)–SB(1)	78.06(2)
RU(1)–CL(1)	2.4090(8)	CL(2)–RU(1)–SB(1)	86.58(2)
RU(1)–CL(2)	2.4232(8)	CL(2)–RU(1)–CL(1)	164.54(3)
RU(1)–C(1)	2.203(3)	C(2)–RU(1)–SB(1)	116.7(1)
RU(1)–C(2)	2.220(4)	C(2)–RU(1)–CL(1)	103.1(1)
RU(1)–C(4)	2.231(4)	C(2)–RU(1)–CL(2)	85.2(1)
RU(1)–C(7)	2.240(3)	C(8)–RU(1)–SB(1)	117.2(1)
RU(1)–C(8)	2.236(3)	C(8)–RU(1)–CL(1)	84.8(1)
RU(1)–C(10)	2.224(4)	C(8)–RU(1)–CL(2)	100.9(1)
C(1)–C(2)	1.410(5)	C(8)–RU(1)–C(2)	126.1(1)
C(2)–C(4)	1.399(6)		
C(7)–C(8)	1.398(6)		
C(10)–C(8)	1.429(6)		

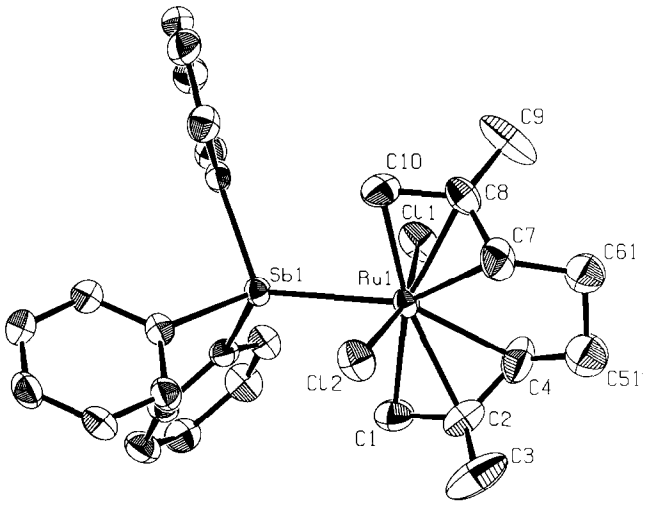


Fig. 3. PLATON [18] plot of **2a** showing the atomic numbering with the thermal ellipsoids drawn at the 50% probability level. The disorder of the ethylene bridge is not outlined (C51, C61, C52, C62). Hydrogen atoms are omitted for clarity.

fore principally electronic less steric influences are important in the interaction between $Sb(C_6H_5)_3$ and the ruthenium atom.

2.3. Results of catalysis

Complexes **2a** and **2b** catalyze the ring-opening polymerization of norbornene with high activity which is dependent on the monomer concentration, temperature and the nature of the neutral ligand L. Fig. 4 shows the conversion-time diagram of the polymerization with **2a** as catalyst.

Under the given reaction conditions, the conversion increased linearly with increasing reaction time. At conversions of about 60% the polymerization solution gells and these results have been disregarded because the reaction rate is controlled by diffusion. **2a** shows at 25°C an activity of 450–500 mol PNB/(mol Ru · h) (related to precipitated *polynorbornene*), so that the polymerization rate is constant up to conversions of 60%. The *cis* selectivity amounts to 24–30% (by ^1H, ^{13}C). The quantitative determination of unsaturation by integration of the ^1H NMR spectra showed that the

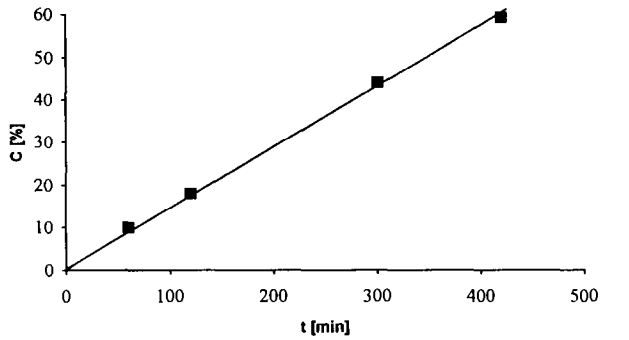


Fig. 4. Conversion-time diagram of catalysis with **2a** (conditions: [NB] = 2.0 M; [Ru] = 2.0×10^{-4} M; [NB]:[Ru] = 5000; solvent: toluene; T = 25°C).

