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Review

Vinylideneruthenium complexes in catalysis

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Contents

Abstract

Vinylideneruthenium complexes with the general formula $[RuCl_2(=C=CHR)L_2]$ (L = PPr^i_3, PCy_3, etc.) have been found to serve as good catalyst precursors with high efficiencies for ring-opening metathesis polymerization of cyclic olefins, ring-opening/cross-metathesis between norbornene derivatives and vinyl chalcogenides, ring-closing metathesis of α,ω-dienes, and (*Z*)-selective dimerization of terminal alkynes. The complexes are easily prepared in high yields from $[RuCl_2(p\text{-cymene})]_2$, L, and RC≡CH, which are all commercially available. Electron-donating substituents (R) at the β-carbon facilitate the alkyne–vinylidene tautomerization from both kinetic and thermodynamic points of view.

Keywords: Vinylidene complex; Ruthenium; Catalysis; Terminal alkyne; Olefin-metathesis; Ring-opening metathesis polymerization; Alkyne-dimerization

1. Introduction

Highly reactive, short-lived organic molecules may be effectively stabilized by coordination to transition metals and invested with novel chemical properties that are useful for selective organic transformations. The chemistry of vinylidene complexes displays a representative example [1]. Thus, the vinylidene (:C=CHR) is a high-energy tautomer of alkyne (RC≡CH) in the free state, but it becomes a more stabilized species on most of transition metals (Scheme 1). The resulting complexes exhibit a variety of reactivities, which are rationalized by taking electrophilicity of α-vinylidene carbon, nucleophilicity of β-vinylidene carbon, and highly unsaturated structures of the vinylidene ligands into consideration (Scheme 2).

Vinylidene complexes have proven to be useful for catalysis as well. Pioneering works in this area until 1998 have been reviewed [2]. It has been documented that vinylidene complexes of group 6–10 metals often serve as key intermediates for catalytic conversion of alkynes. The represen-

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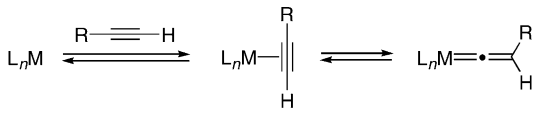
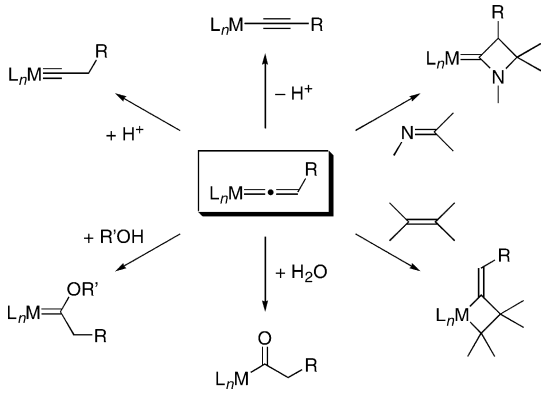


M = Ta, Cr, Mo, W, Mn, Re, Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt
L = ancillary ligand

Scheme 1. Formation of vinylidene complexes.



Scheme 2. Typical reaction patterns of vinylidene complexes.

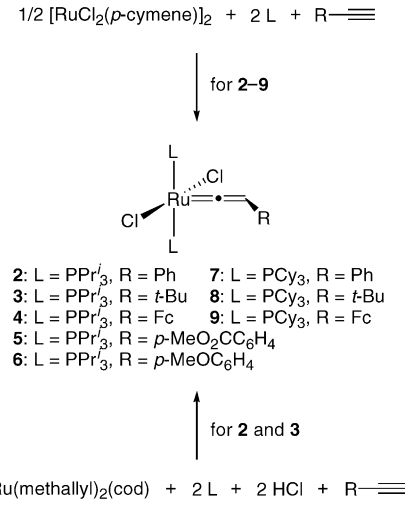
tative examples include dimerization of terminal alkynes [3], cycloaromatization of conjugated enediynes [4], and addition of oxygen, nitrogen, and carbon nucleophiles to alkynes [5]. Furthermore, some vinylidene complexes have been used as catalyst precursors for olefin-metathesis reactions [6].

In the last five years, we have examined synthesis and catalytic properties of ruthenium vinylidene complexes bearing basic and bulky tertiary phosphine ligands (e.g., PPr^i_3 and PCy_3). The complexes have been successfully applied to olefin-metathesis and alkyne-dimerization reactions. This article describes those results, together with related studies reported by other research groups.

2. Synthesis and structures of vinylideneruthenium(II) complexes

In 1979, Bruce et al. disclosed that $[CpRuCl(PPh_3)_2]$ reacts with PhC≡CH in the presence of NH_4PF_6 to afford a cationic vinylidene complex $[CpRu(=C=CHPh)(PPh_3)_2][PF_6]$ in 88% yield [7]. Following this report, a variety of vinylideneruthenium complexes have been prepared using terminal alkynes as vinylidene sources. Most of them have Cp and related ligands, and they are coordinatively saturated, 18-electron species.

On the other hand, there have been scattering reports for 16-electron complexes until recently, despite their potential reactivities derived from the coordinatively unsaturated structures. In 1991, Wakatsuki et al. reported an early example of 16-electron complex with the general formula $[RuX_2(=C=CHR)L_2]$ [8]. They prepared the PPh_3 complexes $[RuX_2(=C=CHBu^t)(PPh_3)_2]$ (X = Cl (**1**), Br) by the treatment of $[RuX_2(PPh_3)_3]$ with *t*-BuC≡CH. Later Werner and co-workers synthesized the PPr^i_3-coordinated analogue $[RuCl_2(=C=CHPh)(PPr^i_3)_2]$ by the reaction of $[RuH_2Cl_2(PPr^i_3)_2]$ with PhC≡CH [9–11], whereas Caulton reported that $[RuHCl(=C=CHPh)(PBu^t_2Me)_2]$ is formed by the insertion of PhC≡CH into $[RuHCl(H_2)(PBu^t_2Me)_2]$, followed by 1,2-hydrogen migration on the resulting styrylruthenium complex [12].



2: L = PPr^i_3, R = Ph **7**: L = PCy_3, R = Ph
3: L = PPr^i_3, R = *t*-Bu **8**: L = PCy_3, R = *t*-Bu
4: L = PPr^i_3, R = Fc **9**: L = PCy_3, R = Fc
5: L = PPr^i_3, R = *p*-$MeO_2CC_6H_4$
6: L = PPr^i_3, R = *p*-$MeOC_6H_4$

Scheme 3. Synthetic routes to $[RuCl_2(=C=CHR)L_2]$.

We have developed two synthetic routes to vinylideneruthenium complexes (Scheme 3) [13]. One is the reaction of $[Ru(methallyl)_2(cod)]$ with PPr^i_3, HCl, and RC≡CH. This reaction proceeds through an $[RuCl_2(PPr^i_3)_2]_n$ intermediate. The other one constitutes a more general and convenient approach. Thus, heating a toluene solution of $[RuCl_2(p\text{-cymene})]_2$, L (2 eq./Ru), and RC≡CH (1 eq./Ru) at 80 °C leads to selective formation of the vinylidene complexes **2**–**9**. All starting materials are commercially available. The PCy_3 complexes **7**–**9** may be isolated as crystals, simply by cooling the reaction solutions.

The latter method may be operative with a variety of alkynes and ancillary ligands, giving the corresponding vinylidene complexes cleanly and in high yields (Fig. 1). Thus, the treatment of $[RuCl_2(p\text{-cymene})]_2$ with PCy_3 and PhC≡$CSiMe_3$ causes 1,2-silyl migration to give the β-silylvinylidene complex $[RuCl_2\{=C=C(SiMe_3)Ph\}(PCy_3)_2]$ (**10**) [13]. The allenylidene complex **11** is synthesized with 1,1-diphenyl-2-propyn-1-ol as an alkyne reagent [14]. When a less bulky phosphine like PMe_2Ph is employed instead of PCy_3 or PPr^i_3, the coordinatively saturated complex **12** is formed [15]. The synthesis of **13**–**15** containing pincer-type tridentate ligands is also successful [16,17]. Furthermore, bi- and tri-metallic vinylidene complexes (**16**, **17**) are formed in high yields [13,18].

