Active Catalysts in Alkene Metathesis

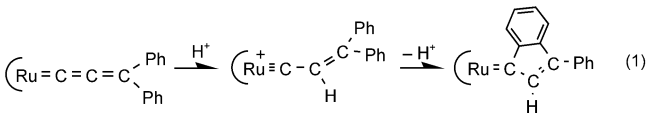
Highly Active Catalysts in Alkene Metathesis: First Observed Transformation of Allenylidene into Indenylidene via Alkenylcarbyne—Ruthenium Species**

*Ricardo Castarlenas and Pierre H. Dixneuf**

Dedicated to Professor Jean-Pierre Genet, on the occasion of his 60th Birthday

Alkene metathesis has recently led to remarkable applications in organic synthesis as well as in polymer science through ring-opening-metathesis polymerization (ROMP).[1] Since the advent of functional group tolerant ruthenium alkylidene catalysts,[2] this reaction has reached a tremendous level of development for the production of a variety of macromolecules with both C=C bonds and functional groups regularly placed.[3] Ruthenium catalysts for alkene metathesis are not restricted to alkylidene precursors of type $L_nRu{=}CHR$. The ionic 18 electron ruthenium allenylidene complexes $[RuCl(=C{=}C{=}CAr_2)(PR_3)(p\text{-cymene})][X]$[4] ($X = PF_6, BPh_4, CF_3SO_3$) promote ring-closing metathesis (RCM) of dienes and enynes[5] as well as ROMP.[6] Indenylidene derivatives of type $RuCl_2(PCy_3)(L)$(indenylidene) ($L = PCy_3$, imidazolylidene), expected to result from the corresponding allenylidene although this has not been fully demonstrated, have also shown good activity in RCM.[7] Werner and co-workers reported that coordinatively unsaturated ionic carbyne ruthenium precursors,[8] and especially hydridocarbyne ruthenium complexes,[9] are active in ROMP of cyclooctene and cross-metathesis.

Tremendous efforts are currently made to produce more efficient and stable catalysts to decrease the process cost and the level of metal traces in fine chemicals and polymers.[10] Herein we report the first observation that alkenylcarbyne ruthenium intermediates, easily obtained from allenylidene ruthenium arene complexes, are the key intermediates for metal–indenylidene complex formation [Eq. (1)] and that the latter show impressive turn-over frequencies (TOFs) for the polymerization of cyclooctene and cyclopentene under mild conditions as well as RCM reactions.



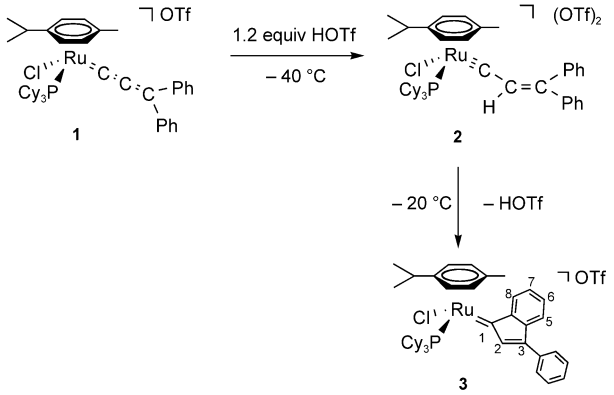
(1)

In the course of our study on cyclooctene polymerization promoted by allenylidene ruthenium(II) complexes, we have observed that the addition of a strong acid to the initiator $[RuCl(=C{=}C{=}CPh_2)(PCy_3)(\eta^6\text{-}p\text{-cymene})][CF_3SO_3]$ (**1**) largely increases the rates of polymerization. Thus, when five equivalents of HBF_4 or CF_3SO_3H are added to catalytic solutions of **1**, TOF values increase by three orders of magnitude (Table 1, entries 1–3). To understand the nature of the catalytic species and control their synthesis, low temperature NMR studies of protonated complex **1** have been undertaken. The addition of 1.2 equivalents of triflic acid to CD_2Cl_2 solutions of **1** at −40 °C led to a change from dark red to dark orange, while a new $^{31}P\{^1H\}$ NMR signal appeared at $\delta = 78.6$ ppm during the disappearance of that of **1** at $\delta = 57.6$ ppm. The conversion was completed in 20 min at −40 °C. The $^{13}C\{^1H\}$ and ^1H NMR data are consistent with the alkenylcarbyne derivative $[RuCl(\eta^6\text{-}p\text{-cymene})(\equiv C\text{-}CH{=}CPh_2)(PCy_3)][CF_3SO_3]_2$ (**2**) resulting from protonation at the C_β of the allenylidene ligand (Scheme 1). Indeed, the $^{13}C\{^1H\}$