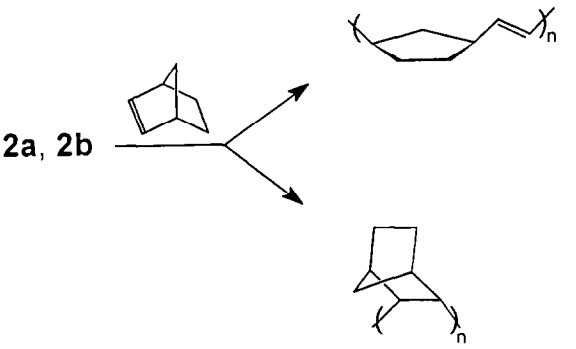
polymers contained 20–30% bicyclo[2.2.1.]hept-2.3-ylene units (see Eq. (2)) [11].

The addition of ten equivalents of free $Sb(C_6H_5)_3$ ligand at the beginning of the catalysis with **2a** inhibits the polymerization completely (Table 3, No 1).

In protic solvents like ethanol the activity decreases at 60 mol PNB/(mol Ru · h) and the *cis* selectivity decreases at 12%, while the bicyclo[2.2.1.]hept-2.3-ylene units remain unchanged (Table 3, No 2).

By increasing the reaction temperature to 50°C the activity increases to 3200 mol PNB/(mol Ru · h) (Table 3, No 3), while the *cis* selectivity and the bicyclo [2.2.1.]hept-2.3-ylene units are unchanged.

By decreasing the concentration of both the ruthenium and the monomer at 50°C (Table 3, No 4) the activity decreases (TON ≈ 420) and is comparable with



(2)

Table 3
Results of catalysis under varied reaction conditions with **2a** as catalyst (solvent: toluene)

Nr.	[NB]:[Ru]	[Ru] · 10^4	[NB]	T (°C)	t (min)	Yield (%)	TON	*cis* (%) [a]	(%) [b]
1	5000	4 + 10 L [c]	2	25	300	–	–	–	–
2 [d]	5000	4	2	50	420	8	60	12	17
3	5000	4	2	50	10	10	3200	26	20
4	5000	1,4	0,7	50	90	12	420	20	15
5	5000	4	2	25	60	10	500	24	20

[a] Double bonds determined by ^1H NMR analysis of olefinic protons in polymers. Assignments: δ = 5.33 ppm (olefin-H, *trans*), δ = 5.19 ppm (olefin-H, *cis*), δ = 2.76–1.02 ppm (alipatic-H). [b] Bicyclo[2.2.1.]hept-2,3-ylene-units. [c] L = $Sb(C_6H_5)_3$. [d] Solvent: ethanol.

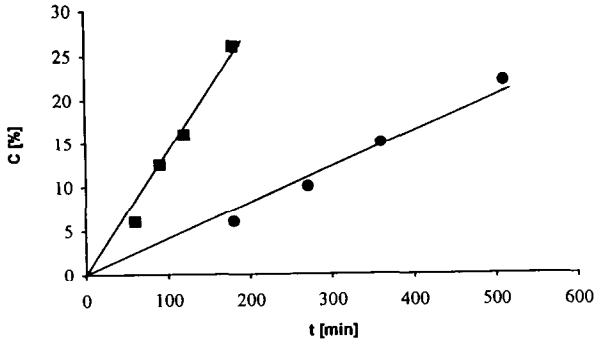


Fig. 5. Conversion-time diagram of catalysis with **2a** (■) and with **2b** (●) (conditions: [NB] = 0.7 M; [Ru] = 1.4×10^{-4} M; [NB]:[Ru] = 5000; solvent: toluene; T = 50°C).

the activity of **2a** at 25°C and at higher concentrations of ruthenium and the norbornene (Table 3, No 5 and Fig. 4).

Fig. 5 shows the conversion-time diagram of the polymerization with **2a** and **2b** as catalysts at 50°C. Under the given conditions the complex **2a** shows an activity of 350–450 mol PNB/(mol Ru · h). The polymerization rate of the complex **2b** is clearly smaller (TON 100–130 mol PNB/(mol Ru · h)). Both catalysts show unchanged *cis* selectivities (24–30%) and bicyclo[2.2.1.]hept-2.3-ylene units (20–30%) under these conditions.

The molecular weight of the polymers obtained with **2a** at 50°C was determined by GPC. The molecular weight distribution is monomodal, while the polydispersity ranges from 2.4 to 5.3. This suggests that only one reaction centre is present for the chain growing and that chain transfer reactions take place besides the chain propagation reaction.

