Convenient Route to Fischer-Type Carbene Ruthenium Complexes: Highly Selective Catalysts for Ring Opening/Cross-Metathesis of Norbornene Derivatives

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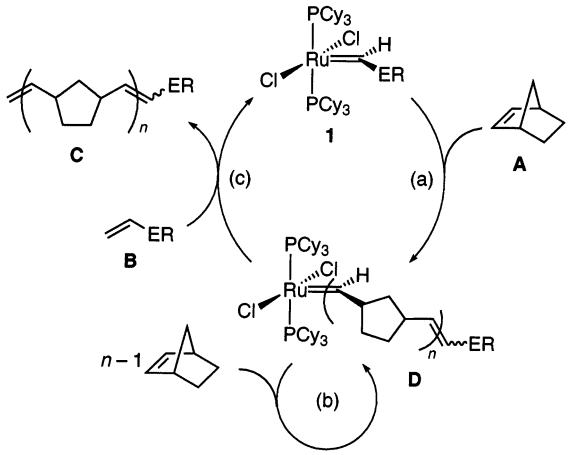
Received September 16, 2002

The Fischer-type ruthenium carbene complexes $RuCl_2\{=C(H)ER\}(PCy_3)_2$ (ER = SPh (**1a**), SC_6H_4Me-*p* (**1b**), SC_6H_4Cl-*p* (**1c**), SC_6H_4OMe-*p* (**1d**), SePh (**1e**)) have been prepared by the reactions of Ru(*p*-cymene)(cod), PCy_3, and the corresponding dichloromethyl chalcogenides (Cl_2CHER) in 47−80% yields. The starting Ru(*p*-cymene)(cod) is readily synthesized in high yield from $[RuCl_2(p\text{-cymene})]_2$. The X-ray structures of **1b** and **1e** are reported. Complexes **1a** and **1e** serve as highly selective catalysts for ring opening/cross-metathesis of norbornene derivatives with vinyl chalcogenides.

Introduction

We recently found a highly selective catalysis for ring opening/cross-metathesis (ROCM) of norbornene derivatives, which proceeds via a catalytic cycle involving the Fischer-type ruthenium carbene complexes $RuCl_2\{=C(H)ER\}(PCy_3)_2$ (**1**, E = O, S, Se) as key intermediates (Scheme 1).[1−3] Reactions of norbornene **A** with vinyl chalcogenide **B** in the presence of **1** or its precursor complex afford the ROCM product **C** having CH_2=CH− and −CH=CHER groups at each terminus. The ratio of **A** to **B** incorporated into **C** may be controlled from 1:1 to 100:1 (i.e., n = 1−100 in **C**) by the choice of ER group as well as the ratio of substrates employed in the reaction. This method has been applied to the synthesis of monofunctional macroinitiators, which are useful for constructing block copolymers.[4] The selectivity of this catalysis is mainly due to the regioselectivity of the cross-metathesis process (path c) between alkylidene intermediate **D** and vinyl chalcogenide **B**. Reflecting a much higher thermodynamic stability of the Fischer-type carbene complex than the corresponding alkylidene analogue,[5] this process adopts exclusively the regiochemistry given in Scheme 1.

Scheme 1



The Fischer-type ruthenium carbene complexes **1** may be generated in situ from the vinylidene complex $RuCl_2\{=C=C(H)Bu^t\}(PCy_3)_2$ as a catalyst precursor.[1] These complexes have also been synthesized by the reactions of the Grubbs complex $RuCl_2\{=C(H)Ph\}(PCy_3)_2$ with vinyl chalcogenides.[2,5] However, considering the rather unique catalytic properties and utility in olefin metathesis reactions described above, we wished to develop a more convenient route to **1**, starting from common ruthenium complexes.

An attractive protocol for ruthenium carbene synthesis is the treatment of ruthenium(0) complexes with dichloromethane derivatives.[6] This method has been examined for the synthesis of the Grubbs alkylidene complexes.[7] However, owing to the difficulty in preparation and handling of the starting complexes (e.g., Ru(cod)(cot) and $Ru(H)_2(H_2)_2(PCy_3)_2$), it has not been used as a practical synthetic route. On the other hand, we found in this study that the Fischer-type complexes **1** bearing thio- and selenocarbene ligands are readily

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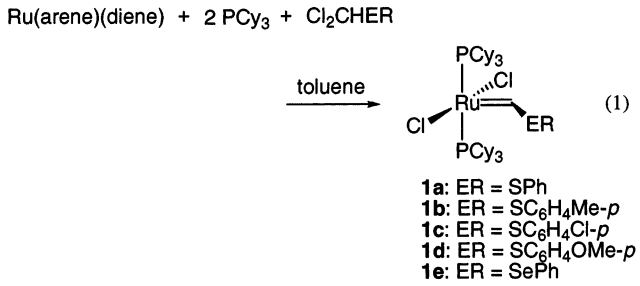
10.1021/om020772z CCC: $25.00
Publication on Web 01/07/2003