Table 1: Cyclooctene polymerisation at room temperature.[a]

Entry	Cat.	Ratio[b]	Acid[c]	Time	Yield	$10^{-3} \times \bar{M}_n$[d]	PDI[e]	% cis[f]	TOF[g]
1	**1**	1.000	–	15 h	95%	143	1.9	27	63
2	**1**	1.000	HBF_4 (5 equiv)	1 min	92%	224	1.7	40	55200
3	**1**	1.000	HOTf (5 equiv)	1 min	95%	238	1.6	38	57200
4	**1**	10000	HOTf (5 equiv)	5 min	97%	387	1.5	28	116400
5	**1**	100000	HOTf (100 equiv)	5 min	88%	857	1.4	35	1096000
6	**4**	10000	HOTf (5 equiv)	10 min	73%	220	1.8	25	43800
7	**5**	10000	HOTf (5 equiv)	8 h	25%	107	1.9	22	312
8	**6**	10000	HOTf (5 equiv)	5 min	92%	286	1.6	26	110000

[a] 4.5×10^{-3} mol of cyclooctene in 2.5 mL of PhCl. [b] [cyclooctene]/[Ru]. [c] Related to complex. [d] determined by GPC in THF versus polystyrene standards. [e] Polydispersity index $\bar{M}_w/\bar{M}_n$. [f] determined by ^{13}C NMR. [g] Turnover frequency in moles per hour. Cat. = catalyst.



Scheme 1. The formation of indenylidene species at low temperature.

[*] Prof. Dr. P. H. Dixneuf, R. Castarlenas
Institut de chimie de Rennes, UMR 6509 CNRS
Université de Rennes
Organométalliques et Catalyse
Campus de Beaulieu, 35042, Rennes (France)
Fax: (+33) 2-2323-6939
E-mail: pierre.dixneuf@univ-rennes1.fr

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NMR spectrum displays a doublet at 328.1 ppm ($^2J_{P\text{-}C}$ = 11 Hz) for the Ru≡C carbon and C_β (δ = 130.5 ppm) and C_γ (δ = 193.2 ppm) correlate with the olefinic proton (δ_H = 7.05 ppm) in ^1H–^{13}C HMQC and HMBC experiments, respectively. The ^1H NMR spectrum of **2** also displays two doublets at δ = 6.75 and 6.61 ppm showing the retention of the coordinated *p*-cymene ligand.

When the temperature was raised to −20 °C a new signal appeared at δ = 48.3 ppm in the $^{31}P\{^1H\}$ spectrum. Complete conversion was achieved in 30 min with a color change to violet. The nature of this intermediate was consistent with the indenylidene ruthenium complex [RuCl(η⁶-*p*-cymene){=C−CH=C(Ph)C$_6$H$_4$}(PCy$_3$)][CF$_3$SO$_3$] (**3**) containing both PCy$_3$ and *p*-cymene groups (Scheme 1). Complex **3** results from phenyl substitution by the electrophilic C_α carbon of **2**, thus a contribution of the canonical form **2B** favors this rearrangement.

[Ru⁺≡C−CH=CPh$_2$ (**2A**)↔Ru=C⁺−CH=CPh$_2$ (**2B**)].

