A typical procedure for polymerization (entry 3) is as follows. An orange solution of **5**, which was prepared by the reaction of **1** (9.30 mg, 10 μmol) with $H(OEt_2)_2BAr_4$ (10.7 mg, 10 μmol) in chlorobenzene (5 mL) at room temperature, was transferred by cannula into a 150 mL pressure bottle and diluted with chlorobenzene (15 mL). Ethylene gas was charged, and the mixture was mechanically stirred at 70 °C for 1 h under a constant pressure (10 $kgf\,cm^{-2}$; 1 kgf = 9.81 N). At this stage, the reaction system was a clear orange solution containing a small quantity of white precipitates. The mixture was poured into MeOH (80 mL), and the resulting precipitates were collected by filtration and dried under vacuum to give a white solid of polyethylene (1.34 g). The reaction could be carried out in 1,2-dichloroethane in place of chlorobenzene at almost the same catalytic activity (124 $kg\,h^{-1}\,(mol\,cat)^{-1}$). In this case, however, precipitation of polymer from the reaction solution was considerable and the molecular weight was lowered ($M_w = 12.9\ kg\,mol^{-1}$, $M_w/M_n = 7.1$).

As seen from entries 3, 7, and 8 in Table 1, the catalytic activity was highly sensitive to the R groups of the diphosphinidenecyclobutene ligands; the phenyl-substituted catalyst **5** derived from **1** exhibited much higher activity than the others. The activity thus observed is similar to the level of the diimine-based palladium catalysts.[6] Higher pressure tends to improve the catalytic activity but causes a drop in the molecular weight (entries 2–4). The activity reached the maximum at around 70 °C (entry 3).

Noteworthy is that the present catalysts bearing diphosphinidenecyclobutene ligands possess extremely high thermal stability in the reaction solutions; no sign of decomposition was observed even at 100 °C (entry 6). This property is remarkable when compared with the diimine analogues[10] and may be attributed to good coordination ability of the phosphorus-based ligands with a soft palladium center.

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[7] Crystallographic data for **4**: $C_{54}H_{74}P_2Pt$, $M_r = 980.22$, orthorhombic, space group *Pbcn* (No. 60), $a = 17.9602(2)$, $b = 18.3428(2)$, $c = 15.2851(2)$ Å, $V = 5035.5(1)$ Å^3, $Z = 4$, $\varrho_{calcd} = 1.293\ g\,cm^{-3}$, $\mu(Mo_{K\alpha}) = 28.71\ cm^{-1}$, $T = 296$ K, $R(F^2)$ $(R_w(F^2)) = 0.031$ (0.042) for 3202 data with $I > 3\sigma(I)$. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-147540. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[9] The formation of **5** in solution was supported by NMR spectroscopy. The monomethyl structure of **5** was further confirmed by using its acetonitrile adduct which was isolated. ^1H NMR (300 MHz, CD_2Cl_2): $\delta = 1.39$ (dd, $J_{P,H} = 9.3$, 3.3 Hz, 3H; PdMe), 1.44, 1.45, 1.59, 1.60, 1.60, 1.61 (each s, each 9H; *t*Bu), 2.30 (s, 3H; MeCN), 6.78 (d, $J_{H,H} = 7.8$ Hz, 2H; *o*-Ph), 6.84 (d, $J_{H,H} = 8.1$ Hz, 2H; *o*-Ph), 6.97 (t, $J_{H,H} = 8.1$ Hz, 2H; *m*-Ph), 6.98 (t, $J_{H,H} = 7.8$ Hz, 2H; *m*-Ph), 7.24 (t, $J_{H,H} = 7.8$ Hz, 2H; *p*-Ph), 7.57 (s, 4H; BAr), 7.61 (d, $J_{P,H} = 2.7$ Hz, 2H; PAr), 7.71 (d, $J_{P,H} = 4.2$ Hz, 2H; PAr), 7.73 (s, 8H; BAr); $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2): $\delta = 3.4$ (s, *Me*CN), 14.5 (dd, $J_{C,P} = 94$, 3 Hz, PdMe), 31.3, 31.5, 33.8, 33.8, 34.1, 34.1 (each s, C*Me*$_3$), 35.8, 36.0, 38.7, 38.7, 39.8, 39.9 (each s, *C*Me$_3$), 122.7 (s, N*C*Me); $^{31}P\{^1H\}$ NMR (121 MHz, CD_2Cl_2): $\delta = 133.6$, 159.9 (each d, $J_{P,P} = 30$ Hz); elementary analysis calcd (%) for $C_{87}H_{86}BF_{24}NP_2Pd$: C 58.68, H 4.87, N 0.79, found: C 58.25, H 4.75, N 0.73.

