ELSEVIER

Journal of Molecular Catalysis A: Chemical 182–183 (2002) 577–583

JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL

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Preparation of new ruthenium–allenylidene catalysts and their use in polymerisation of cyclic olefins

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Received 20 August 2001; accepted 17 October 2001

Abstract

A variety of ruthenium–allenylidene complexes were produced in two steps from the simple $RuCl_2(dmso)_4$ precursor: the neutral $RuCl_2(=C=C=CR_2)(PCy_3)_n(dmso)_m$ and the cationic $[RuCl(=C=C=CR_2)(PCy_3)_n(dmso)_m]TfO$ complexes. Some of them have been evaluated for polymerisation of norbornene and cyclooctene, and constitute the first example of active $Ru=C=C=CR_2$ catalysts for ring opening metathesis polymerisation (ROMP). The most active system is the cationic $[RuCl(=C=C=CPh_2)(PCy_3)(dmso)_2]TfO$ complex **5** which leads in PhCl at 80 °C to 90% of polycyclooctene with a polydispersity of 1.89 and 69% of *cis*-configuration of CH=CH bonds. The presence of an electron-donating group on the aryl substituents (*p*-OMe) drastically favours both yield and low polydispersity of the polymer.

Keywords: Allenylidene–ruthenium; Ruthenium catalyst; ROMP; Polymerisation; Cyclic olefins

1. Introduction

Well-defined 16 electron alkylidene-ruthenium complexes have been revealed, during the last decade, as efficient tools in fine synthesis as alkene metathesis catalyst precursors [1–3], whereas several coordinatively unsaturated ruthenium species have promoted the ring opening metathesis polymerisation (ROMP) of cyclic olefins [4–7]. Recently, arene–ruthenium–allenylidenes [8] and related systems [9] were shown to efficiently promote ring closing metathesis of dienes [8–10] and enynes [11], whereas their activity for ROMP was modest. Consequently, we have attempted to generate arene-free $Ru=C=C=CR_2$ complexes but with labile ligands in order to produce more active species for ROMP.

We now report a variety of new neutral and cationic allenylidene–ruthenium systems of type $RuCl_2(=C=C=CR_2)(PCy_3)_n(dmso)_m$ and $[RuCl(=C=C=CR_2)(PCy_3)_n(dmso)_m]TfO$ ($3 \leq n+m \leq 4$) and their use to promote ROMP of cyclic alkenes.

2. Results

2.1. Synthesis of ruthenium–allenylidene complexes

It was shown previously that the 18 electron, cationic complexes $[RuCl(=C=C=CPh_2)(PCy_3)(p\text{-cymene})]X$ were transformed into an active alkene metathesis catalyst after preliminary loss of the arene ligand [8], thus generating a highly coordinatively unsaturated species. We thus consider $RuCl_2(dmso)_4$

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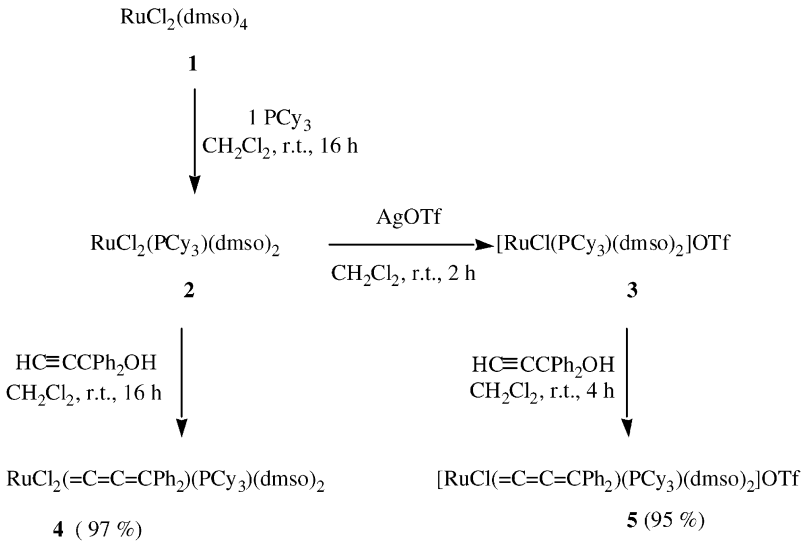
1381-1169/02/$ – see front matter
PII: S1381-1169(01)00498-8



Scheme 1.