The number average molecular weight, M_n, increases with increasing the reaction time, see Fig. 6. Assuming that the whole amount of ruthenium in the used catalyst **2a** is catalytically active and no chain transfer reactions takes place (theoretical chain length),

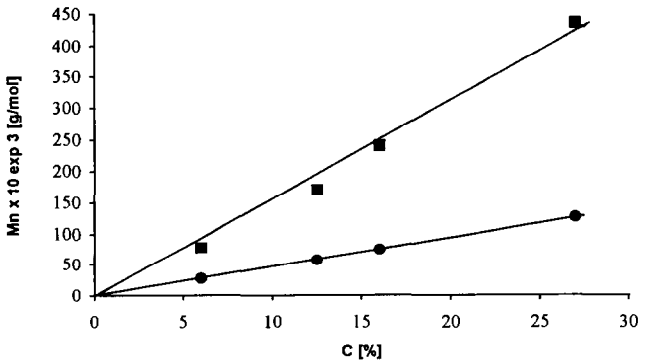
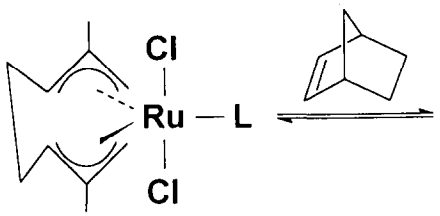
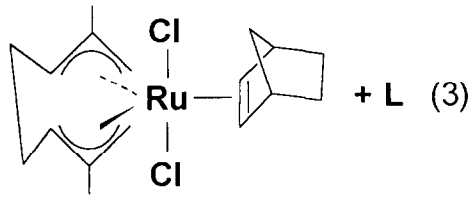


Fig. 6. Comparison between calculated M_n (●) (assuming that a whole amount of Ru is active and no chain transfer reactions takes place) and measured M_n (■) (GPC).



2a, b



the calculated M_n is clearly smaller than the measured M_n. Therefore only a small amount of the precatalyst **2a** converts into an catalytically active species.

Neither ^1H or ^{13}C NMR spectroscopic investigations could find any signs for the course of the catalysis. At the start of the catalysis only the resonances of **2a** and of the free norbornene were observed. In the course of the catalytic cycle the resonances of polynorbornene appears to that degree to which the resonances of the free norbornene decrease. Furthermore, the resonances of **2a** are unchanged during the complete course of the catalysis. Additional signals could not be observed. One may conclude from this that the concentration of the catalytically active ruthenium is below NMR detection (less than 5%).

3. Discussion

From our experimental investigations of the catalytic properties of **2a** and **2b** we conclude an equilibrially formation of a norbornene-ruthenium complex in the catalytic cycle of the norbornene polymerization, see eqn. (3).

The catalytic activity of **2a** and **2b** is primarily determined by the electronic properties of the ligand L, because the activity increases with easier displacement of the ligand by norbornene and consequent decreasing of the coordinatively ligand-ruthenium bond strength. A dependence from the effective donor strength of the ligands L is not recognizable, because the $Sb(C_6H_5)_3$ with a larger donor effect than $P(OC_6H_5)_3$ results in higher catalytical activity. A decreasing bond stability independent from the donor effect is a well-known fact [16]. In these special cases a simple ^1H and ^{31}P NMR following experiment presents the easier displacement

of $Sb(C_6H_5)_3$ from the ruthenium complex compared with $P(OC_6H_5)_3$. Reaction of **2a** with one equivalent $P(OC_6H_5)_3$ yields 65% of **2b** after 1 h reaction time, while **2b** + $Sb(C_6H_5)_3$ produces only 15% of **2a** under the same reaction conditions.

By rudimentary LCAO-MO theory the correlation of the coordinative bond strength with donor strength can only be expected at comparable overlap conditions of the participating valence orbitals. If that is not the case, because of the variation of the stick atom at **2a** and **2b**, respectively, the bond strength and the donor strength can be changed regardless of each other.

The assumed norbornene complex must be available in such a small concentration that it is not detectable by NMR spectroscopy. Even if the growing polymer chain at the ruthenium is not detectable because of small concentration, it must be assumed that the given equilibrium (eqn. (3)) is shifted to the left-hand side of the equation. The concentration of the norbornene complex therefore limits the catalytic activity thermodynamically. Accordingly the turn over numbers of the $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})LCl_2]$ complexes **2a** and **2b** are larger by a factor of ten in comparison to $[\{Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})(\mu\text{-}Cl)Cl\}_2]$ **1** [11,12], because in complex **1** the effective positive charge is reduced by additional coordination of chloride and so the coordination of the norbornene is more difficult.

The complete prevention of polymerization by addition of the ligand is explainable with a shift of the mentioned equilibrium to the starting complexes **2a** and **2b**. A similar effect is observed by the change to stronger donor solvents such as ethanol.

