The New Possibility of Vinylideneruthenium(II) Complexes Derived from Terminal Alkynes: Ring-Opening Metathesis Polymerization of Norbornene Derivatives

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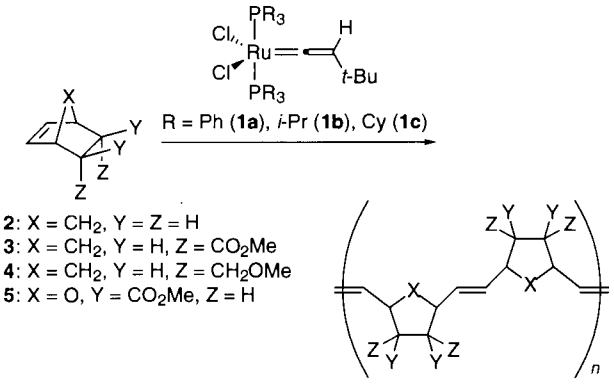
(Received October 2, 1997; CL-970762)

Vinylideneruthenium(II) complexes $RuCl_2[=C=CH(t\text{-}Bu)](PR_3)_2$ (R = Ph, *i*-Pr, Cy) serve as good catalyst precursors for the ring-opening metathesis polymerization of norbornene derivatives.

Transition metal vinylidene complexes have attracted significant recent interest, mainly due to their facile synthesis from alkynes and the novel chemical properties.[1] The reactions most frequently observed are nucleophilic attack to the α-carbon or electrophilic attack to the β-carbon of vinylidene ligand.[1,2] Cycloaddition of unsaturated hydrocarbons to the $C^{\alpha}=C^{\beta}$ bond has also been observed for some instances.[3] On the other hand, despite the alkylidene-like structures of vinylidene ligands, their applications to metallacycle formation and olefin metathesis are extremely limited.[4,5]

We report herein that vinylideneruthenium complexes of the type $RuCl_2[=C=CH(t\text{-}Bu)](PR_3)_2$ (R = Ph (**1a**), *i*-Pr (**1b**), *t*-Bu (**1c**)) serve as good catalyst precursors for the ring-opening metathesis polymerization (ROMP)[5-7] of norbornene derivatives (Scheme 1). The catalytic activity of an analogous complex $RuCl_2(=C=CH_2)(PCy_3)_2$ toward ROMP has been briefly described without concrete examples by Grubbs and his co-workers.[5] However, this non-substituted vinylidene complex was synthesized by a rather inconvenient method starting from an alkylideneruthenium complex and 1,2-propadiene. We found that complexes **1a**–**1c**, which are more readily accessible via tautomerization of *t*-BuC≡CH on ruthenium, can be used as the catalyst precursors for ROMP.



Scheme 1.

$RuCl_2[=C=CH(t\text{-}Bu)](PPh_3)_2$ (**1a**) was synthesized in a quantitative yield by the reaction of $RuCl_2(PPh_3)_3$ with *t*-BuC≡CH according to the literature.[8] Treatment of **1a** with P(*i*-Pr)$_3$ and PCy_3 in Et_2O afforded $RuCl_2[=C=CH(t\text{-}Bu)](PR'_3)_2$ (R' = *i*-Pr (**1b**), Cy (**1c**)), respectively. The ligand substitution took place instantly at room temperature with 2 equivalents of phosphines for both cases and the complexes were isolated as deep purple crystals by recrystallization from cold Et_2O. The presence of vinylidene ligand was confirmed by the appearance of characteristic signals in the ^1H (δ 3.14 (**1b**), 3.16 (**1c**)) and $^{13}C\{^1H\}$ NMR spectra (δ 335.2 and 115.8 (**1b**), 337.1 and 115.5 (**1c**)).[9] The signals of vinylidene α-carbons at δ 335.2 (**1b**) and 337.1 (**1c**) were observed as a triplet with a relatively small $^2J_{PC}$ coupling (15 Hz), respectively, indicating the structures bearing two phosphine ligands in mutually trans positions.