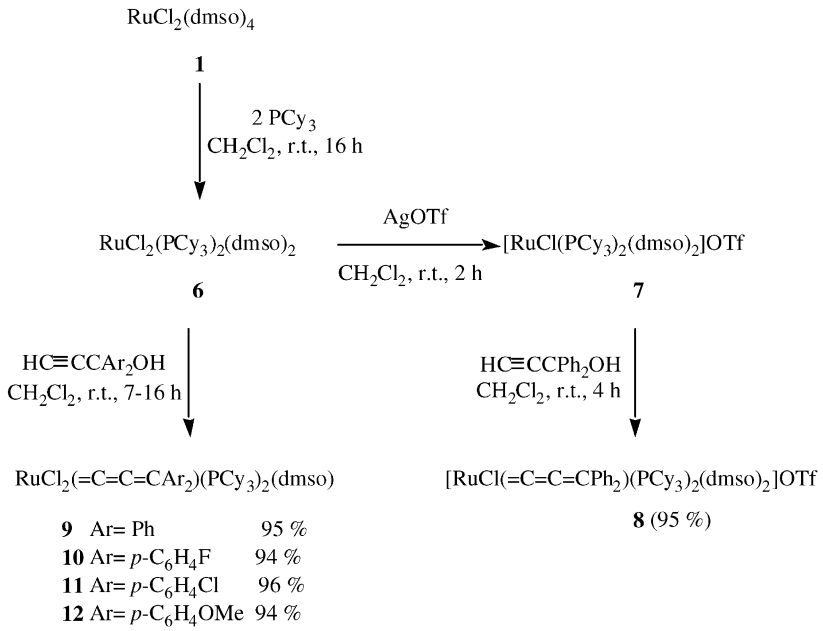
as a possible source of alkene metathesis ruthenium catalysts by linking to the Ru site both a bulky, electron-rich ligand and a carbene-type moiety such as an allenylidene ligand.

$RuCl_2(dmso)_4$ **1** [12] was reacted with 1 equiv. of PCy_3 and gave a stable complex **2** containing, as indicated by ^1H NMR, a PCy_3 ligand for two dmso ligands (Scheme 1). This simple reaction of the bulky PCy_3 group displacing two dmso ligands contrasts with the reaction of **1** with smaller bidentate ligands leading to $RuCl_2(dmso)_2(Me_2NCH_2CH_2NMe_2)$ [13]. This complex **2** on treatment with 1 equiv. of AgOTf leads to a salt of which the formula is consistent with $[RuCl(PCy_3)(dmso)_2]OTf$ **3**, but likely in its dimeric form, as this 14-electron cationic species is expected to easily dimerise into a dication with two chloride bridges. Both complexes **2** and **3** were reacted with 1 equiv. of $HC{\equiv}CCPh_2OH$ at room temperature. Complex **2** slowly but quantitatively afforded the neutral purple derivative **4** containing one allenylidene ligand ($\nu(C{=}C{=}C) = 1935\,cm^{-1}$). Complex **3** reacted faster to afford the purple derivative **5** ($\nu(C{=}C{=}C) = 1942\,cm^{-1}$) (Scheme 1).

Alternatively, when $RuCl_2(dmso)_4$ was reacted with 2 equiv. of PCy_3 the yellow complex $RuCl_2(PCy_3)_2(dmso)_2$ **6** was formed. The latter which possesses equivalent PCy_3 (^{31}P NMR, $\delta = 51.3$ ppm) and dmso ligands (^1H NMR, $\delta = 3.48$ ppm (12H)) reacted with 1 equiv. of AgOTf to give a brown species $[RuCl(PCy_3)_2(dmso)_2]OTf$ **7** (Scheme 2) displaying non-equivalent *cis*-phosphine ligands (^{31}P NMR, two doublets at $\delta = 43.65$ and 37.60 ppm, $^2J_{PP}$=34.7 Hz) and non-equivalent dmso ligands (^1H NMR, two singlets at $\delta = 3.36$ (2Me) and 3.50 (2Me) ppm).

Complex **7** reacted with $HC{\equiv}CCPh_2OH$ and afforded the purple allenylidene complex **8**, containing non-equivalent groups for both PCy_3 and dmso ligands. Consequently, the chloride and allenylidene ligands cannot be in *trans*-positions as in $[RuCl(=C=C=CPh_2)(Ph_2P(CH_2)_nPPh_2)_2]PF_6$ ($n = 1$) [14] and ($n = 2$) [15]. The data are consistent with the relative *cis*-position of the PCy_3 ligands and of the dmso groups. Under similar conditions, the complex **6** afforded the neutral allenylidene complex **9** resulting from the displacement of one labile dmso ligand (Scheme 2). The latter reaction of **6** was performed with various propargylic alcohols $HC{\equiv}CCAr_2OH$ (Ar = *p*-C_6H_4–F, *p*-C_6H_4–Cl and *p*-C_6H_4–OMe) and the neutral allenylidene complexes **10**–**12** analogous to **9** were successively obtained in quantitative yields.