[10] It was found that the diimine complex $[PdMe\{Ar'N{=}C(Me)\text{-}C(Me){=}NAr'\}]^+[BAr_4]^-$ ($Ar' = 2,6\text{-}(i\text{Pr})_2C_6H_3$)[5a] under the reaction conditions of entry 3 in Table 1 immediately starts to decompose giving metallic palladium and loses all catalytic activity within 15 min, 1.10 g of a sludgy, dark polymer was obtained using 10 μmol of the catalyst.

Highly Selective Ring-Opening/Cross-Metathesis Reactions of Norbornene Derivatives Using Selenocarbene Complexes as Catalysts**

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Tsuneo Nishioka, Chikaya Wada, Masato Nagao, and
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With the advent of well-defined alkylidene catalysts of molybdenum[1] and ruthenium,[2] olefin-metathesis has been invested with a great deal of utility in synthetic organic

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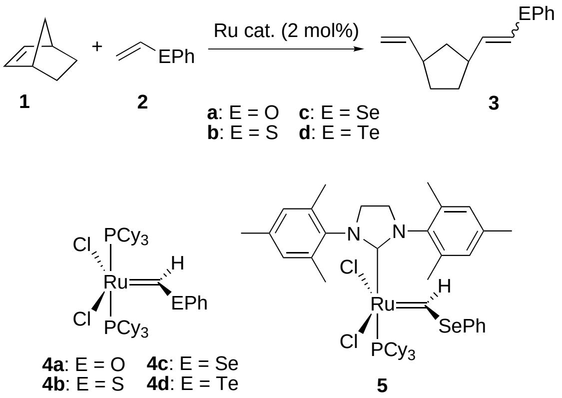
chemistry.[3] This transformation includes several reaction patterns which are dependent on the olefinic substrates employed. The most extensively investigated is the ring-opening metathesis polymerization (ROMP) of cyclic olefins. Ring-closing metathesis (RCM) of dienes or enynes has also found a number of applications in organic synthesis. Very recently, a highly efficient catalyst for inter- and intramolecular cross-metathesis (CM) of acyclic olefins has been developed.[4]

While the intermolecular coupling between cyclic olefins and acyclic olefins by a sequence of ring-opening/cross-metathesis reactions (ROCM) should be another useful variation of olefin metathesis, selective systems for this tandem protocol are rare.[5] A major problem is the concurrent self-metathesis of cyclic olefins, giving the ROMP products. The polymer formation is particularly pronounced when highly reactive cyclic olefins such as norbornene and 7-oxanorbornene are employed. Consequently, ROCM is usually conducted in a dilute solution using an excess of acyclic olefin,[5] and, on occasion, it is necessary to reduce the reactivity of cyclic olefin by steric protection.[5a] In contrast, we found in this study that a highly selective ROCM of norbornene (**1**) could be performed without such devices, by using phenyl vinyl selenide **2c** as an acyclic olefin and selenocarbene ruthenium **4c** as a catalyst (Scheme 1).[6]



Scheme 1. Catalytic ROCM of norbornene with vinyl chalcogenides.