The further mechanistic course of catalysis is still uncertain. A ring-opening polymerization under metathesis for **2a** and **2b**, such as that detected for **1** by the characterization of oligomers of norbornene-olefin copolymers [11] can be assumed by analogy. This is possible only by separation of the bisallyl ligand from the ruthenium under the condition of catalysis. However the bisallyl group is strongly bonded to the ruthenium as shown by experiments.

Further explanation of the course of catalysis and the optimization of the precatalyst is the aim of future investigations.

4. Experimental details

All reactions and manipulations were carried out under a nitrogen atmosphere. Norbornene (MERCK) was distilled from calcium hydride under nitrogen prior to use. The solvents were distilled from calcium hydride or Na/benzophenone under nitrogen and stored over molecular sieves.

$[\{Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})(\mu\text{-}Cl)Cl\}_2]$ **1** was prepared by published methods [5]. Elemental analysis were performed in the Microanalytical Laboratory of our institute (M. Barth).

NMR spectra were obtained on a Jeol JMN-GX 400 and a Bruker AC 250 spectrometer. IR spectra were recorded by a FT-IR Perkin Elmer spectrometer and MS spectra were obtained by a Finnigan MAT 90.

4.1. Preparations

4.1.1. $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})\{Sb(C_6H_5)_3\}Cl_2]$ 2a

A solution of 0.62 g (1.0 mmol) $[\{Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})(\mu\text{-}Cl)Cl\}_2]$ in 10 ml of methylene chloride was treated with 0.7 g (2.0 mmol) $Sb(C_6H_5)_3$. The colour of the solution changed quickly from pink to orange. After stirring for 1 h at room temperature the methylene chloride was reduced in vacuum to ca. 0.25 vol. By addition of 15 ml of pentane orange crystals were precipitated. These were isolated by filtration, washed with pentane and dried in vacuum. The compound is stable in air and very soluble in methylene chloride, chloroform and THF, soluble in diethyl ether, toluene, methanol and ethanol, and less soluble in pentane. Yield: 1.25 g (95%), m.p. 185–187°C (decomposition under nitrogen).

Elemental Anal.: Found: C, 50, 44; H, 4, 61; Cl, 10, 46; Ru, 14, 80; Sb, 19, 69. calc. for $C_{28}H_{31}Cl_2RuSb$: C, 50, 83; H, 4, 69; Cl, 10, 74; Ru, 15, 28; Sb, 18, 46%.

IR (KBr-disc): 3048(m), 2913(m), 1575(m), 1479(s), 1453(m), 1431(vs), 1380(m), 1184(m), 1064(m), 1021(m), 998(m), 735(vs), 696(vs), 464(s).

EI-MS (70 eV): $m/z = 352$ ($[SbPh_3]^+$, 12%), 308 ($[C_{10}H_{16}RuCl_2]^+$, 0,9%), 275 ($[SbPh_2]^+$, 10%), 273 ($[C_{10}H_{16}RuCl]^+$, 5%), 237 ($[C_{10}H_{16}Ru]^+$, 0,6%), 198 ($[SbPh]^+$, 74%), 154 ($[C_4H_6Ru]^+$, 100%), 136 ($[C_{10}H_{16}]^+$, 39%), 121 ($[C_9H_{13}]^+$, 39%), 107 ($[C_8H_{10}]^+$, 12%), 92 ($[C_7H_8]^+$, 46%), 82 ($[C_6H_{10}]^+$, 14%), 77 ($[Ph]^+$, 62%), 69 ($[C_5H_8]^+$, 36%), 54 ($[C_4H_6]^+$, 49%).

4.1.2. $[Ru(\eta^3,\eta^3\text{-}C_{10}H_{16})\{P(OC_6H_5)_3\}Cl_2]$ 2b

A solution of 0.62 g (1.0 mmol) $[\{Ru(\eta^3,\eta^3\text{-}C_{10}H_{16})(\mu\text{-}Cl)Cl\}_2]$ in 10 ml of methylene chloride was treated with 0.53 ml (2.0 mmol) of $P(OC_6H_5)_3$. The colour of the solution changed from pink to yellow. The solution was reduced in vacuum to ca. 0.25 vol. and pentane was added. Yellow crystals were obtained and dried in vacuum. The solubility and stability of **2b** is similar to **2a**. Yield: 1.19 g (96%), m.p. 155°C (decomposition under nitrogen).

Elemental anal.: Found: C, 54, 00; H, 5, 01; Cl, 11, 99; Ru, 15, 89; O, 7, 78; P, 4, 96; calc. for $C_{28}H_{31}Cl_2RuO_3P$: C, 54, 37; H, 5, 02; Cl, 11, 49: Ru, 16, 34; O, 7, 77; P, 5, 02%.