The ^{31}P NMR analysis of each complex **9**–**12** shows equivalent phosphines as in the precursor **6**. The ^{13}C NMR spectrum of **12** showed three allenylidene carbon atoms at $\delta = 312.5$ (Cα), 269.7 (Cβ) and 193.0 (Cγ) ppm. These data can be compared with those of $[RuCl(=C=C=CPh_2)(Ph_2PCH_2CH_2PPh_2)_2]PF_6$ [15]



Scheme 2.

δ: 308.6 (Cα), 215.9 (Cβ) and 161.4 C(γ) ppm. These data are consistent with the *trans* position of the PCy_3 ligands, both of them being *cis* to the allenylidene ligands.

2.2. Polymerisation of norbornene and cyclooctene by Ru=C=C=CR_2 catalysts

The above ruthenium–allenylidene complexes were evaluated as catalysts in ROMP of cyclic olefins. The ROMP of norbornene and cyclooctene has been attempted with the two cationic ruthenium–allenylidenes **5** and **8** and the neutral complexes **9**, **11** and **12**.

The reaction was first performed with 1 g of norbornene in the presence of 0.28 mol% of ruthenium catalyst in chlorobenzene at 60 °C for 4 h and the resulting polymer was precipitated in methanol. The data in Table 1 show that among the cationic precursors only **5** gives decent yields (70%) but with high polydispersity (3.97) and low percentage of *cis*-CH=CH configuration as shown by ^{13}C NMR [16]. Among the neutral derivatives, only **12** gives a good compromise between activity (yield 96%) and polydispersity (1.61); also it shows a drastic influence of an electron-donating group on the phenyl group (*p*-OMe) with respect to **11** (*p*-Cl) (80%, PDI = 2.66). However, the molecular weights remain modest.

The polymerisation of the unstrained cyclooctene, usually more difficult to perform, was then attempted. The reaction was performed, at 80 °C but for longer time (16 h), with 0.33 mol% of catalyst in 5 ml of chlorobenzene and the resulting polymer was precipitated in methanol. Table 2 shows that the cationic precursor **5** is also the best catalyst as it leads to 90% of polymer with a rather narrow polydispersity (1.89) and the ^{13}C NMR shows 69% of *cis*-configuration of the –CH=CH– bonds [16].

Table 1
Polymerisation of norbornene with Ru=C=C=CR_2 catalysts[a]

Catalyst	Yield (%)	Mw (1×10^{-3})	Mn (1×10^{-3})	Mw/Mn	Percent *cis*[b]
5	70	149.5	37.6	3.97	15
8	22	66.1	17.0	3.88	13
9	56	66.1	15.9	4.15	
11	80	53.3	20.0	2.66	
12	96	73.1	45.2	1.61	52

[a] 3×10^{-5} mol (0.28 mol%) of ruthenium–allenylidene catalyst in 5 ml of PhCl and 10.6×10^{-3} mol of norbornene, at 60 °C for 4 h.

[b] Determined by ^{13}C NMR [16].

Table 2
Polymerisation of cyclooctene with $Ru{=}C{=}C{=}CR_2$ catalysts[a]

Catalyst	Yield (%)	Mw (1×10^{-3})	Mn (1×10^{-3})	Mw/ Mn	Percent *cis*[b]
5	90	133.6	70.6	1.89	69
8	20	133.5	70.6	1.89	–
9	65	173.3	95.3	1.81	60
11	10	70.0	41.6	1.68	–
12	92	57.0	36.5	1.56	54

[a] 3×10^{-5} mol (0.33 mol%) of ruthenium–allenylidene catalyst in 5 ml of PhCl and 9.1×10^{-3} mol of cyclooctene, at 80 °C for 16 h.

[b] Determined by ^{13}C NMR [16].

Among the neutral systems, the catalyst precursor **12** with *p*-C_6H_4–OMe groups leads to high yield (90%) but with low molecular weight, whereas compound **11** (with *p*-C_6H_4–Cl groups) only affords 10% of polymer. Actually derivative **9** gives the best compromise for yield (65%), molecular weight and polydispersity 1.81, with 60% of *cis*-configuration for the CH=CH bonds.