A dichloromethane solution of **1** and **2c** (each 0.25 M) was treated with a catalytic amount of **4c** (2 mol%) at room temperature for 2 h. GLC analysis revealed selective formation of the ROCM product **3c** ($E/Z = 65/35$), which was isolated in 92% yield by column chromatography. Complex **4c** was the sole ruthenium species observed by $^{31}P\{^{1}H\}$ NMR spectroscopy throughout the reaction and recovered almost quantitatively from the system.

The ROCM reaction could be conducted using $[Ru(=CHPh)Cl_2(PCy_3)_2]$ (**6**)[2a] or $[Ru(=C=CHtBu)Cl_2(PCy_3)_2]$ (**7**)[8] in place of **4c**. The reaction with **6** (2 mol%), which is the precursor of **4c**,[6] proceeded at a comparable rate, giving **3c** ($E/Z = 64/36$) in 89% yield. In this case, treatment of **6** with **2c** prior to mixing with **1** was essential for the high product yield; otherwise a considerable amount of poly(**1**) was formed. While complex **7** was less reactive than **4c** and **6**, the ROCM product **3c** was still obtained in good yield (83%; $E/Z = 62/38$) at elevated temperature (60 °C, 4 h).

The reactions of **1** with a series of phenyl vinyl chalcogenides are summarized in Table 1. The vinyl selenide **2c** (entry 4) is much more effective in ROCM than the others. Thus the reactions with vinyl ether **2a** (entries 1 and 2) and sulfide **2b** (entry 3) were accompanied by considerable ROMP of **1**.[9] The reaction with telluride **2d** was sufficiently selective but incomplete because of decomposition of the ruthenium catalyst (entry 5).

Table 1. Ruthenium-catalyzed ROCM of norbornene (**1**) with the vinyl chalcogenides **2**.

Entry[a]	$H_2C{=}CHEPh$	Catalyst	Reaction time [h]	Yield of **3**[b] [%]	E/Z[c]
1	**2a** (E = O)	**4a**	1	0[d]	–
2	**2a** (E = O)[e]	**4a**	5	17	15/85
3	**2b** (E = S)	**4b**	6	63	63/37
4	**2c** (E = Se)	**4c**	2	92	65/35
5	**2d** (E = Te)	**4d**	18	34 (98)[f]	46/54

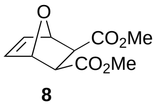
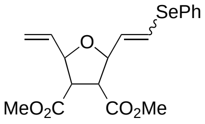
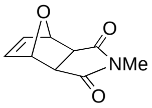
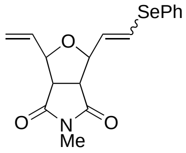
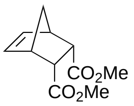
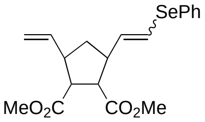
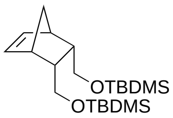
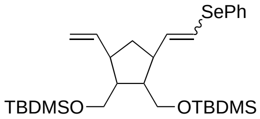
[a] Initial concentration: [**1**] = [**2**] = 0.25 M, [catalyst] = 5.0 mM. Conditions: in CH_2Cl_2 at room temperature. [b] Isolated yield. [c] Determined by ^{1}H NMR spectroscopy. [d] See ref [9]. [e] 1.3 M of **2a** was used. [f] Conversion in parentheses.

Although the ROCM of **1** was further examined with several α-olefins, no selective systems were found out. For example, the reaction with styrene or 1-hexene in the presence of **6** (2 mol%) at room temperature rapidly afforded a quantitative yield of poly(**1**) which was isolated by precipitation from MeOH. The reaction with allyltrimethylsilane, which has been reported as a good cross-metathesis reagent,[5] also gave the polymer in 85% yield. In addition, several types of cross-metathesis products as well as a homodimer of allyltrimethylsilane were formed (see the GCMS chart in Supporting Information).