Complexes **2**–**9** in Scheme 3 have been converted to the complexes with various ligands (Fig. 2). Treatment of **8** with 1,3-dimesitylimidazol-2-ylidene (IMes) or its saturated

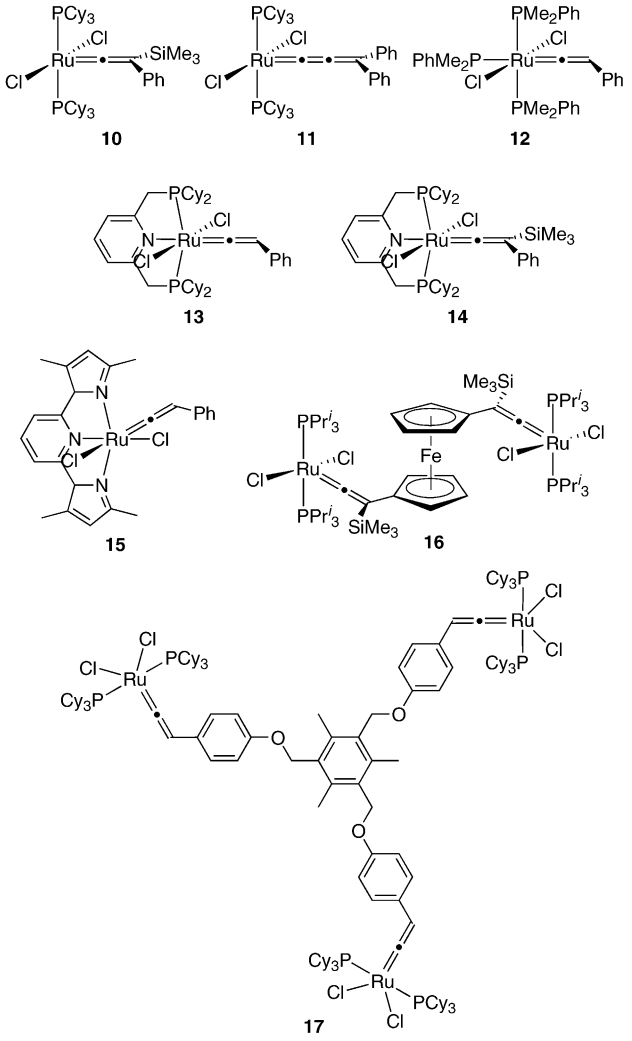


Fig. 1. Vinylideneruthenium(II) complexes prepared from $[RuCl_2(p\text{-cymene})]_2$, alkynes, and ancillary ligands.

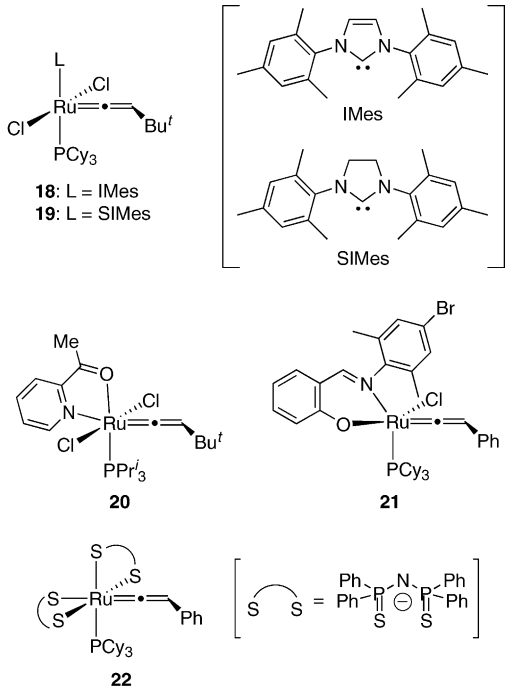


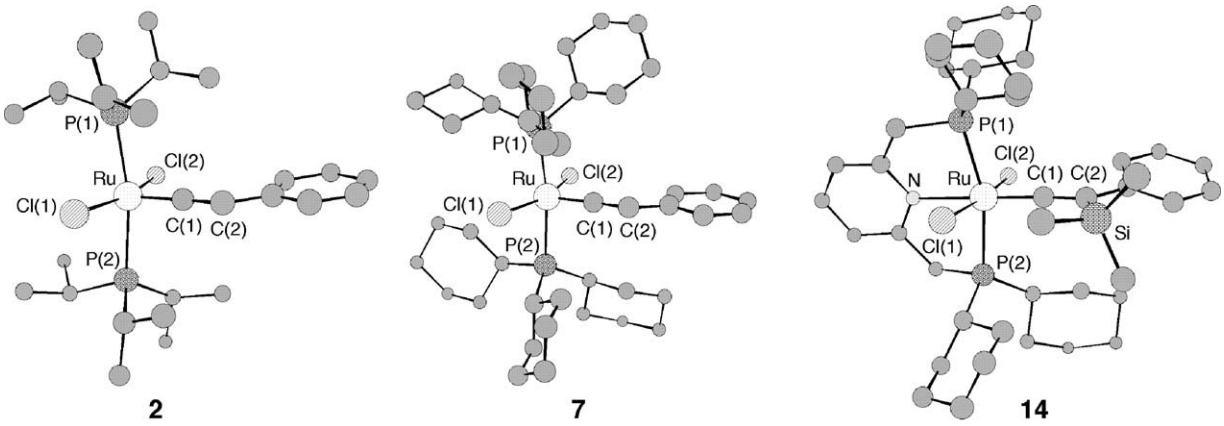
Fig. 2. Vinylideneruthenium(II) complexes with mixed ligand sets.

derivative (SIMes) leads to a rapid displacement of one of the PCy_3 with the carbene ligand to give **18** or **19**, respectively [19,20]. Similarly, the *N*,*O*-chelate **20** is obtained from **3** and 2-acetylpyridine [15]. The Schiff-base and (thiophosphoryl)imide complexes (**21** and **22**, respectively) are synthesized by the reactions of **7** with the corresponding metal salts of the ligands [20,21].

Fig. 3 compares molecular structures of three vinylideneruthenium complexes [10,13,16]. The five-coordinate complexes **2** and **7** adopt distorted square pyramidal geometry having the vinylidene ligand at the apical position, whereas the six-coordinate complex **14** has an octahedral structure with meridional coordination of the dcpmp ligand (dcpmp $= C_5H_3N(CH_2PCy_2)_2$). The Ru–C(1) distances in **2** and **7** (1.750(4) and 1.761(2) Å, respectively) are comparable to each other and to that of $RuBr_2(=C=CHBu^t)(PPh_3)_2$ with an analogous five-coordinate structure (1.768(17) Å) [22], but clearly shorter than those of the six-coordinate complexes **14** (1.845(4) Å), $[CpRu(=C=CMePh)(PPh_3)_2][I]$ (1.863(10) Å) [23], and $[RuCl(=C=CHPh)(\kappa^2(P,O)\text{-}Pr^i_2PCH_2CH_2OMe)_2][OTf]$ (1.790(3) Å) [24]. Thus, the variation in the bond distances is due to the presence or absence of a donor ligand trans to the vinylidene ligands. The vinylidene groups lie approximately on the least-squares plane composed of Ru, Cl(1), Cl(2), and C(1) atoms. A similar structural feature has been observed for the alkylidene complex $[RuCl_2(=CHC_6H_4Cl\text{-}p)(PCy_3)_2]$ [25].

Vinylidene complexes are essentially in equilibrium with the parent π-alkyne complexes (Scheme 1). Accordingly, kinetic and thermodynamic features of this interconversion must significantly affect catalytic reactions involving vinylidene intermediates. In this respect, we have examined effects of the R groups on the formation of $[RuCl_2(=C=CHR)(dcpmp)]$ and $[RuCl_2(=C=CHR)(PPr^i_3)_2]$ by kinetic experiments [16,26].