Thus, these results show that the above $Ru{=}C{=}C{=}CR_2$ complexes are active for ROMP but that the simple cationic precursor **5** offer the best compromise for yield, molecular weight narrow dispersity and high percentage of *cis*-CH=CH configuration for both norbornene and cyclooctene. They also give evidence for a drastic favourable influence of the electron-donating capability of the aryl groups linked at the carbon C(γ) of the allenylidene ligand in neutral systems such as **9** and **12**. This observation strongly suggests that the allenylidene ligand behaves as an ancillary ligand rather than being involved in the coupling with the cyclic olefin in the first step.

Whereas several ruthenium catalyst precursors have been used to polymerise cyclic olefins, such as carbene [5,6] and vinylidene [7] complexes or highly coordinatively unsaturated ruthenium species [4], these results provide the first example of ROMP polymerisation of a cycloalkene by ruthenium–allenylidene catalyst.

3. Experimental

3.1. General methods and chemicals

(a) *ROMP of norbornene*. In a Schlenk tube containing 3×10^{-5} mol (0.28 mol%) of ruthenium complex under an argon atmosphere, 5 ml of degassed chlorobenzene and 1 g (10.6 mmol) of norbornene were added. The reaction was heated at 60 °C for 4 h. The polymer was then precipitated in 600 ml of methanol, filtrated and dried under vacuum.

(b) *ROMP of cyclooctene*. In a Schlenk tube containing 3×10^{-5} mol (0.33 mol%) of ruthenium complex under an argon atmosphere, 5 ml of degassed chlorobenzene and 1 g (9.1 mmol) of cyclooctene were added. The reaction was heated at 80 °C for 16 h. The polymer was then precipitated in 600 ml of methanol, filtrated and dried under vacuum.

4. Synthesis

4.1. Synthesis of complexes containing one tricyclohexylphosphine ligand

4.1.1. Synthesis of $RuCl_2(PCy_3)(dmso)_2$ (**2**)

In a Schlenk tube under an argon atmosphere, 1 g (2.06 mmol) of $RuCl_2(dmso)_4$, 0.578 g (2.06 mmol) of tricyclohexylphosphine and 15 ml of degassed dichloromethane were introduced. The solution was stirred at room temperature for 16 h. The solvent was then distilled under reduced pressure and 1.385 g of a yellow powder was obtained (yield 98%).

^1H NMR (200.130 MHz, $CDCl_3$): δ 1.00–2.03 (m, 30H, $15CH_2PCy_3$), 2.04–2.42 (m, 3H, $3CHPCy_3$), 3.42 (s, 12H, $2CH_3SOCH_3$) ppm. ^{31}P NMR: (81.019 MHz, $CDCl_3$), δ 50.97 (s, PCy_3) ppm. ^{13}C NMR: (50.332 MHz, $CDCl_3$), δ 25.6 (s, δ-CH_2PCy_3), 26.5 (d, $^3J_{PC} = 26.1$ Hz, β-CH_2PCy_3), 26.9 (d, $^2J_{PC} = 11.5$ Hz, γ-CH_2PCy_3), 35.0 (d, $^1J_{PC} = 60.1$ Hz, $CHPCy_3$), 46.1 (CH_3SOCH_3) ppm.

4.1.2. Synthesis of $[RuCl(PCy_3)(dmso)_2]^+TfO^-$ (**3**)

In a Schlenk tube under an argon atmosphere, 500 mg (0.82 mmol) of $RuCl_2(PCy_3)(dmso)_2$, 225 mg (0.82 mmol) of silver triflate and 10 ml of degassed dichloromethane were introduced. The solution was stirred at room temperature for 2 h. The solution was filtrated with a cannula, the solvent was distilled under reduced pressure, and 552 mg of a brown powder was obtained (yield 93%).

^{1}H NMR (200.130 MHz, $CDCl_3$): δ 1.09–2.02 (m, 33H, PCy_3), 3.41 (s, 12H, $2CH_3SOCH_3$) ppm. ^{31}P NMR: (81.019 MHz, $CDCl_3$), δ 60.32 (s, PCy_3) ppm.

*4.1.3. Synthesis of $RuCl_2(=C=C=CPh_2)(PCy_3)(dmso)_2$ (**4**)*

In a Schlenk tube under an argon atmosphere, 500 mg (0.82 mmol) of $RuCl_2(PCy_3)(dmso)_2$, 171 mg (0.73 mmol) of 1,1-diphenylpropynol and 10 ml of degassed dichloromethane were introduced. The solution was stirred at room temperature for 16 h. The solvent was distilled under reduced pressure and 623 mg of a purple powder was obtained (yield 95%).