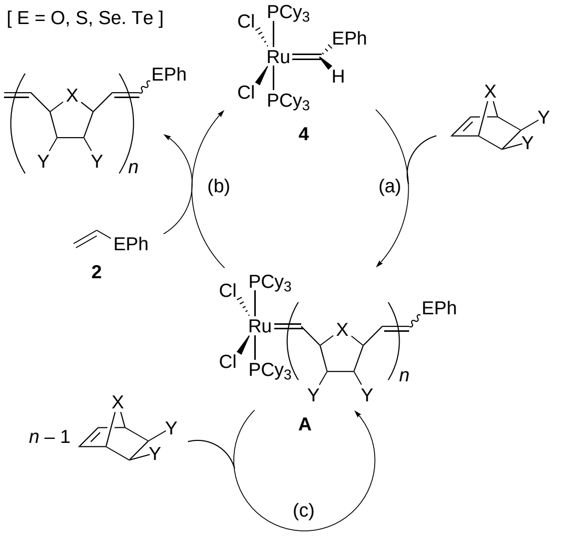
The catalytic ROCM system using vinyl selenide **2c** could be applied to several norbornene derivatives. The representative results are given in Table 2. 7-Oxanorbornene derivatives (**8** and **10**) reacted at room temperature to give the corresponding ROCM products (**9** and **11**, respectively) in high yields (entries 1 and 2). The reactions of less reactive *endo*-5,6-disubstituted norbornenes (**12** and **14**) were successfully conducted at 40 °C using catalyst **5** bearing a 1,3-dimesityl-4,5-dihydroimidazol-2-ylidene ligand (see Scheme 1).[7]

The variation in the product-selectivity depending on the sort of chalcogen atoms (Table 1) may be rationalized by the catalytic mechanism depicted in Scheme 2, where the Fischer-type carbene complex **4** is proposed as a key intermediate. Although Fischer-type complexes are considered to have little reactivity toward olefin metathesis,[10] complexes **4a**–**4d** based on the Grubbs' catalyst **6** were so reactive as to readily catalyze the ROMP of norbornene (**1**) and *exo*-5,6-bis(methoxycarbonyl)-7-oxanorbornene (**8**) at room temperature.[11] Process (a) giving the alkylidene intermediate **A** ($n = 1$) is the common initiation step for both ROCM and ROMP, which subsequently invoke processes (b) and (c), respectively. Therefore, it is possible that **A** further reacts with norbornene

Table 2. Ruthenium-catalyzed ROCM of norbornene derivatives with **2c**.

Entry[a]	Substrate	Product	Yield[b] [%]	E/Z[c]
1	 **8**	 **9**	99	84/16
2	 **10**	 **11**	82	72/28
3	 **12**	 **13**	96	55/45
4	 **14**	 **15**	91	58/42

[a] All reactions were run in CH_2Cl_2 for 20–48 h. Initial concentration: [substrate] = [**2c**] = 0.25 M, [catalyst] = 5.0 mM. Catalyst: **4c** (entries 1, 2), **5** (entries 3, 4). Reaction temperature: room temperature (entries 1, 2), 40 °C (entries 3, 4). [b] Isolated yield. [c] Determined by ^1H NMR spectroscopy. TBDMS = $SiMe_2tBu$.



Scheme 2. Proposed mechanism for catalytic ROCM reactions, a), b), and c) are explained in the text.

derivatives according to process (c) to form the ROMP products. However, when vinyl chalcogenide **2** is sufficiently more reactive than the norbornene derivatives, intermediate **A** selectively undergoes process (b) to afford the ROCM products. Thus the catalytic reactions using phenyl vinyl selenide **2c** produces no notable amounts of polymers and the ROCM products are obtained in high yields.

There is another condition for the selective ROCM: the cross-metathesis between **A** ($n = 1$) with **2** must be a highly regioselective process, regenerating **4** exclusively. Thus the greater thermodynamic stability of the Fischer-type complex **4** compared with the corresponding Schrock-type analogue $[Ru(=CH_2)Cl_2(PCy_3)_2]$ should provide this high regioselectivity, leading to the well-controlled ROCM reactions.[12]

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