The acetonitrile complex $[RuCl_2(NCMe)(dcpmp)]$ (**23**) cleanly reacts with a variety of terminal alkynes at 50 °C to give the corresponding vinylidene complexes in quantitative yields. The kinetic data suggested the mechanism and kinetic expression given in Scheme 4. Vinylidene complexes are formed by the sequence of three elementary processes: i.e., dissociation of MeCN, coordination of alkyne, and tautomerization of alkyne ligand to vinylidene ligand. For the reaction of **23** with PhC≡CH, the k_1 and k_{-1}/k_2 values were estimated to be $2.9(1) \times 10^{-3}$ s^{-1} and 20(2), respectively. Furthermore, a moderate kinetic isotope effect ($k_H/k_D = 1.69(5)$) was observed for the reaction with PhC≡CD. These results indicate a significant contribution

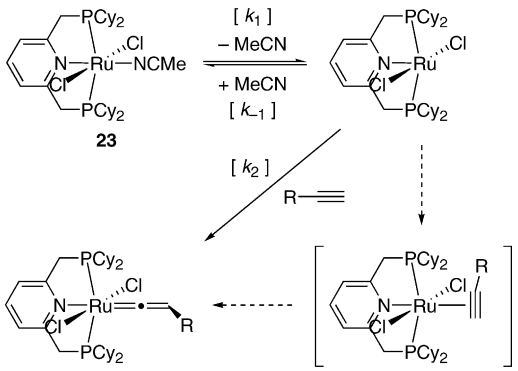


2		7		14	
Ru–C(1)	= 1.750(4) Å	Ru–C(1)	= 1.761(2) Å	Ru–C(1)	= 1.845(4) Å
Ru–Cl(1)	= 2.338(1) Å	Ru–Cl(1)	= 2.3668(7) Å	Ru–Cl(1)	= 2.4152(9) Å
Ru–Cl(2)	= 2.3541(9) Å	Ru–Cl(2)	= 2.3623(7) Å	Ru–Cl(2)	= 2.4023(9) Å
Ru–P(1)	= 2.421(1) Å	Ru–P(1)	= 2.4241(6) Å	Ru–P(1)	= 2.3595(9) Å
Ru–P(2)	= 2.424(1) Å	Ru–P(2)	= 2.4080(6) Å	Ru–P(2)	= 2.3635(9) Å
C(1)–C(2)	= 1.329(5) Å	C(1)–C(2)	= 1.334(3) Å	C(1)–C(2)	= 1.301(5) Å
Ru–C(1)–C(2)	= 177.1(3)°	Ru–C(1)–C(2)	= 178.5(2)°	Ru–C(1)–C(2)	= 177.2(3)°
Cl(1)–Ru–Cl(2)	= 158.63(4)°	Cl(1)–Ru–Cl(2)	= 156.93(2)°	Cl(1)–Ru–Cl(2)	= 167.22(3)°
P(1)–Ru–P(2)	= 169.17(3)°	P(1)–Ru–P(2)	= 170.94(2)°	P(1)–Ru–P(2)	= 162.10(3)°

Fig. 3. Chem3D views of the X-ray structures of **2** ($R = 0.033$), **7** ($R = 0.033$), and **14** ($R = 0.054$).

of the alkyne–vinylidene tautomerization toward overall reaction rates, while the dissociation of MeCN from **23** constitutes the slowest step.

Table 1 lists the k_{obsd} values for the reactions of **23** with various terminal alkynes. More electron-rich and less sterically demanding alkynes tend to provide higher reaction rates. A similar tendency is observed for the reactions of $[RuCl_2(NCMe)_2(PPr^i_3)_2]$ (**24**) with terminal alkynes to give $[RuCl_2(=C=CHR)(PPr^i_3)_2]$ [26]. It has been also confirmed that thermodynamic stability of the related β-silylvinylidene complex $[RhCl\{=C=C(SiMe_3)R\}\text{-}(PPr^i_3)_2]$ in the equilibrium with the corresponding π-alkyne complex $[RhCl(RC{\equiv}CSiMe_3)\text{–}(PPr^i_3)_2]$ increases as the electron-donating ability of the R group increases [27].



$$\frac{1}{k_{obsd}} = \frac{k_{-1}[MeCN]}{k_1 k_2[RC{\equiv}CH]} + \frac{1}{k_1}$$

Scheme 4. Proposed mechanism for the formation of dcpmp-coordinated vinylideneruthenium complexes from **23** and terminal alkynes.

Table 1
Pseudo-first-order rate constants for the reactions of $[RuCl_2(NCMe)(dcpmp)]$ (**23**) and $[RuCl_2(NCMe)_2(PPPPr^i_3)_2]$ (**24**) with various terminal alkynes

Alkyne	$10^4 k_{obsd}$ (s^{-1})	
	For **23**[a]	For **24**[b]
p-$MeO_2CC_6H_4C{\equiv}CH$	Very slow	7.56 (5)
p-$BrC_6H_4C{\equiv}CH$	2.89 (4)	n.d.[c]
$PhC{\equiv}CH$	4.71 (6)	8.14 (3)
p-$MeC_6H_4C{\equiv}CH$	4.14 (3)	n.d.[c]
p-$MeOC_6H_4C{\equiv}CH$	6.06 (8)	13.4 (1)
t-$BuC{\equiv}CH$	3.10 (4)	1.20 (2)
$FcC{\equiv}CH$	7.4 (2)	17.8 (4)

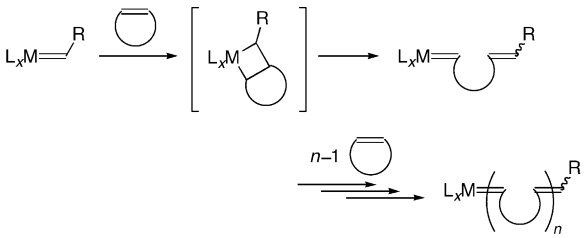
[a] In $ClCH_2CH_2Cl$ at 50 °C. Initial concentration: $[\mathbf{23}]_0 = 15$ mM, $[alkyne]_0 = 0.15$ M, $[MeCN]_0 = 40$ mM.
[b] In CH_2Cl_2 at 40 °C. Initial concentration: $[\mathbf{24}]_0 = 30$ mM, $[alkyne]_0 = 0.30$ M.
[c] Not determined.

3. Catalytic properties

3.1. Olefin-metathesis and related reactions

3.1.1. Vinylideneruthenium catalysts in olefin-metathesis: general considerations

Olefin-metathesis reactions catalyzed by transition metal complexes have brought about great advance in organic and polymer synthesis [6]. The rapid progress in recent years is due to the advent of well-defined alkylidene catalysts of molybdenum [28] and ruthenium [25]. Especially, the Grubbs' alkylideneruthenium catalysts exhibit excellent fuctional group tolerance and have remarkably extended the scope of applications of olefin-metathesis reactions in synthetic chemistry.



Scheme 5. A general reaction scheme for ROMP.

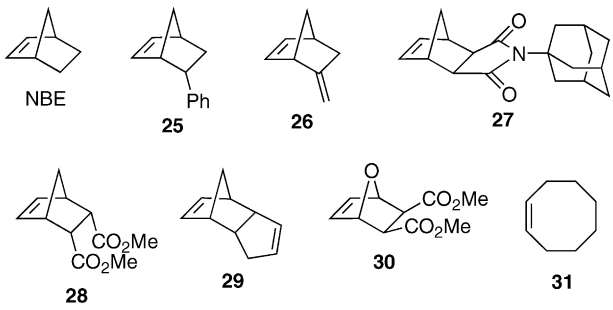
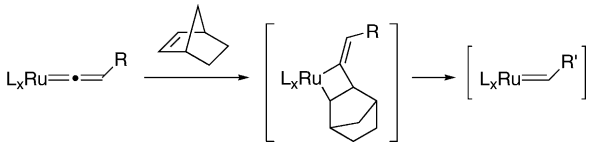


Fig. 4. Monomers for ROMP.



Scheme 6. Possible process for the initiation of polymerization.

Following the discovery of the Grubbs catalysts, a variety of ruthenium complexes bearing a metal–carbon multiple bond (i.e. vinylidene, allenylidene, and Fischer-type carbene complexes) have been examined as precursors of olefin-metathesis catalysts. Grubbs et al. first pointed out the metathesis activity of the non-substituted vinylidene complex $[RuCl_2(=C=CH_2)(PCy_3)_2]$, which was synthesized from $[RuCl_2(=CHPh)(PCy_3)_2]$ and 1,2-propadiene [25]. Afterward, others and we employed vinylideneruthenium complexes, which are more easily prepared from terminal alkynes. Complexes **3** and **8** constitute representative examples. Unlike the alkylidene analogues, they are fairly stable in solution as well as in the solid state. Thus, no notable decomposition takes place in neat toluene at 80 °C for 1 day. The solid samples can be stored in air for several months at ambient temperature.