^{1}H NMR (200.130 MHz, $CDCl_3$): δ 1.05–1.98 (m, 30H, PCy_3), 3.49 (s, 6H, CH_3SOCH_3), 7.11–7.38 (m, 6H, *meta*- and *para*-C*H* in C_6H_5), 7.51–7.62 (m, 4H, *ortho*-C*H* in C_6H_5) ppm. ^{31}P NMR (81.019 MHz, $CDCl_3$): δ 51.07 (s, PCy_3) ppm. IR (KBr): 1935 (Ru=C=C=C) cm^{-1}.

*4.1.4. Synthesis of $[RuCl(=C=C=CPh_2)(PCy_3)(dmso)_2]^+TfO^-$ (**5**)*

In a Schlenk tube under an argon atmosphere, 500 mg (0.69 mmol) of $[RuCl(PCy_3)(dmso)_2]^+TfO^-$, 144 mg (0.69 mmol) of 1,1-diphenylpropynol and 10 ml of degassed dichloromethane were introduced. The solution was stirred at room temperature for 4 h. The solvent was distilled under reduced pressure and 613 mg of a purple powder was obtained (yield 97%).

^{1}H NMR (200.130 MHz, $CDCl_3$): δ 1.05–2.08 (m, 33H, PCy_3), 3.42 (s, 12H, CH_3SOCH_3), 7.18–7.35 (m, 6H, *meta*- and *para*-C*H* in C_6H_5), 7.50–7.61 (m, 4H, *ortho*-C*H* in C_6H_5) ppm. ^{31}P NMR (81.019 MHz, $CDCl_3$): δ 61.20 (s, PCy_3) ppm. IR (KBr): 1942 (Ru=C=C=C) cm^{-1}.

4.2. Synthesis of complexes containing two tricyclohexylphosphine ligands

*4.2.1. Synthesis of $RuCl_2(PCy_3)_2(dmso)_2$ (**6**)*

In a Schlenk tube under an argon atmosphere, 1 g (2.06 mmol) of $RuCl_2(dmso)_4$, 1.578 g (4.12 mmol) of tricyclohexylphosphine and 20 ml of degassed dichloromethane were introduced. The solution was stirred at room temperature for 16 h. The solvent was distilled under reduced pressure and 1.756 g of a yellow powder was obtained (yield 96%).

^{1}H NMR (200.130 MHz, $CDCl_3$): δ 1.01–2.24 (m, 66H, PCy_3), 3.48 (s, 12H, CH_3SOCH_3) ppm. ^{31}P NMR (81.019 MHz, $CDCl_3$): δ 51.3 (s, PCy_3) ppm.

*4.2.2. Synthesis of $[RuCl(PCy_3)_2(dmso)_2]^+TfO^-$ (**7**)*

In a Schlenk tube under an argon atmosphere, 150 mg (0.17 mmol) of $RuCl_2(PCy_3)_2(dmso)_2$, 35 mg (0.17 mmol) of silver triflate and 10 ml of degassed dichloromethane were introduced. The solution was stirred at room temperature for 2 h. The solution was filtrated with a cannula, the solvent was removed under reduced pressure, and 161 mg of a brown powder was obtained (yield 95%).

^{1}H NMR (200.130 MHz, $CDCl_3$): δ 1.06–2.05 (m, 60H, $15CH_2PCy_3$), 2.05–2.33 (m, 6H, $6CHPCy_3$), 3.36 (6H, CH_3SOCH_3), 3.50 (s, 6H, CH_3SOCH_3) ppm. ^{31}P NMR (81.019 MHz, $CDCl_3$): δ 43.65 (d, $^2J_{PP}$ = 34.7 Hz), 37.60 (d, $^2J_{PP}$ = 34.7 Hz) ppm.

*4.2.3. Synthesis of $[RuCl(=C=C=CPh_2)(PCy_3)_2(dmso)_2]^+TfO^-$ (**8**)*

In a Schlenk tube under an argon atmosphere, 150 mg (0.21 mmol) of $[RuCl(PCy_3)_2(dmso)_2]^+TfO^-$, 43 mg (0.21 mmol) of 1,1-diphenylpropynol and 10 ml of degassed dichloromethane were introduced. The solution was stirred at room temperature for 4 h. The solvent was distilled under reduced pressure and 180 mg of a purple powder was obtained (yield 95%).