The $^{13}C\{^1H\}$ NMR spectrum shows a doublet ($^2J_{P\text{-}C}$ = 10 Hz) at δ = 334.1 ppm corresponding to Ru=C carbon atom as well as signals for every carbon of indenylidene group (see experimental section). The ^1H spectrum displays a singlet at δ = 6.88 ppm that correlates with C_2 (δ = 143.1 ppm) in a HMQC experiment and with C_1 and C_3 (δ = 154.6 ppm) in a HMBC experiment. Indeed, the unambiguous presence of the indenylidene ligand arises from the correlation of C_1 and H_8 of the indenylidene ligand in the HMBC experiment, which is not observed for its alkenylcarbyne precursor **2**. Four doublets between δ = 6.36 and 6.15 ppm were observed for the four arene protons of the coordinated *p*-cymene ligand. Attempts to isolate complex **3** were unsuccessful because of slow decomposition of the complex at room temperature by loss of *p*-cymene ligand and formation of [HPCy$_3$][CF$_3$SO$_3$] as observed in ^1H and $^{31}P\{^1H\}$ NMR spectra.

Whereas alkenylcarbyne osmium[11] complexes have been fully described, only two types of unstable dicationic alkenylcarbyne ruthenium intermediates were recently reported on the protonation of the corresponding allenylidene ruthenium complexes, [RuCl(≡CCH=CPh$_2$)(κ²-P,O-Cy$_2$PCH$_2$CH$_2$OCH$_3$)(κ-P-Cy$_2$PCH$_2$CH$_2$OCH$_3$)][BF$_4$,PF$_6$] by Werner et al.[12] and [Cp*Ru(dippe)(≡CCH=CPh$_2$)][B(Ar$_F$)$_4$]$_2$ by Valerga and co-workers.[13] No formation of related indenylidene complexes was observed in these examples. It is noteworthy that the formation of indenylidene ruthenium derivatives [RuCl$_2$(PR$_3$)$_2$(indenylidene)] was observed while attempting to produce the corresponding allenylidene ruthenium complex.[7c] However, the rearrangement of allenylidene into the indenylidene ligand was never directly observed.[7] Thus, the above results show for the first time the direct intramolecular transformation of an allenylidene ruthenium species into an indenylidene species on protonation via an alkenylcarbyne intermediate.

The activity in ROMP of the in situ prepared species **3** was thus evaluated. To quickly generate species **3**, complex **1** was first treated with CF$_3$SO$_3$H at room temperature. When 10000 equivalents of cyclooctene (1.46 M) in PhCl were added, complete gelatification was observed within 1 minute, but the reaction was stirred for a further 5 min before being quenched with ethyl vinyl ether (Table 1, entry 4). The isolation of low polydispersed polyoctenamer showed a conversion of 97 % corresponding to a calculated TOF value of 116000 mol per hour. Indeed, a tremendous increase in the TOF value to more than 1000000 mol per hour was reached when 100000 equivalents of monomer were loaded (entry 5). It was verified that polymerization does not take place with CF$_3$SO$_3$H in the absence of the ruthenium catalyst.

Slight modifications of the starting allenylidene complex were made by changing subtituents in the phenyl groups [RuCl(η⁶-*p*-cymene){=C=C=C(***p*-OMe-Ph**)$_2$}(PCy$_3$)][CF$_3$SO$_3$] (**4**), in the phosphane [RuCl(η⁶-*p*-cymene)(=C=C=CPh$_2$)(**PPh$_3$**)][CF$_3$SO$_3$] (**5**) or in the η⁶-arene ligand [RuCl)(η⁶-**1,2,4,5-tetramethylbenzene**)(=C=C=CPh$_2$)(PCy$_3$)][CF$_3$SO$_3$] (**6**). The addition of five equivalents of triflic acid to solutions of **4**–**6** also promoted the formation of cyclooctenamer (entries 6–8). Only precursor **6** led to similar results as those of **1**, thus showing that either the less electron-donating phosphane PPh$_3$ (**5**) or the introduction of electron releasing groups in the phenyl rings (**4**) reduces catalytic activity.