Table 1 summarizes typical results for the polymerization. Upon heating a CH_2Cl_2 solution of norbornene (**2**) (1.0 M) and **1a** (1 mol%, 10 mM) at 40 °C, the initially homogeneous solution gradually became viscous. After 24 h, the solution was poured into vigorously stirred MeOH containing 0.1% of 2,6-di-*tert*-butyl-4-methylphenol to give a white precipitate of poly(norbornene), which was subsequently purified by column chromatography (SiO_2, CH_2Cl_2) (83% yield) (entry 1). GPC analysis revealed the molecular weight (M_n) of 10.6×10^4 (M_w/M_n = 2.31). IR and NMR analyses indicated the trans geometry around the C=C bond of main chain in over 90% regularity.[10]

Dichloromethane was among the most suitable solvents tested (entries 1–3). The P(*i*-Pr)$_3$ and PCy_3 complexes (**1b** and **1c**) exhibited much higher catalytic activity than the PPh_3 complex (**1a**); both reaction systems set to gel within a few minutes at 25 °C and nearly or almost quantitative yield of the polymer was obtained (entries 4 and 5). A similar tendency regarding the effect of tertiary phosphine ligands has been reported for the alkylideneruthenium-catalyzed reactions.[6] Norbornene derivatives **3**, **4**, and **5** could be polymerized in high yields in the present systems (entries 6–8).

The vinylidene complexes exhibited the catalytic activity without isolation. Complex **1a** generated in situ from $RuCl_2(PPh_3)_3$ and *t*-BuC≡CH (10 equiv.) in CH_2Cl_2 provided poly(norbornene) in 72% yield at 40 °C for 48 h ($M_n = 5.6 \times 10^4$, M_w/M_n = 2.89). The polymerization of **2** more readily proceeded at room temperature using **1b** or **1c** as the catalyst. In these cases the catalysts were prepared in situ from **1a** and the corresponding phosphines (2 equiv.). The polymer was isolated in almost quantitative yields: [with **1b**] 95% yield, $M_n = 3.6 \times 10^4$, M_w/M_n = 3.72; [with **1c**] >99% yield, $M_n = 4.5 \times 10^4$, M_w/M_n = 2.86.

Table 2 compares the catalytic activities of a variety of vinylidene catalysts bearing PPh_3 ligands, which were prepared by the treatment of $RuCl_2(PPh_3)_3$ with the corresponding alkynes RC≡CH (10 equiv.) in CH_2Cl_2 at room temperature and employed to the catalytic systems without isolation.[11] It is seen that the catalytic activity is clearly dependent upon the nature of substituent R in the parent alkyne and trimethylsilyl group provides the highest reactivity (entry 1). Although exact reason for the variation is presently uncertain, the particularly high activity of the trimethylsilyl derivative may be associated with its thermodynamic stability in the equilibrium between vinylidene and alkyne complexes. The high stability of silylvinylidene complexes has been documented for rhodium

Table 1. Polymerization of norbornene derivatives **2–5** catalyzed by vinylideneruthenium complexes **1a–1c**[a]

Entry	Catalyst	Monomer	Solvent	T/°C	Yield/%	M_n[b]/10^4	M_w/M_n[b]
1	**1a**	**2**	CH_2Cl_2	40	83	10.6	2.31
2	**1a**	**2**	benzene	40	52	3.0	3.68
3	**1a**	**2**	THF	40	22	2.6	3.63
4	**1b**	**2**	CH_2Cl_2	25	97	4.7	4.14
5	**1c**	**2**	CH_2Cl_2	25	>99	45.2	2.63
6	**1b**	**3**	$ClCH_2CH_2Cl$	60	87	18.0	2.81
7	**1b**	**4**	$ClCH_2CH_2Cl$	60	95	5.5	2.59
8	**1b**	**5**	CH_2Cl_2	25	97	66.5	2.14

[a]Initial concentration: $[catalyst]_0$ = 10 mM, $[monomer]_0$ = 1.0 M. Reaction time: [entries 1–3, 6, 8] 24 h; [entries 4, 5] 2 h; [entry 7] 48 h. [b]Determined by GPC based on polystyrene standards.