^{1}H NMR (200.130 MHz, $CDCl_3$): δ 1.06–2.03 (m, 66H, $2PCy_3$), 3.35 (s, 6H, CH_3SOCH_3), 3.42 (s, 6H, CH_3SOCH_3), 7.20–7.38 (m, 6H, *meta*- and *para*-C*H* in C_6H_5), 7.52–7.61 (m, 4H, *ortho*-C*H* in C_6H_5) ppm. ^{31}P NMR (81.019 MHz, $CDCl_3$): δ 33.25 (d, $^2J_{PP}$ = 35.1 Hz), 39.38 (d, $^2J_{PP}$ = 35.1 Hz) ppm. IR (KBr): 1941.9 (Ru=C=C=C) cm^{-1}.

*4.2.4. Synthesis of $RuCl_2(=C=C=CPh_2)(PCy_3)_2(dmso)$ (**9**)*

In a Schlenk tube under an argon atmosphere, 150 mg (0.17 mmol) of $RuCl_2(PCy_3)_2(dmso)_2$, 35 mg (0.17 mmol) of 1,1-diphenylpropynol and 10 ml of degassed dichloromethane were introduced. The solution was stirred at room temperature for 7 h. The solvent was distilled under reduced pressure and 160 mg of a purple powder was obtained (yield 95%).

^{1}H NMR (200.130 MHz, $CDCl_3$): δ 0.98–2.20 (m, 66H, $2PCy_3$), 3.38 (s, 6H, CH_3SOCH_3), 7.11–7.31 (m, 6H, *meta*- and *para*-C*H* in C_6H_5), 7.52–7.64 (m, 4H,

ortho-C*H* in C_6H_5). ^{31}P NMR (81.019 MHz, $CDCl_3$): δ 50.84 (s, PCy_3) ppm. ^{13}C NMR (50.332 MHz, CD_2Cl_2): δ 26.6 (δ-*C*H_2PCy_3), 26.9 (d, $^3J_{PC}$ = 28.2 Hz, β-*C*H_2PCy_3), 27.4 (γ-*C*H_2PCy_3), 35.5 (d, $^1J_{PC}$ = 61.3 Hz, *C*HPCy_3), 46.3 (*C*H_3SOCH_3), 126.4, 127.7, 128.4 (*C*H arom.), 146.3 (ipso-*C*), 218.2 (*C*γ), 263.5 (*C*β), 309.3 (*C*α) ppm. IR (KBr): 1934.3 (Ru=C=C=C) cm^{-1}.

4.2.5. Synthesis of
*$RuCl_2$(=C=C=C(p-C_6H_4F)$_2$)(PCy_3)$_2$(dmso) (**10**)*

In a Schlenk tube under an argon atmosphere, 150 mg (0.17 mmol) of $RuCl_2(PCy_3)_2(dmso)_2$, 41 mg (0.17 mmol) of propargyl alcohol HC≡CC(*p*-$C_6H_4F)_2$ OH and 10 ml of degassed dichloromethane were introduced. The solution was stirred at room temperature for 16 h. The solvent was evaporated under reduced pressure and 165 mg of a purple powder was obtained (yield 94%).

^{1}H NMR (200.130 MHz, $CDCl_3$): δ 0.92–2.19 (m, 66H, PCy_3), 3.44 (s, 6H, CH_3SOCH_3), 9.92 (d, 4H, $^3J_{HH}$ = 8.5 Hz, 4C*H*C_6H_4), 7.51 (d, 4H, $^3J_{HH}$ = 8.5 Hz, 4C*H*C_6H_4) ppm. ^{31}P NMR (81.019 MHz, $CDCl_3$): δ 51.27 (s, PCy_3) ppm. IR (KBr): 1933.3 (Ru=C=C=C) cm^{-1}.

4.2.6. Synthesis of
*$RuCl_2$(=C=C=C(p-C_6H_4Cl)$_2$)(PCy_3)$_2$(dmso) (**11**)*

In a Schlenk tube under an argon atmosphere, 150 mg (0.17 mmol) of $RuCl_2(PCy_3)_2(dmso)_2$, 47 mg (0.17 mmol) of propargyl alcohol HC≡CC(*p*-$C_6H_4Cl)_2$ OH and 10 ml of degassed dichloromethane were introduced. The solution was stirred at room temperature for 16 h. The solvent was distilled under reduced pressure and 173 mg of a purple powder was obtained (yield 96%).