Due to the high activity of the indenylidene complex, **3**, for the ROMP of cyclooctene, the polymerization of the less reactive cyclopentene was evaluated. A Schlenk tube was charged with allenylidene complexes (**1, 4**, or **6**), 1000 equivalents of cyclopentene (2.33 M), PhCl, and 5 equivalents of triflic acid at 0 °C (Figure 1). To make a comparison of

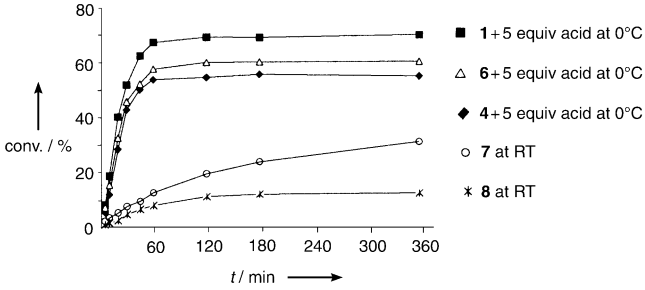


Figure 1. Cylopentene polymerization with different catalysts and monitored by ^1H NMR experiments. Conv. = conversion

the activity of these catalysts, experiments with the well-known stable ruthenium alkylidene catalysts RuCl$_2$(=CHPh)(PCy$_3$)$_2$ (**7**)[2c] and RuCl$_2$(=CHPh)-(PCy$_3$)$_2${=CN(Mes)CH$_2$CH$_2$N(Mes)} (**8**)[2a] were carried out at room temperature. The analysis of calculated TOF values clearly demonstrates the excellent catalytic performance of in situ generated indenylidene species from **1, 4**, or **6** with TOF values lying between 540 and 670, eight times more than those observed for the catalyst **8** (Table 2). In addition, when five equivalents of triflic acid were added to vessel containing **8**, even lower yields and lower TOF values were observed, which is in agreement with the previous observation that the addition of HCl does not increase activity of pure **8**.[14] It was described that with Schrock-type initiators of such as [W(=CH*t*Bu)(O*t*Bu)$_2$(NAr)], the polymerization of cyclopentene took place at temperatures below −40 °C ([cata-

Table 2: Cyclopentene polymerization with the catalytic system RuCl(η⁶-*p*-cymene)(=C=C=CR₂)(PR′₃)][CF₃SO₃] + HOSO₂CF₃.[a]

Entry	Complex	*T* [°C]	Acid[b]	Time	Yield	$10^{-3}\times\bar{M}_n$[c]	PDI[d]	% *cis*[e]	TOF[f]
1	**1**	0	5 equiv	1 h	67%	106	1.5	15	670
2	**4**	0	5 equiv	1 h	54%	90	1.8	18	540
3	**6**	0	5 equiv	1 h	60%	88	1.7	16	600
4	**7**	20	–	3 h	12%	31	1.5	21	40
5	**8**	20	–	3 h	24%	60	1.6	19	80
6[h]	**1**	−40	5 equiv	15 min	91%	–	–	–	44444

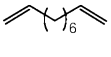
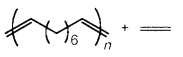
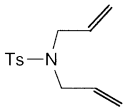
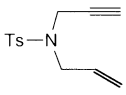
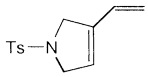
[a] 7.3×10^{-3} mol of cyclopentene in 2.5 mL of PhCl [cyclopentene]/[Ru] = 1000. [b] Related to Ru complex. [c] determined by GPC in THF versus polystyrene standards. [d] Polydispersity index $\bar{M}_w/\bar{M}_n$. [e] determined by ^{13}C NMR. [f] Turnover frequency in moles per hour. [g] bulk polymerization, [cyclopentene]/[Ru] = 10000.

The above results show for the first time that the direct intramolecular transformation of an allenylidene ruthenium complex into an indenylidene ruthenium derivative, on protonation via an alkenylcarbyne compound. Moreover they show the birth of a new in situ generated 18 electron, ionic arene indenylidene ruthenium catalytic species, highly active for ROMP of cyclooctene and cyclopentene, RCM or ADMET reactions even operating at 0 °C and arising from easily made allenylidene complexes.

lyst]:[monomer] = 1:200, 4 h, 95% conversion).[15] At this temperature, the in situ generated complex **3** was able to polymerize in fifteen minutes up to 90% of cyclopentene in bulk conditions with extremely low loading of the catalyst (1:10000) showing even better activity (Table 2, entry 6). The above experiments constitute the first evidence of an indenylidene–metal catalyst precursor for ROMP.