Table 1. Synthesis of 1a by the Reactions of Ruthenium(0) Complexes with Cl_2CHSPh and PCy_3[a]

run	Ru(0) complex[b]	temp (°C)	time (h)[c]	yield (%)[d]
1	Ru(*p*-cymene)(cod)	60	24	80
2	Ru(benzene)(cod)	60	16	70
3	Ru(naphthalene)(cod)	40	24	75
4	Ru(*p*-cymene)(chd)	60	18	50
5	Ru(benzene)(chd)	60	6	70

[a] All reactions were carried out in toluene. Initial concentration: $[Ru(0)]_0$ = 22 mM, $[PCy_3]_0$ = 44 mM, $[Cl_2CHSPh]_0$ = 30 mM. [b] Definitions: *p*-cymene = *p*-$CH_3C_6H_4CH(CH_3)_2$, cod = 1,5-cyclooctadiene, chd = 1,3-cyclohexadiene. [c] Time required for complete conversion of Ru(0) complex. [d] Isolated yield.

prepared in high yields by the treatment of common ruthenium(0) complexes with dichloromethyl chalcogenides (eq 1).



(1)

Results and Discussion

Synthesis of Fischer-Type Carbene Complexes 1. When a mixture of Ru(*p*-cymene)(cod), Cl_2CHSPh (1.4 equiv), and PCy_3 (2.0 equiv) in toluene was stirred at 60 °C for 24 h, the initially reddish brown solution gradually darkened. $^{31}P\{^1H\}$ NMR analysis of the reaction solution revealed the formation of a single product (δ 31.7) with complete conversion of free PCy_3. The product was isolated as a purple solid in 80% yield by removal of volatile materials followed by washing the residue with acetone and MeOH. The ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra measured in $CDCl_3$ were identical with those reported for $RuCl_2\{=C(H)SPh\}(PCy_3)_2$ (**1a**).[2,5a]

Similarly, several ruthenium(0) complexes bearing arene and diene ligands were tested as the starting materials. The results are summarized in Table 1. Ru(benzene)(cod) afforded **1a** in 70% yield (run 2). Ru(naphthalene)(cod), which is known to be reactive toward arene exchange in solution,[8] cleanly reacted with Cl_2CHSPh at 40 °C to give a 75% yield of **1a** (run 3). 1,3-Cyclohexadiene (chd) complexes also formed **1a** in good to high yields (runs 4 and 5). Ru(benzene)(chd) was especially reactive, and the reaction was complete after 6 h at 60 °C (run 5).

Taking these observations and the ease of preparation and handling of the ruthenium(0) complexes into consideration, we concluded that Ru(*p*-cymene)(cod) was the starting complex of choice. This complex is fairly stable toward air and moisture and is synthesized in 83% isolated yield, simply by the treatment of $[RuCl_2(p\text{-cymene})]_2$ with 1,5-cyclooctadiene (10 equiv/Ru) and Na_2CO_3 (3 equiv/Ru) in EtOH under reflux. All substrates and reagents employed are commercially available.

Table 2. Synthesis of Fischer-Type Carbene Complexes Using Ru(*p*-cymene)(cod)[a]

run	Cl_2CHER	time (h)[b]	yield (%)[c]
1	Cl_2CHOPh	24	0
2	$Cl_2CHSC_6H_4Me$-*p*	51	47
3	$Cl_2CHSC_6H_4Cl$-*p*	21	56
4	$Cl_2CHSC_6H_4OMe$-*p*	46	77
5	Cl_2CHSCH_2Ph	24	0
6	$Cl_2CHSePh$	36	71

[a] All reactions were carried out in benzene at 60 °C. Initial concentration: $[Ru(p\text{-cymene})(cod)]_0$ = 22 mM, $[PCy_3]_0$ = 44 mM, $[Cl_2CHER]_0$ = 30 mM. [b] Time required for complete conversion of Ru(*p*-cymene)(cod). [c] Isolated yield.

Table 3. Selected Bond Distances (Å) and Angles (deg) for 1b and 1e

	1b	**1e**
Ru−C(1)	1.826(6)	1.825(3)
Ru−Cl(1)	2.387(2)	2.3942(9)
Ru−Cl(2)	2.405(2)	2.3923(9)
Ru−P(1)	2.422(2)	2.4312(8)
Ru−P(2)	2.419(2)	2.4079(8)
C(1)-E	1.725(7)	1.886(3)
Cl(1)−Ru−Cl(2)	174.47(7)	168.54(4)
P(1)−Ru−P(2)	161.61(6)	165.81(3)
Ru−C(1)−E	130.0(4)	128.1(2)
C(1)−E−C(2)	102.7(3)	99.0(2)

Table 2 summarizes results of the reactions of Ru(*p*-cymene)(cod) with PCy_3 and several dichloromethyl chalcogenides. Benzenethiolates bearing three kinds of para substituents formed the corresponding thiocarbene complexes (**1b**−**d**) in 47−77% yields (runs 2−4). Dichloromethyl benzeneselenolate also gave the selenocarbene complex **1e** in 71% yield (run 6). On the other hand, Cl_2CHOPh and Cl_2CHSCH_2Ph were unreactive (runs 1 and 5).