^{1}H NMR (200.130 MHz, $CDCl_3$): δ 0.94–2.21 (m, 66H, 2PCy_3), 3.45 (s, 6H, CH_3SOCH_3), 7.20 (d, 4H, $^3J_{HH}$ = 8.6 Hz, 4C*H*C_6H_4), 7.47 (d, 4H, $^3J_{HH}$ = 8.6 Hz, 4C*H*C_6H_4) ppm. ^{31}P NMR (81.019 MHz, $CDCl_3$): δ 51.07 (s, PCy_3) ppm. IR (KBr): 1924.4 (Ru=C=C=C) cm^{-1}.

4.2.7. Synthesis of
*$RuCl_2$(=C=C=C(p-C_6H_4OMe)$_2$)(PCy_3)$_2$(dmso) (**12**)*

In a Schlenk tube under an argon atmosphere, 150 mg (0.17 mmol) of $RuCl_2(PCy_3)_2(dmso)_2$, 45 mg (0.17 mmol) of propargyl alcohol HC≡CC(*p*-$C_6H_4OMe)_2$OH and 10 ml of degassed dichloromethane were introduced. The solution was stirred at room temperature for 16 h. The solvent was distilled under reduced pressure and 170 mg of a purple powder was obtained (yield 95%).

^{1}H NMR (200.130 MHz, CD_2Cl_2): δ 0.98–2.21 (m, 66H, 2PCy_3), 3.38 (s, 6H, CH_3SOCH_3), 3.71 (s, 6H, 2OCH_3), 6.77 (d, 4H, $3J_{HH}$ = 8.8 Hz, 4C*H*C_6H_4), 7.44 (d, 4H, $3J_{HH}$ = 8.8 Hz, 4C*H*C_6H_4) ppm. ^{31}P NMR (81.019 MHz, $CDCl_3$): δ 50.94 (s, PCy_3) ppm. ^{13}C NMR (50.332 MHz, CD_2Cl_2): δ 26.2 (δ-*C*H_2PCy_3), 26.5 (d, $^3J_{PC}$ = 25.1 Hz, β-*C*H_2PCy_3), 27.0 (γ-*C*H_2PCy_3), 35.1 (d, $^1J_{PC}$ = 60.9 Hz, *C*HPCy_3), 45.9 (*C*H_3SOCH_3), 55.2 (O*C*H_3), 113.2, 127.2 (*C*HC_6H_5), 138.2 (ipso-*C*), 158.9 (ipso-OCH_3*C*), 193.0 (*C*γ), 269.7 (*C*β), 312.5 (*C*α) ppm. IR (KBr): 1943 (Ru=C=C=C) cm^{-1}.

5. Conclusion

The above results offer a novel family of ruthenium–allenylidene complexes containing both bulky PCy_3 and labile dmso ligands. They are easily made in two or three steps with high yields from $RuCl_2(dmso)_4$ and they are expected to be key starting derivatives for the access to a variety of ruthenium–allenylidene complexes. These simple ruthenium–allenylidene complexes appear to be efficient catalyst precursors for the ROMP polymerisation of cyclic olefins. The coordinatively unsaturated complex [RuCl(=C=C=CPh_2)(PCy_3)$(dmso)_2$]OTf **5** is the most active catalyst for the ROMP polymerisation of both norbornene and cyclooctene. Among the neutral complexes $RuCl_2$(=C=C=CAr_2)(PCy_3)$_2$(dmso), **12** (Ar = *p*-C_6H_4OMe) gives by far the best compromise for the norbornene polymerisation for yields (96%) narrow polydispersity (1.61) and *cis*-configuration of the CH=CH bonds (56%). Whereas both complexes **9** (Ar = C_6H_5) and **12** constitute efficient catalysts for cyclooctene polymerisation.

Acknowledgements

The authors are grateful to the University of El Jadida for a stay of IAA in Rennes, and to Prof. Mernari and Guesmi for helpful discussions, the

European Union for support via COST-Chemistry Program D17 and Network POLYCAT, and the Region Bretagne for its programme on Catalysis PRIR (No. 169 AOC).

References

[1] S.T. Nguyen, L.K. Johnson, R.H. Grubbs, J. Am. Chem. Soc. 114 (1992) 3974;
P. Schwab, M.B. France, J.W. Ziller, R.H. Grubbs, Angew. Chem. Int. Ed. Engl. 34 (1995) 2039.

[2] A. Fürstner (Ed.), Alkene Metathesis in Organic Synthesis, Springer, Berlin, Angew. Chem. Int. Ed. Engl. 39 (2000) 3013;
M. Schuster, S. Blechert, Angew. Chem. Int. Ed. Engl. 36 (1997) 2036;
R.H. Grubbs, S. Chang, Tetrahedron 54 (1998) 4413;
T.M. Trnka, R.H. Grubbs, Acc. Chem. Res. 34 (2001) 18.