The indenylidene species **3** is also an active catalyst precursor in other typical alkene metathesis reactions. Monitoring the RCM of diallyltosylamide with the catalytic system made from **1** and five equivalents of CF_3SO_3H was carried out in an NMR tube. Initially, the mixture was cooled to −40 °C. The formation of **2** was observed by $^{31}P\{^1H\}$ NMR but no RCM product was formed after 1 hour at −40 °C. At 0 °C the formation of **3** was observed and the RCM reaction took place at 0 °C reaching 99% of conversion in 30 min. Other typical alkene metathesis reactions like acyclic diene metathesis (ADMET) of decadiene and ring closing metathesis of allylpropargyltosylamide were carried out, thus showing versatility of catalyst **3** (Table 3). Therefore, the

Table 3: Alkene metathesis with *in situ* prepared catalyst **3** from RuCl(η⁶-*p*-cymene)(=C=C=CPh₂)(PCy₃)][CF₃SO₃] (**1**) + HOSO₂CF₃ at 0 °C.[a]

	Substrate	Product	Time	Yield	TOF[b]
ADMET			12 h	94%	4
RCM			30 min	99%	98
Enyne metathesis			3 h	75%	12.5

[a] 4.5×10^{-6} mol of **1** + 22.5×10^{-6} mol of $HOSO_2CF_3$ in 0.5 mL of CD_2Cl_2 [substrate/[Ru] = 50. [b] Turnover frequency in moles per hour.

activity of 18 electron, ionic indenylidene-arene complex **3** seems higher than that of previously reported 16 electron, neutral diphosphane indenylidene or phosphane imidazolylidene indenylidene ruthenium complexes[7] probably because the *p*-cymene ligand is easily released, thus generating active initiators.

Experimental Section

Preparation of **2**: A dark-red solution of **1** (40 mg, 0.045 mmol) in CD_2Cl_2 (0.5 mL) in an NMR tube under argon atmosphere at 233 K was treated with triflic acid (5 μL 0.056 mmol). The solution immediately turned dark orange and after sealing the NMR tube under argon atmosphere measurements were made. ^{1}H NMR (300 MHz, CD_2Cl_2, 233 K): $\delta = 8.12$ (vt, $J_{H\text{-}H} = 7.0$ Hz, 2H, $H_{meta\text{-}Ph}$), 7.8–7.3 (m, 6H, H_{Ph}), 7.05 (s, 1H, Ru≡C−CH=), 6.92 (vt, $J_{H\text{-}H} = 7.5$ Hz, 2H, $H_{meta\text{-}Ph}$), 6.75 and 6.61 (both d, $J_{H\text{-}H} = 6.0$ Hz, 4H, η⁶-*p*-cymene), 2.9–2.6 (m, 4H, ^{i}Pr and PCH), 2.28 (s, 3H, CH_3), 2.1–0.9 ppm (m, 36H, Cy and *i*Pr). $^{13}C\{^1H\}$ NMR + DEPT, HMQC and HMBC (75.4 MHz, CD_2Cl_2, 233 K): $\delta = 328.1$ (d, $J_{C\text{-}P} = 11$ Hz, Ru≡C), 193.2 (s, CH=*C*Ph₂), 140.5 and 137.6 (both s, $C_{ipso\text{-}Ph}$), 136.0, 134.8, 134.2, 130.3, 129.4, and 127.8 (all s, C_{Ph}), 130.5 (s, Ru≡C−*C*H=), 128.2 and 125.8 (both s, $C_{ipso\text{-}p\text{-}cymene}$), 120.4 (c, $J_{C\text{-}F} = 320.0$ Hz, CF_3), 111.8, 108.7 (both s, $C_{p\text{-}cymene}$), 33.3 (s, CH_{iPr}), 31–24 (br, Cy), 25.1, 22.2 (s, $CH_{3\text{-}iPr}$), 19.9 ppm (s, CH_3). $^{31}P\{^1H\}$ NMR (121.4 MHz, CD_2Cl_2, 233 K): $\delta = 78.6$ ppm (s).