Table 2. Polymerization of norbornene **2** catalyzed by $RuCl_2(=C=CHR')(PPh_3)_2$[a]

Entry	R'	Yield/%	M_n[b]/10^4	M_w/M_n[b]
1	Me_3Si	95	4.1	2.07
2	Fc	54	6.9	1.43
3	*t*-Bu	19	5.0	2.15
4	*n*-Bu	0	—	—
5	Ph	13	14.2	1.69
6	*p*-$MeCOC_6H_4$	9	5.6	2.22
7	*p*-$MeO_2CC_6H_4$	8	6.6	2.33
8	*p*-$O_2NC_6H_4$	20	1.2	3.08

[a]Polymerization conditions: $[catalyst]_0$ = 10 mM, $[2]_0$ = 1.0 M, at 40 °C, for 24 h. See text for the preparation of catalysts. [b]Determined by GPC based on polystyrene standards.

systems.[12]

The ^1H NMR spectrum of poly(norbornene) isolated from the reaction system using FcC≡CH (Fc = ferrocenyl, entry 2) exhibited characteristic signals for the ferrocenyl moiety at δ 4.51 and 4.34 (each triplet, J = 1.8 Hz) and at δ 4.28 (s). The molecular weight calculated from the relative peak integration of vinylic protons of the main chain and ferrocenyl protons was *ca.* 4.7 × 10^4, which was in agreement with the value determined by GPC based on polystyrene standards (M_n = 6.9 × 10^4). This result clearly indicates the presence of ferrocenyl group at the terminus of polymer chain.

In conclusion, we have found that the vinylidene-ruthenium(II) complexes derived from terminal alkynes serve as good catalyst precursors for ROMP of norbornene derivatives. Although the initiation of the present catalysis was slow and the polydispersities of the resulting polymers were lower than those observed with alkylideneruthenium catalysts,[5] the present systems still have an advantage that a variety of terminal functional groups may be easily introduced to poly(norbornene) chains by using terminal alkynes as suggested by the reaction with ferrocenylacetylene. Further studies on the effect of substituent R of starting alkyne and the scope of applications of this readily prepared catalyst are now under investigation.

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9 Spectroscopic data are as follows. **1b**: ^1H NMR (C_6D_6) δ 3.14 (t, $^4J_{PH}$ = 3.9 Hz, 1H, =C=C*H*(*t*-Bu)), 2.93–2.85 (m, 6H, PC*H*CH_3), 1.35 (doublet of virtual triplets, $^3J_{HH}$ = 7.1 Hz, J = 5.9 Hz, 36H, PCHC*H*$_3$), 1.20 (s, 9H, *t*-Bu); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 335.2 (t, $^2J_{PC}$ = 15 Hz, Ru=*C*=C), 115.8 (s, Ru=C=*C*), 32.3 (s, *t*-Bu), 23.3 (virtual triplet, J = 9.9 Hz, P*C*HCH$_3$), 20.2 (s, PCH*C*H$_3$); $^{31}P\{^1H\}$ NMR (C_6D_6) δ 27.4 (s). **1c**: ^1H NMR (C_6D_6) δ 3.16 (t, $^4J_{PH}$ = 3.7 Hz, 1H, =C=C*H*(*t*-Bu)), 2.92–2.85, 2.33–2.29, 1.87–1.78, 1.34–1.19 (each m, 66H, Cy), 1.29 (s, 9H, *t*-Bu); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 337.1 (t, $^2J_{PC}$ = 15 Hz, Ru=*C*=C), 115.5 (br, Ru=C=*C*), 33.5 (virtual triplet, J = 10 Hz, C^1 of Cy), 32.3 (s, C^3 of Cy), 30.6 (s, *t*-Bu), 28.1 (br, C^2 of Cy), 27.0 (s, C^4 of Cy); $^{31}P\{^1H\}$ NMR (C_6D_6) δ 18.4 (s).

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11 In order to compare the catalytic activities, particularly at the initiation step, the reactions in Table 2 were examined under controlled reaction conditions (at 40 °C, for 24 h). For elongated reaction times, the catalytic systems afforded almost quantitative yields of polymers except for entry 4, which showed no catalytic activity.

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