3.1.2. Ring-opening metathesis polymerization (ROMP)

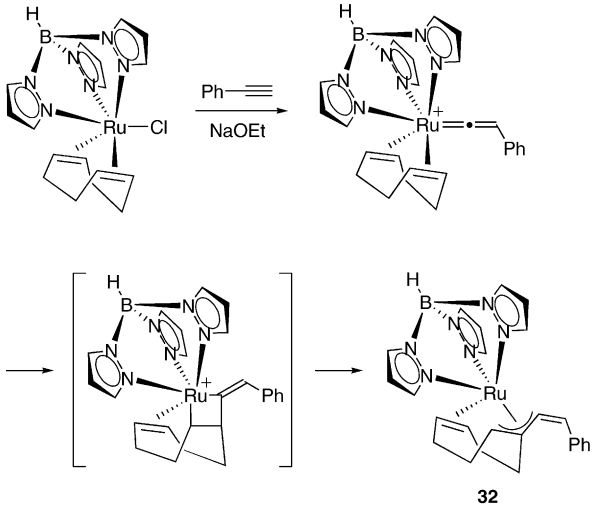
ROMP of cyclic olefins is among the central subjects of olefin-metathesis reactions because of its capability of producing the polymers that are unable to be prepared by other polymerization methods (Scheme 5) [6,29]. Table 2 summarizes representative results of vinylideneruthenium-catalyzed ROMP. All monomers listed in Fig. 4 are polymerized in high yields. The catalytic activity of $[RuCl_2(=C=CHBu^t)L_2]$ is enhanced according to the ligand (L) in the order: **1** (PPh_3) ≪ **3** (PPr^i_3) < **8** (PCy_3) < **19** (PCy_3 and SIMes). Although the vinylidene complexes are much less reactive than the Grubbs' alkylidene catalysts, the polymerization proceeds rapid enough for practical use, and the resulting polymers have the molecular weights and polydispersity comparable to those obtained from the alkylidene-catalyzed systems.

As judging from the M_n values in Table 2, the polymers synthesized with the vinylidene precursors have significantly higher molecular weights than those expected from the monomer to catalyst precursor ratios. This fact indicates low efficiency of the vinylidene complexes as the initiators (i.e., the slow initiation compared with the propagation). Indeed, an approximately 95% of **3** was recovered from the reaction solution of ROMP of norbornene after the polymerization [30]. The complex thus obtained exhibited the catalytic activity almost identical with pure **3**, giving

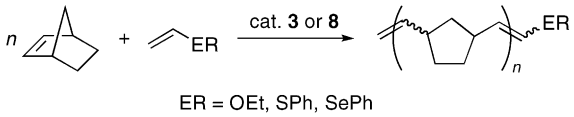
Table 2
ROMP of cyclic olefins using vinylideneruthenium complexes as catalyst precursors

Entry	Monomer (eq.)	Catalyst precursor	Temperature (°C)	Time	Yield (%)	M_n[a]/10^4	M_w/M_n[a]	Refs.
1	NBE (100)	**1**	40	24 h	83	10.6	2.31	[30]
2	NBE (100)	**3**	r.t.	10 min	98	59.9	1.44	[30]
3	NBE (100)	**8**	r.t.	10 min	> 99	48.3	2.03	[30]
4	NBE (2000)	**19**	r.t.	5 min	100	98	2.3	[20]
5	NBE (800)	**21**	80	30 min	100	63.4	1.70	[20]
6	NBE (795)	$[Ru(=C=CHPh)(NN'N)(PPh_3)][BF_4]_2$[b]	80	1 h	100	96.8	1.16	[31]
7	NBE (100)	$[TpRuCl(=C=CHPh)(PPh_3)]$	80	24 h	76	3.0	5.01	[32]
8	**25** (2000)	**19**	60	2 h	87	214	1.67	[20]
9	**26** (2000)	**19**	60	30 min	100	209	1.90	[20]
10	**27** (100)	**8**	50	3 h	85	59	1.2	[33]
11	**28** (100)	**3**	60	24 h	87	18.0	2.81	[30]
12	**29** (2000)	**19**	60	2 h	97	–[c]	–[c]	[20]
13	**30** (100)	**3**	r.t.	24 h	97	66.5	2.14	[30]
14	**31** (5000)	**19**	60	30 min	90	474	1.54	[20]

[a] Determined by GPC.
[b] NN'N = κ^3-$C_5H_3N(CH_2NMe_2)_2$.
[c] Insoluble.



Scheme 7. Coupling of PhC≡CH with 1,5-cyclooctadiene through metallacyclobutane formation.



Scheme 8. ROMP of norbornene in the presence of CTAs.

poly(norbornene) (PNBE) with M_n of 68.6 × 10^4 (M_w/M_n = 1.81) in 94% yield under the same reaction conditions as entry 2 in Table 2.

There are several possibilities for the initiation process. Careful observation of the ^{1}H NMR spectrum of PNBE isolated from the reaction system using [$RuCl_2$(=C=CHFc)(PPh_3)$_2$] (Fc: ferrocenyl) as a catalyst precursor indicated the presence of Fc group at the terminus of polymer chain [30]. Accordingly, the mechanism involving [2+2] cycloaddition between the Ru=C bond and norbornene was proposed (Scheme 6). Kirchner and co-workers have documented this type of process in a stoichiometric reaction using a Tp-coordinated ruthenium complex (Scheme 7) [34].

Table 3
ROMP of norbornene (NBE) in the presence of CTAs[a]

Entry	CTA ([NBE]$_0$/[CTA]$_0$)	Time (h)	Yield (%)	M_n[b]/10^4	M_w/M_n[b]
1	H_2C=CHOEt (100/2)	24	90	6.32	2.38
2	H_2C=CHOEt (100/4)	24	87	2.51	2.94
3	H_2C=CHOEt (100/6)	24	93	1.88	2.96
4	H_2C=CHOEt (100/10)	24	80	1.38	2.55
5	H_2C=CHOEt (100/20)	48	88	0.87	2.19
6	H_2C=CHOEt (100/40)	72	77	0.61	1.99
7	H_2C=CHOAc (100/10)	48	61	0.42	1.47
8	H_2C=CHSPh (100/10)	2	84	0.36	1.30
9	H_2C=CHSePh (100/10)	2	88	0.30	1.90

[a] All reactions were run at room temperature in CH_2Cl_2 using 2 mol% of **3** as the catalyst precursor.
[b] Determined by GPC.

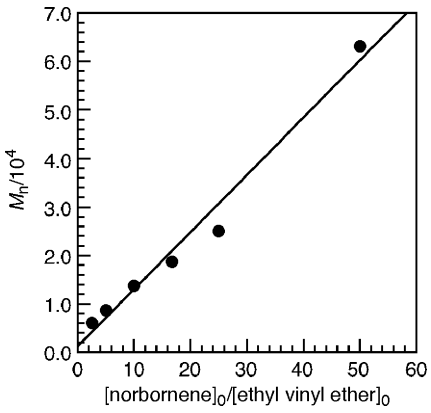
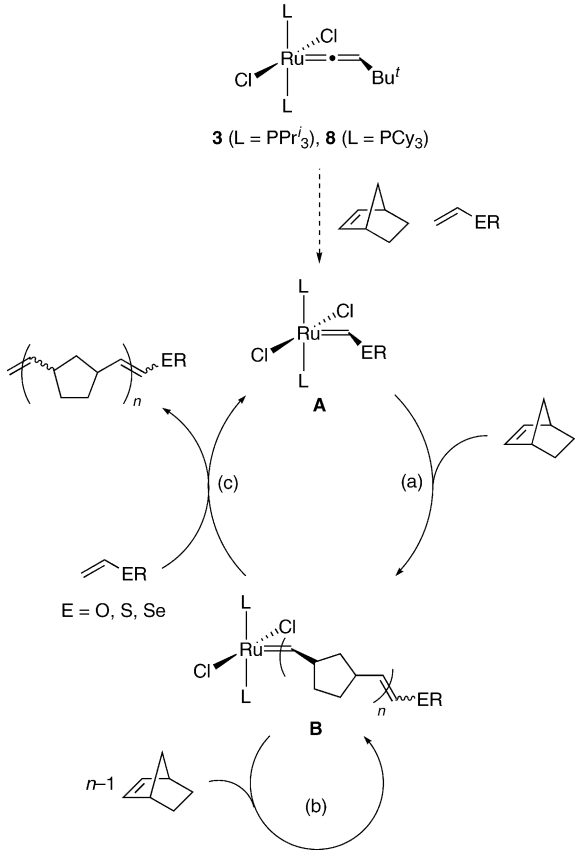


Fig. 5. Plot of the M_n values of poly(norbornene) vs. the ratio of norbornene to ethyl vinyl ether (entries 1–6 in Table 3).