Preparation of **3**: A dark-red solution of **1** (40 mg, 0.045 mmol) in CD_2Cl_2 (0.5 mL) in an NMR tube under argon atmosphere at 253 K was treated with triflic acid (5 μL 0.056 mmol). The tube was sealed under argon and reaction was monitored by ^{31}P NMR. The formation of **2** was first observed and a new species, **3**, was progressively formed. The formation of **3** was completed in 20 min. ^{1}H NMR (300 MHz, CD_2Cl_2, 233 K): $\delta = 8.33$ (m, 1H, $H_{8\text{-}ind}$), 7.84 (d, $J_{H\text{-}H} = 7.5$ Hz, 2H, $H_{orto\text{-}Ph}$), 7.75 (t, $J_{H\text{-}H} = 7.5$ Hz, 1H, $H_{para\text{-}Ph}$), 7.60 (vt, $J_{H\text{-}H} = 7.5$ Hz, 2H, $H_{meta\text{-}Ph}$), 7.42 (m, 2H, $H_{7\text{-}ind}$ and $H_{6\text{-}ind}$), 7.13 (m, 1H, $H_{5\text{-}ind}$), 6.88 (s, 1H, Ru=C−CH=), 6.36, 6.31, 6.19, and 6.15 (all d, 4H, $J_{H\text{-}H} = 6.0$ Hz, η⁶-*p*-cymene), 2.83 (m, 1H, ^{i}Pr), 2.78 (m, 3H, PCH), 2.31 (s, 3H, CH_3), 2.1–0.9 ppm (m, 36H, Cy and *i*Pr). $^{13}C\{^1H\}$ NMR + DEPT, HMQC and HMBC (75.4 MHz, CD_2Cl_2, 233 K): $\delta = 334.1$ (d, $J_{C\text{-}P} = 10$ Hz, Ru = C), 154.6 (s, $C_{3\text{-}ind}$), 146.8 (s, $C_{9\text{-}ind}$), 143.1 (d, $J_{C\text{-}P} = 2$ Hz, $C_{2\text{-}ind}$), 136.5 (s, $C_{4\text{-}ind}$), 134.7 (s, $C_{7\text{-}ind}$), 133.4 (s, $C_{8\text{-}ind}$), 132.7 (s, $C_{6\text{-}ind}$), 132.5 (s, $C_{para\text{-}Ph}$), 131.7 (s, $C_{ipso\text{-}Ph}$), 130.0 (s, $C_{meta\text{-}Ph}$), 127.8 (s, $C_{orto\text{-}Ph}$), 126.3 and 125.3 (both s, $C_{ipso\text{-}p\text{-}cymene}$), 121.2 (s, $C_{5\text{-}ind}$), 120.4 (c, $J_{C\text{-}F} = 320.0$ Hz, CF_3), 103.6 and 99.7 (both s, $C_{p\text{-}cymene}$), 33.8 (s, CH_{iPr}); 30–24 (br, Cy); 24.2 and 22.8 (both s, $CH_{3\text{-}iPr}$); 19.6 ppm (s, CH_3). $^{31}P\{^1H\}$ NMR (121.4 MHz, CD_2Cl_2, 233 K): $\delta = 48.3$ ppm (s).

Polymerisation of cyclolefins: **1** (8 mg 9 μmol) was dissolved in PhCl (0.5 mL) at 253 K and 4 μL (45 μmol) of triflic acid was added. After 30 min at this temperature desired amount of freshly prepared catalyst was transferred to a vessel at chosen temperature containing PhCl (2.5 mL) and monomer (500 mg; 4.5 mmol of cyclooctene, 1.46 M; 7.3 mmol of cyclopentene 2.33 M). After the reaction had finished, the resulting viscous mixture was dissolved with $CHCl_3$ containing 0.1% of 2,6-di-*tert*-butyl-4-methylphenol (BHT; 20 mL) and vinyl ethyl ether (0.3 mL). This solution was poured into methanol (300 mL) to precipitate the polymer, which was collected by filtration, dried under vacuum, and characterized by ^{1}H and ^{13}C NMR. Average molecular weights were determined using gel-

permeation chromatography GPC calibrated with polystyrene standards.

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