IR (KBr-disc): 3074(m), 3047(m), 3002(m), 2897(m), 2852(m), 1588(s) 1489(vs), 1454(m), 1381(m), 1218(s), 1185(vs), 1164(s), 1070(m), 1027(m), 934(vs), 758(vs), 689(s), 588(m), 488(s).

EI-MS (70 eV): $m/z = 273$ ($[C_{10}H_{16}RuCl]^+$, 4%), 136 ($[C_{10}H_{16}]^+$, 100%), 121 ($[C_9H_{13}]^+$, 84%), 107 ($[C_8H_{10}]^+$, 29%), 94 ($[C_6H_5O]^+$, 96%), 91 ($[C_7H_8]^+$, 53%), 82 ($[C_6H_{10}]^+$, 39%), 69 ($[C_5H_8]^+$, 71%), 55 ($[C_4H_6]^+$, 58%).

4.2. NMR spectroscopic observation of the catalysis

[NB]:[Ru] = 20; 30 mg **2a** (4.5×10^{-5} mol 9.0×10^{-2} M); 84 mg norbornene (9.0×10^{-4} mol; 1.8 M) in 0.5 ml $CDCl_3$.

4.3. Crystal structure determination

Crystals were obtained from a CH_2Cl_2/Et_2O solution (1:2) at room temperature. A dark-orange crystal was mounted in a glass capillary on an Enraf-Nonius CAD4 diffractometer with Kappa geometry. Final lattice parameters were obtained by least-squares refinement of 25 reflections ($45.7° < 2\Theta < 53.2°$, $\lambda = 0.70930$ Å-Mo-($K\alpha_1$)). Empirical absorption corrections were applied to the dataset [22]. The structure was solved by the Patterson method (SHELXS-86) [23] and refinements were carried out using the program CRYSTALS [24].

The ethylene bridge is disordered (C51, C61, C52, C62). Nearly all hydrogen atoms could be found by difference Fourier techniques, missing hydrogen positions were calculated with ideal geometry. H2 and the disordered hydrogen atoms were fixed during refinement. A summary of the structural data is given in Table 4 [25*].

Table 4
Crystallographic data

Formula	$C_{28}H_{31}Cl_2Ru_1Sb_1$
Fw	661.28
Size (mm^3)	$0.23 \times 0.15 \times 0.15$
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	10.556(6)
b (Å)	10.823(5)
c (Å)	13.156(7)
α (°)	93.34(4)
β (°)	108.47(3)
γ (°)	112.64(3)
V (Å^3)	1288(2)
Z	2
D_{calc} (g cm^{-3})	1.71
μ (Mo-Kα) (cm^{-1})	18.6
F(000)	656
Diffractometer	Enraf Nonius CAD4
Radiation (Å)	Mo-Kα, $\lambda = 0.71073$
2Θ range (°)	2–50
Scan mode	ω-scan
Temperature (°C)	-80 ± 4
No. of reflections measured total	4736
No. of unique reflections	4173
No. of reflections used for refinement, $I/\sigma(I) > 2.0$	3785
Number of refined parameters	391
Weighting scheme	Tukey and Prince [26] with five parameters $p1 = 0.90$, $p2 = -0.636$, $p3 = 0.722$, $p4 = -0.171$, $p5 = 0.140$
Maximum and minimum electron density in ΔF map (e Å^{-3})	+0.94, −0.41
R	0.024
R_w	0.021
Data/parameter	9.7

4.4. Polymerizations

In a typical polymerization run 2.8 mg (4.2×10^{-6} mol) of the catalyst (**2a**) was put in a schlenk tube having a central neck and a side arm, which was connected to a vacuum-nitrogen system. A toluene solution of norbornene with mole ratio [2.0 g (2.0×10^{-2} mol) norbornene in 31 ml toluene (0.7 molar)] was introduced into the schlenk tube. The tube was set in a bath maintained at constant temperature (25 or 50 ± 0.5°C) with stirring. The polymerization was terminated by pouring the reaction mixture into an excess of methanol (ca. 80 ml) with a small amount of HCl and di-tert.-butyl-*p*-kresol as antioxidant.

4.5. Molecular weight determination

Molecular weights were determined by gel permeation chromatography with a modular compound GPC-apparatus (Fa. KNAUER GmbH) by using linear WATERS ULTRASTYRAGEL column. As mobile phase toluene was used with a flow rate of 0.5 ml min^{-1}. The measurement temperature was 25°C.

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