3.1.3. Ring-opening metathesis polymerization using chain-transfer agents (ROMP/CT)

Vinylideneruthenium complexes **3** and **8** serve as good catalyst precursors for ROMP of norbornene in the presence of vinyl chalcogenides as chain-transfer agents (CTAs) (Scheme 8) [30,35]. As seen from Table 3, the addition of the vinyl compounds reduces the molecular weight of PNBE to a great extent (entry 2 in Table 2). The molecular weight may be controlled in a wide range by changing the ratio of CTAs to norbornene (entries 1–6). Thus, plot



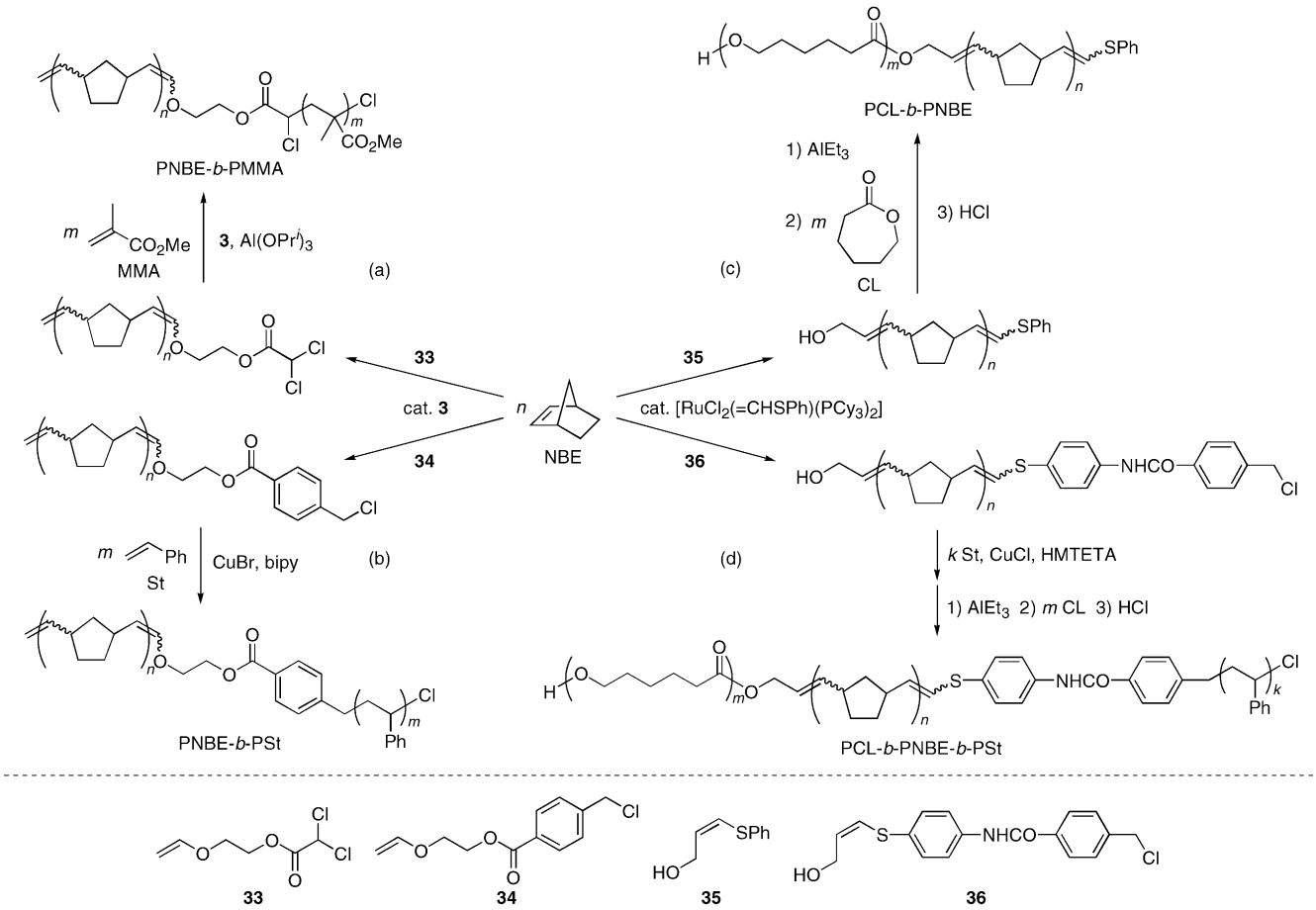
Scheme 9. Mechanism for ROMP/CT reaction.

of the M_n value against the ratio of monomer to ethyl vinyl ether exhibits a linear correlation (Fig. 5). End-group analysis of the polymer by ^{1}H NMR spectroscopy clearly indicated the presence of vinyl and –CH=CHOEt groups at each terminus. Phenyl vinyl sulfide and selenide are particularly reactive and the polymerization is completed within 2 h (entries 8 and 9). The reaction of NBE with phenyl vinyl selenide causes 1:1 coupling of the substrates, and the ring-opening/cross-metathesis (ROCM) product ($n = 1$; ER = SePh) was obtained in 83% yield [36].

Scheme 9 shows the mechanism of ROMP/CT reaction, which involves a Fischer-type ruthenium carbene complex **A**, generated from vinylidene precursors. Generally, Fischer-type carbene complexes are poorly reactive toward olefin-metathesis. However, complex **A** based on the Grubbs catalyst was sufficiently reactive toward polymerization of norbornene at room temperature, as confirmed with the isolated complexes [$RuCl_2$(= CHEPh)(PCy_3)$_2$] (E = O, S, Se) [36,37]. Thus, **A** reacts with norbornene to form an alkylidene intermediate (**B**, $n = 1$) (step a), which successively undergoes olefin-metathesis with additional norbornenes to give the propagation species **B** (step b). This complex eventually undergoes cross-metathesis with vinyl chalcogenides to give the PNBE having the vinyl and –CH=CHER groups at each terminus, and regenerates **A** (step c). The cross-metathesis proceeds with perfect regioselectivity, reflecting the much higher thermodynamic stability of the Fischer-type carbene complex **A** than the alkylidene alternative [$RuCl_2$(=CH_2)L_2] [38].

The ROMP/CT reaction outlined in Scheme 9 selectively forms the polymer bearing different substituents at α- and ω-ends, respectively. Such heterotelechelic polymers are of great importance from the viewpoint of tailored polymer synthesis and useful for constructing complex macromolecular architectures such as block copolymers and polymeric networks. We have demonstrated that various functionalities are selectively incorporated into the chain-ends of PNBEs by the choice of CTAs. The resulting polymers serve as macroinitiators for the synthesis of AB- and ABC-type block copolymers (Scheme 10) [39,40].

Thus, the ROMP of norbornene in the presence of vinyl ethers (**33**, **34**) afforded PNBEs having halomethyl groups, which initiated metal-mediated atom-transfer radical polymerization (ATRP) of methyl methacrylate (MMA) and styrene (St) to give the AB-type block copolymeres PNBE-*b*-PMMA and PNBE-*b*-PSt, respectively (paths a and b). NMR, VPO, and GPC analyses revealed selective formation of the AB-type block copolymers. The use of



Scheme 10. Synthesis of block copolymers via ROMP/CT reactions.

(*Z*)-1-phenylthio-1-propen-3-ol (**35**) as a CTA enabled selective functionalization of the ω-end of PNBE for hydroxy group (path c). The ω-hydroxy-terminated PNBE thus prepared was subjected to anionic ring-opening polymerization (AROP) of 1-caprolactone (CL) to give the desired diblock copolymer PCL-*b*-PNBE. Integration of mechanistically different, three polymerization methods was also successful using **36** as a CTA (path d). Thus, ROMP/CT of norbornene with **36**, followed by ATRP of styrene and AROP of 1-caprolactone, formed the ABC-type triblock copolymer PCL-*b*-PNBE-*b*-PSt in high yield.

3.1.4. Ring-closing metathesis (RCM)

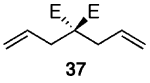
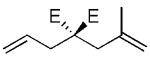
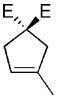
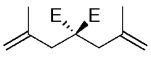
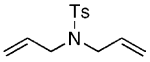
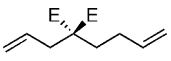
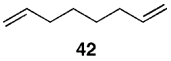
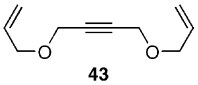
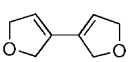
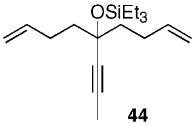
Similarly to the other ruthenium-based ROMP catalysts, the vinylideneruthenium complexes exhibit the catalytic activity toward ring-closing metathesis reactions (RCM) [20,30]. Table 4 summarizes the results using **9**, **19**, and **21** as the catalyst precursors. A variety of dienes (**37**, **40**–**42**) and dienynes (**43**, **44**) are cleanly converted to the corresponding cyclic alkenes in high yields without any detectable side reaction products. The RCM of the more sterically hindered substrates (**38**, **39**) proceeds with the SIMes-coordinated complex **19** albeit in moderate yields.