[3] T. Weskamp, W.C. Schattenmann, M. Spiegler, W.A. Herrmann, Angew. Chem. Int. Ed. Engl. 37 (1998) 2490;
T. Weskamp, F.J. Kohl, W. Hieringer, D. Gleich, W.A. Herrmann, Angew. Chem. Int. Ed. Engl. 38 (1999) 2416;
J. Huang, H.J. Schang, E.D. Stevens, S.P. Nolan, Organometallics 18 (1999) 5375;
M. Scholl, S. Ding, C.W. Lee, R.H. Grubbs, Org. Lett. 1 (1999) 953;
C.W. Bielanski, R.H. Grubbs, Angew. Chem. Int. Ed. Engl. 39 (2000) 2903.

[4] A. Mutch, M. Leconte, F. Lefebvre, J.M. Basset, J. Mol. Catal. A 133 (1998) 191;
P.A. van der Schaaf, A. Hafner, A. Mühlebach, Angew. Chem. Int. Ed. Engl. 35 (1996) 1845.

[5] A.W. Stumpf, E. Saive, A. Demonceau, A.F. Noels, J. Chem. Soc., Chem. Commun. (1995) 1127;
A. Demonceau, A.W. Stumpf, E. Saive, A.F. Noels, Macromolecules 30 (1997) 3127;
L. Delaude, A. Demonceau, A.F. Noels, Chem. Commun. (2001) 986.

[6] S.T. Nguyen, L.K. Johnson, R.H. Grubbs, J. Am. Chem. Soc. 114 (1992) 3974;
R.R. Schrock, Acc. Chem. Res. 23 (1990) 158.

[7] I. del Río, G. van Koten, Tetrahedron Lett. 40 (1999) 1401;
H. Katayama, T. Yoshida, F. Ozawa, J. Organomet. Chem. 562 (1998) 203.

[8] A. Fürstner, M. Picquet, C. Bruneau, P.H. Dixneuf, Chem. Commun. (1998) 1315;
M. Picquet, D. Touchard, C. Bruneau, P.H. Dixneuf, New J. Chem. 23 (1999) 141;
A. Fürstner, M. Liebl, C.W. Lehmann, M. Picquet, R. Kunz, C. Bruneau, D. Touchard, P.H. Dixneuf, Chem. Eur. J. 6 (2000) 1847.

[9] K.J. Harlow, A.F. Hill, J.D.E.T. Wilton-Ely, J. Chem. Soc., Dalton Trans. (1999) 285;
H.J. Schanz, L. Jafarpour, E.D. Stevens, S.P. Nolan, Organometallics 18 (1999) 5187;
A. Fürstner, A.F. Hill, M. Liebl, J.D.E.T. Wilton-Ely, Chem. Commun. (1999) 601.

[10] S.N. Osipov, O.J. Artyuskin, A.F. Kolomiets, C. Bruneau, P.H. Dixneuf, Synlett 7 (2000) 1031;
S.N. Osipov, O.J. Artyuskin, A.F. Kolomiets, M. Picquet, C. Bruneau, P.H. Dixneuf, Eur. J. Org. Chem., (2001) 3891;
S.N. Osipov, C. Bruneau, M. Picquet, A.F. Kolomiets, P.H. Dixneuf, J. Chem. Soc., Chem. Commun. (1998) 2053.

[11] M. Picquet, C. Bruneau, P.H. Dixneuf, J. Chem. Soc., Chem. Commun. (1998) 2249;
D. Sémeril, J. Le Nôtre, C. Bruneau, P.H. Dixneuf, A.F. Kolomiets, S.N. Osipov, New J. Chem. 25 (2001) 16.

[12] J.P. Evans, A. Spencer, G. Wilkinson, J. Chem. Soc., Dalton Trans. (1973) 204.

[13] J.J. Rack, H.B. Gray, Inorg. Chem. 38 (1999) 2.

[14] N. Pirio, D. Touchard, L. Toupet, P.H. Dixneuf, Chem. Commun. (1991) 980;
D. Touchard, N. Pirio, P.H. Dixneuf, Organometallics 14 (1995) 4920.

[15] D. Touchard, P. Haquette, A. Daridor, A. Romero, P.H. Dixneuf, Organometallics 17 (1998) 3844.

[16] K.J. Ivin, J.C. Mol, Olefin Metathesis and Metathesis Polymerization, Academic Press, New York, 1997.