3.1.5. Catalytic reactions via [2+2] cycloaddition of vinylideneruthenium complexes

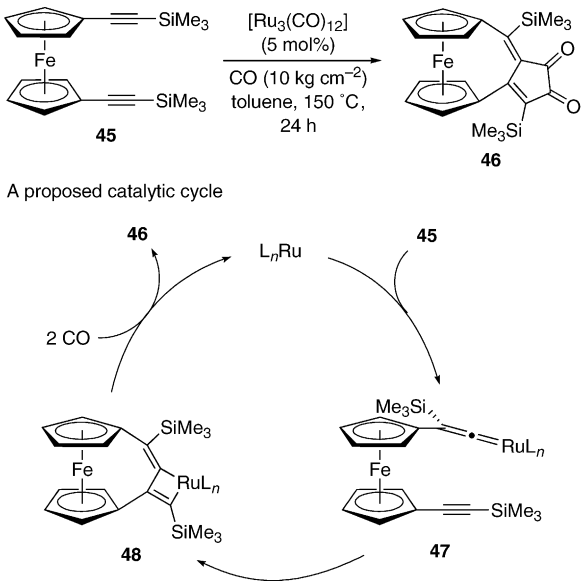
Several examples have been reported for catalytic alkyne–alkyne and alkyne–alkene coupling reactions, probably through a [2+2] cycloaddition of vinylideneruthenium intermediates. Treatment of 1,1′-bis[(trimethylsilyl)ethynyl] ferrocene **45** with a catalytic amount (5 mol%) of $[Ru_3(CO)_{12}]$ under CO pressure (10 kg cm^{-2}) at 150 °C affords the cyclocarbonylation product **46** in 36% yield (Scheme 11) [41]. The structure of **46** strongly suggests the catalytic cycle involving a (β-silylvinylidene)ruthenium(0) intermediate (**47**) (Scheme 11). Intramolecular [2+2] cycloaddition between the Ru=C bond and the remaining C≡C bond in **47** leads to the formation of ruthenacyclobutene **48**. The reaction product **46** is afforded by insertion of two CO molecules into each of the Ru–C bonds of **48**, followed by reductive elimination.

Murakami et al. have developed vinylideneruthenium-catalyzed coupling reactions of terminal alkynes with simple olefins [42,43]. For example, when a pyridine solution of phenylacetylene and 1-octene (10 eq.) is heated at 100 °C in the presence of $[CpRuCl(PPh_3)_2]$ (5 mol%) and $NaPF_6$ (6 mol%), linear and branched dienes (**49a** and **49b**) are

Table 4
ROMP of α,ω-dienes and dienynes using vinylideneruthenium complexes as catalyst precursors

Substrate[a]	Product[a]	Catalyst precursor[b]	Temperature (°C)	Time (h)	Yield[c] (%)	Refs.
 **37**		**9**	60	24	96	[30]
		19	60	2	100	[20]
		21	80	24	96	[20]
 **38**		**19**	60	2	71	[20]
 **39**		**19**	60	10	34	[20]
 **40**		**9**	60	24	90	[30]
 **41**		**9**	60	16	94	[30]
 **42**		**19**	60	1	100	[20]
 **43**		**9**	60	3	99	[30]
 **44**		**9**	60	44	91	[30]

[a] E = CO_2Et.
[b] The amount of catalyst precursors: 2 mol% (**9**), 5 mol% (**19**, **21**).
[c] Determined by ^1H NMR analysis.



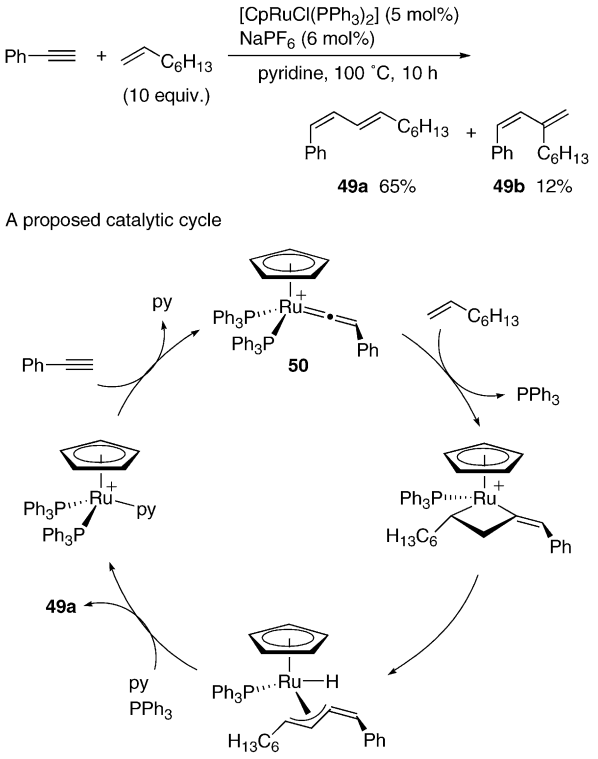
Scheme 11. Ruthenium-catalyzed cyclocarbonylation of 1,1′-bis[(trimethylsilyl)ethynyl]ferrocene **45**.

formed in 65% and 12% yields, respectively. The use of vinylidene complex [CpRu(=C=CHPh)(PPh_3)$_2$][PF_6] (**50**) as a catalyst results in the same reaction outcomes. Consequently, the catalytic cycle involving **50** as an intermediate for the predominant formation of **49a** has been postulated (Scheme 12). Based on this working hypothesis, Murakami and Hori have recently discovered the ruthenium-catalyzed direct alkenylation reaction of pyridines with silylacetylenes [44].

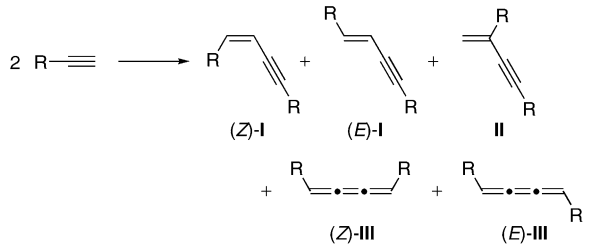
3.2. Alkyne dimerization

Metal-catalyzed dimerization of terminal alkynes is a convenient method of constructing highly unsaturated four carbon skeletons, which are useful building blocks in organic synthesis and active components of conducting and light-emitting polymers [45–47]. This reaction possibly forms five types of isomers, (*Z*)- and (*E*)-1,4-disubstituted-1-buten-3-ynes (**I**), 2,4-disubstituted-1-buten-3-yne (**II**), and (*Z*)- and (*E*)-1,2,3-butatrienes (**III**) (Scheme 13). Among them, the formation of (*Z*)-**I** and (*Z*)-**III** has been considered to involve vinylidene intermediates, as illustrated in Scheme 14 [48–50]. Alkynyl complex **C** is transformed into alkynyl(vinylidene) intermediate **E** via π-coordination of terminal alkyne followed by alkyne-to-vinylidene rearrangement. Intramolecular migration of the alkynyl ligand to the α-vinylidene carbon in **C** forms η^3-butenynyl complex **F**, which is in equilibrium with the η^1 form **G** and the butatrienyl complex **H**, leading to (*Z*)-**I** and (*Z*)-**III**, respectively. The preference for **G** or **H** is strongly dependent on the bulkiness of terminal alkynes employed and ancillary ligands bonded to the metal center.

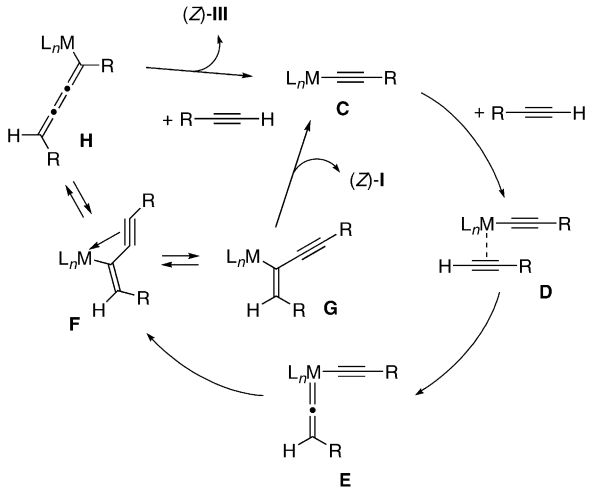
Bianchini et al. have succeeded for the first time in identifying an η^3-butenynyl complex (i.e. **F** in Scheme 14) as the



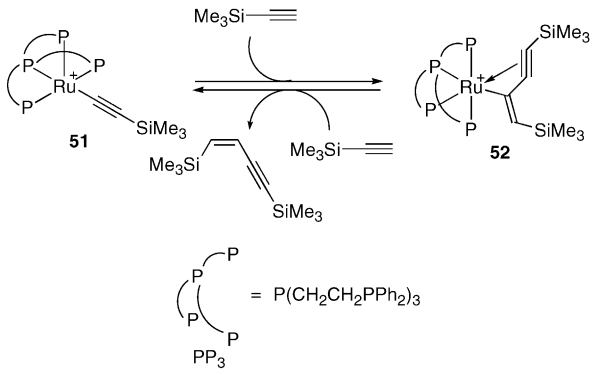
Scheme 12. Ruthenium-catalyzed coupling reaction of phenylacetylene with 1-octene.



Scheme 13. Dimerization of terminal alkynes.



Scheme 14. Catalytic cycle for the formation of (*Z*)-**I** and (*Z*)-**III**.

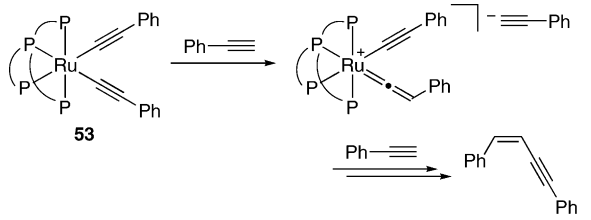


Scheme 15. Dimerization of $Me_3SiC{\equiv}CH$ catalyzed by [$(PP_3)RuC{\equiv}CSiMe_3$][BPh_4] (**51**).

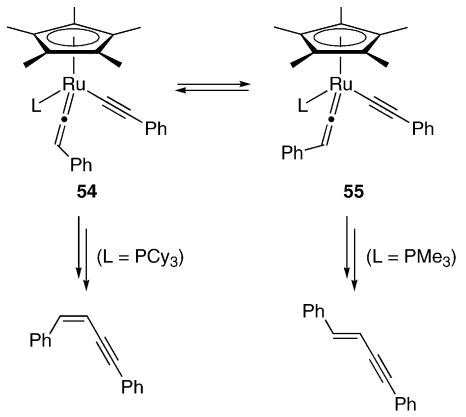
catalytic intermediate for (*Z*)-selective alkyne-dimerization [48]. Thus, the dimerization of $Me_3SiC{\equiv}CH$ catalyzed by (silylethynyl)ruthenium complex **51** having a tripodal phosphine ligand (PP_3) proceeds in up to 95% (*Z*)-selectivity through the η^3-butenynyl intermediate **52**, which was isolated as crystals and characterized by X-ray diffraction analysis (Scheme 15). The use of **52** instead of **51** as the catalyst reproduced the catalytic rate and selectivity.

Later the same research group reported stereoselective dimerization of $PhC{\equiv}CH$ to (*Z*)-butenyne catalyzed by PP_3-coordinated ruthenium dihydride [$(PP_3)RuH_2$] [49]. Detailed mechanistic studies revealed that bis(alkynyl) ruthenium complex [$(PP_3)Ru(C{\equiv}CPh)_2$] (**53**) serves as a catalytic interemediate (Scheme 16). Interestingly, this complex is converted to the alkynyl(vinylidene) intermediate via protonation of the alkynyl ligand by external $PhC{\equiv}CH$.

A remarkable ligand effect on the stereoselectivity has been found for dimerization of $PhC{\equiv}CH$ using Cp*RuL-type catalysts (Cp*: pentamethylcyclopentadienyl) [51]. Thus, [$Cp^*RuH_3(PCy_3)$] results in (*Z*)-selective formation of $PhCH{=}CHC{\equiv}CPh$ (*Z*:*E* = 90:10), whereas [$Cp^*RuH_3(PMe_3)$] having less-sterically demanding PMe_3 selectively forms (*E*)-isomer. These observations have been rationalized by assuming preferential formation of the two rotamers (**54** and **55**), dependent on the steric conditions between the Ph group and phosphine ligands (Scheme 17). The related complexes [Cp*RuCl(ICy)] (ICy = 1,3-dicyclohexylimidazolin-2-ylidene) [52], [TpRuCl$(PPh_3)_2$] (Tp = hydrotris(1-pyrazolyl)borate) [53], and [TpRuCl(=C=CHPh)(PPh_3)] [53] cause (*E*)-selective dimerization. We recently found that **2** in combination



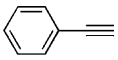
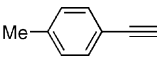
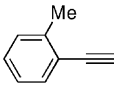
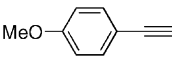
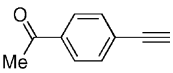
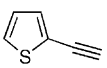
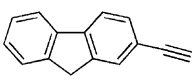
Scheme 16. Dimerization process of $PhC{\equiv}CH$ catalyzed by [$(PP_3)RuH_2$].



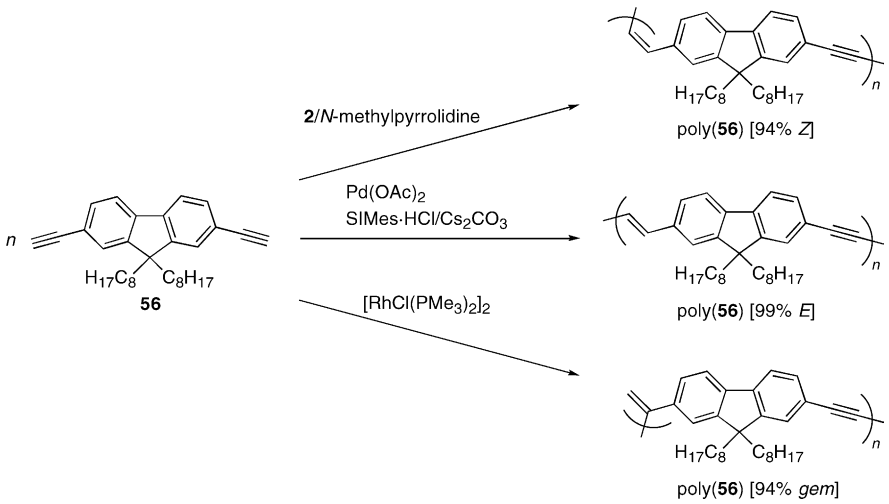
Scheme 17. Rotamers of alkynyl(vinylidene)ruthenium intermediate leading to (*Z*)- and (*E*)-butenynes.

with *N*-methylpyrrolidine catalyzes highly (Z)-selective dimerization of arylacetylenes [54]. As listed in Table 5, various arylacetylenes are readily dimerized at room temperature to the corresponding (*Z*)-1,4-diaryl-1-buten-3-ynes in 91–100% selectivities. The catalytic activity thus observed was much higher than that previously reported for (*Z*)-selective catalysts. The addition of *N*-methylpyrrolidine was of particular importance to develop the highly active catalysis (vide infra). It was also noted that the catalytic activity is rather sensitive to the sorts of phosphine ligands. Complex **2** having bulky and basic triisopropylphosphines exhibited the best performance of vinylideneruthenium complexes examined (**1**–**3**, **7**).

Table 5
Homo-dimerization of arylalkynes and hetero-dimerization between arylalkynes and (trimethylsilyl)acetylene catalyzed by **3**/*N*-methylpyrrolidine[a]

Arylalkyne	Homo-dimerization		Hetero-dimerization	
	GLC yield (%)	Product ratio (*Z*)-**I**:(*E*)-**I**:**II**	GLC yield (%)	Product ratio (*Z*)-**IV**:(*E*)-**IV**:**V**
	>99	96:1:3	83	90:3:7
	>99	92:0:8	86	91:0:9
	>99	93:0:7	72	93:3:4
	96	91:1:8	70	92:3:5
	97	100:0:0	70	93:1:6
	82	97:0:3	81	93:7:0
	99	90:0:10	92	91:0:9

[a] All reactions were run in CH_2Cl_2 at room temperature using 1–5 mol% of **2** and 20 mol% of *N*-methylpyrrolidine.



Scheme 18. Polyaddition of 2,7-diethynyl-9,9-dioctylfluorene **56** using regio- and stereoselective alkyne-dimerization catalysts.

The (*Z*)-selective catalyst derived from **2** and *N*-methylpyrrolidine has been applied to polyaddition of 2,7-diethynyl-9,9-dioctylfluorene (**56**) with the aim of synthesizing tailored π-conjugated polymers (Scheme 18) [55]. Reflecting the nature of the catalyst in the prototype dimerization reactions, the resulting poly(**56**) has (*Z*)-butenyne units in the main chain in 94% geometrical purity. Similarly, (*E*)- and *gem*-rich poly(**56**)s were successfully prepared by using appropriate alkyne-dimerization catalysts, $[Pd(OAc)_2]$/SIMes·HCl/Cs_2CO_3 (SIMes·HCl = 1,3-dimesitylimidazolinium chloride) [56] and $[RhCl(PMe_3)_2]_2$ [57], respectively. The resulting polymers showed markedly different light-absorption and emission properties according to the main-chain structures (Fig. 6).

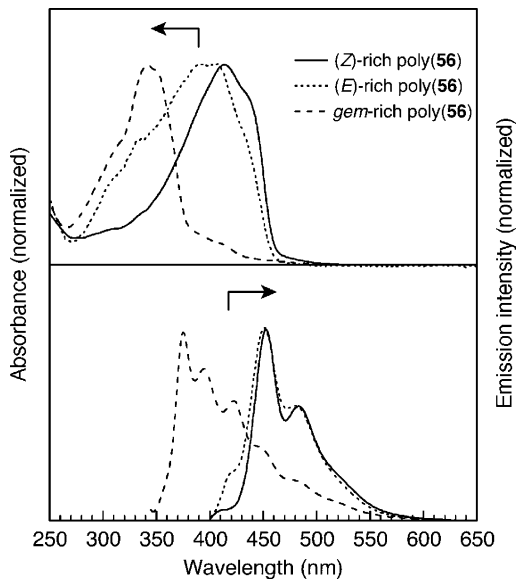
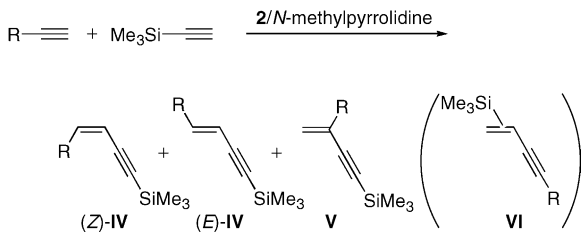


Fig. 6. UV–vis absorption of emission spectra of (*Z*)-, (*E*)-, and *gem*-rich poly(**56**)s.

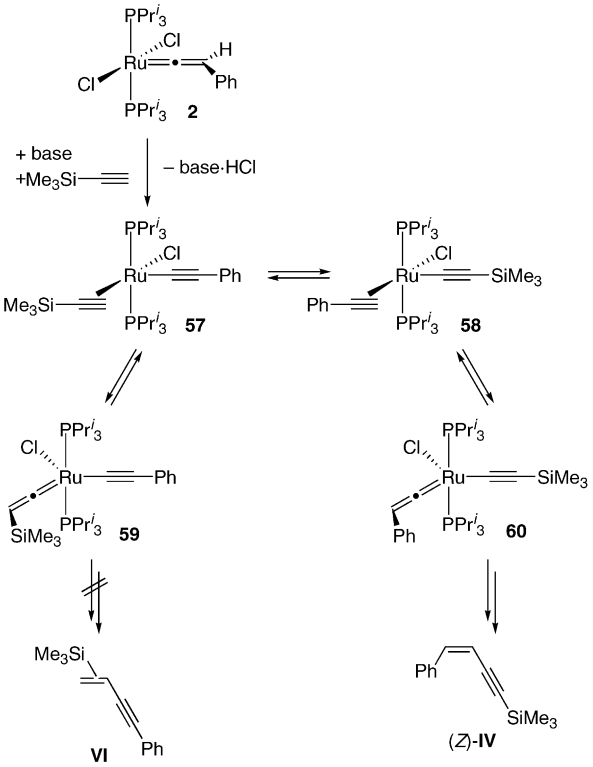
In the reactions of arylacetylenes with $Me_3SiC{\equiv}CH$ in the presence of **2** and *N*-methylpyrrolidine, hetero-dimerization proceeded in regio- and stereoselective manners to afford (*Z*)-butenynes (**IV**) bearing the Me_3Si group at the *sp*-hybridized carbon atom (Scheme 19, Table 5) [54]. Butenynes (**VI**) having the opposite substitution pattern was almost negligible. Base-promoted desilylation of (*Z*)-**IV** proceeded without loss of the stereochemical purity. Thus, the overall process provided a simple and convenient approach to terminal alkenylacetylenes ($RCH{=}CHC{\equiv}CH$) with (*Z*)-configuration.

Scheme 20 shows our proposed mechanism for hetero-dimerization of $PhC{\equiv}CH$ and $Me_3SiC{\equiv}CH$. The catalytically active alkynylruthenium species is generated by the elimination of β-hydrogen of the vinylidene ligand and the chlorido ligand in **2** as HCl. Basic and compact *N*-methylpyrrolidine promotes this process very effectively. The resulting (phenylethynyl)ruthenium intermediate **57** undergoes exchange of the alkynyl ligand with the coordinated $Me_3SiC{\equiv}CH$ to give (silylethynyl)ruthenium **58**, which leads to (*Z*)-**IV** (R = Ph) by the mechanism similarly to Scheme 14.

While 1,2,3-butatriene derivatives (**III**) are thermodynamically much less stable than butenynes, highly selective dimerization of *t*-$BuC{\equiv}CH$ to (*Z*)-*t*-$BuCH{=}C{=}CH$(*t*-Bu) has been developed by Wakatsuki et al. using $[RuH_2(CO)$

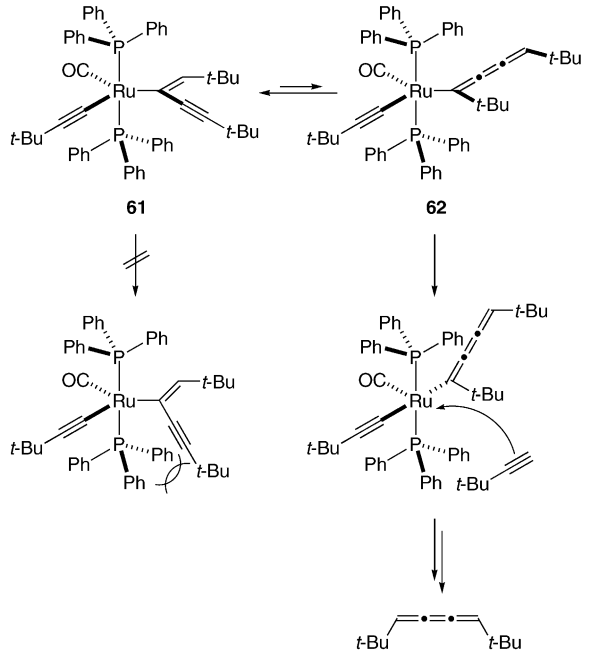


Scheme 19. Hetero-dimerization between arylacetylenes and (trimethylsilyl)acetylene.



Scheme 20. Proposed mechanism for hetero-dimerization between PhC≡CH and Me_3SiC≡CH.

$(PPh_3)_3$] as a catalyst [50]. They successfully carried out a series of model reactions and elucidated the overall reaction process. The essential features are illustrated in Scheme 21. The key to the selective formation of the (*Z*)-1,2,3-butatriene



Scheme 21. Mechanism of 1,2,3-butatriene formation from *t*-BuC≡CH catalyzed by $[RuH_2(CO)(PPh_3)_3]$.

is difference in the reactivities between the butenynyl complex **61** and the butatrienyl complex **62** toward *t*-BuC≡CH. When the butenynyl ligand in **61** is oriented perpendicular to the basal plane of complex so as to open the coordination site for incoming *t*-BuC≡CH, this complex undergoes severe steric repulsion between the PPh_3 ligand and the *t*-BuC≡C- moiety of the butenynyl group. In contrast, the *t*-Bu group in **62** can be bent away from the phosphine to avoid the steric hindrance. Therefore, the butatrienyl complex **62** can be combined with *t*-BuC≡CH, and the subsequent C–H bond formation between the butatriene ligand and the acetylenic proton of *t*-BuC≡CH forms the butatriene.

4. Conclusion

We have shown that coordinatively unsaturated, 16-electron vinylidene ruthenium complexes of the type $[RuCl_2(=C=CHR)L_2]$ ($L = PPr^i_3$, PCy_3, etc.) serve as highly efficient catalyst precursors for ring-opening metathesis polymerization of cyclic olefins, ring-closing metathesis of α,ω-dienes, and homo- and hetero-dimerization of terminal alkynes. The complexes are easily prepared in high yields from $[RuCl_2(p\text{-cymene})]_2$, L, and RC≡CH, which are all commercially available. It has been suggested that electron-donating substituents (R) at the β-carbon facilitate the alkyne–vinylidene tautomerization from both kinetic and thermodynamic points of view.

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