Complexes **1b**−**e** thus obtained were identified by NMR spectroscopy and elemental analysis. The thiocarbene complexes exhibited the ^1H and $^{13}C\{^1H\}$ signals characteristic of carbene ligands at δ 17.52−17.60 and 278.8−282.5, respectively. The selenocarbene complex **1e** showed the corresponding signals at slightly lower magnetic fields: δ 18.50 (^1H) and 285.7 (^{13}C).

The structures of **1b** and **1e** were determined by single-crystal X-ray diffraction studies. Selected bond distances and angles are listed in Table 3. As seen from the ORTEP drawings in Figures 1 and 2, both complexes have a distorted-square-pyramidal structure with the carbene ligand at the apical position. A similar structural feature has been reported for closely related complexes, including $RuCl_2\{=C(H)OEt\}(PCy_3)_2$[5a] and $RuCl_2\{=C(H)C_6H_4Cl\text{-}p\}(PCy_3)_2$.[9] The Ru−C(1) distances (1.826(6) Å for **1b**; 1.825(3) Å for **1e**) are comparable to each other and to that for **1a** (1.829(3) Å).[4a]

Ring Opening/Cross-Metathesis of Norbornene Derivatives. Having the new synthetic route to Fischer-type carbene ruthenium complexes, we next examined ROCM reactions using **1a** and **1e** as catalysts. When the reaction was carried out with an equimolar amount of vinyl sulfide or selenide in combination with norbornene derivatives, 1:1 coupling between the substrates proceeded (Table 4). As already mentioned in a preliminary communication,[2] phenyl vinyl selenide served as

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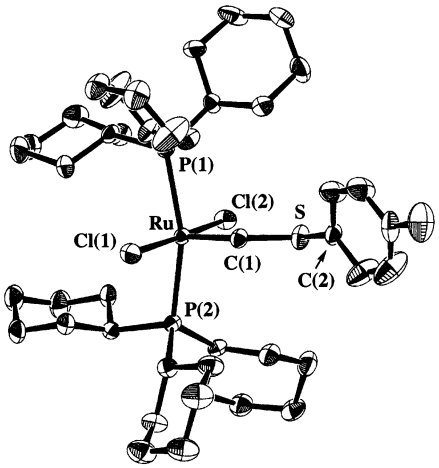


Figure 1. ORTEP diagram of $RuCl_2\{=C(H)SC_6H_4Me\text{-}p\}(PCy_3)_2$ (**1b**). The thermal ellipsoids are drawn at the 30% probability level.

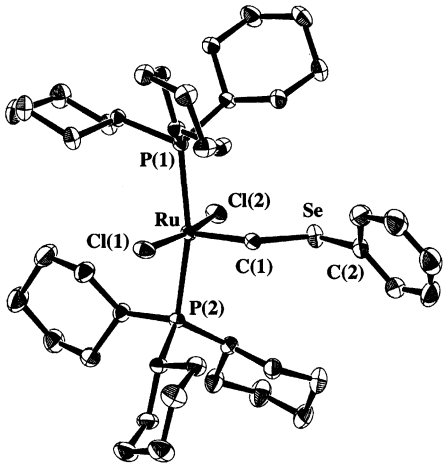
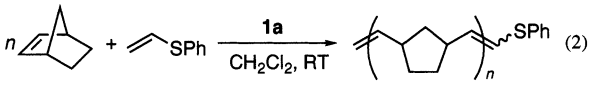


Figure 2. ORTEP diagram of $RuCl_2\{=C(H)SePh\}(PCy_3)_2$ (**1e**). The thermal ellipsoids are drawn at the 30% probability level.

a particularly effective reagent to afford the coupling products in high yields (runs 3, 9, and 10). While vinyl sulfides were less reactive, 1:1 coupling products were obtained in good to high yields (runs 1, 2, and 4−8).

In the present ROCM systems using Fischer-type carbene complexes, vinyl chalcogenides exhibit much higher reactivity than common alkene substrates. Thus, as shown in Scheme 2, vinyl sulfides bearing alkenyl substituents reacted with 2,3-bis(methoxycarbonyl)-7-oxabicyclo[2.2.1]hept-5-ene, exclusively at the $CH_2{=}CHS-$ group. Similarly, the vinyl sulfide having a (trimethylsilyl)ethynyl group selectively underwent reaction at the sulfur-substituted vinyl group.

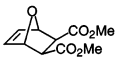
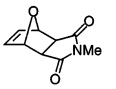
The above-mentioned ROCM giving 1:1 coupling products proceeds via the sequence of elementary processes a and c in Scheme 1. On the other hand, when norbornene was employed in excess of phenyl vinyl sulfide, process b became also effective, and poly(norbornene) bearing $CH_2{=}CH-$ and $-CH{=}CHSPh$ groups at each terminus was obtained (eq 2). The



(2)

polymerization proceeded readily in CH_2Cl_2 at room temperature in the presence of 2 mol % of **1a**, giving the polymer in 89−98% yield. GPC analysis revealed monomodal peak profiles with PDI values of 1.71−2.12. As seen from Figure 3, the number-average molecular weight of polymer (M_n) showed an excellent linear correlation with the initial ratio of substrates. Hence, the well-controlled polymerization of norbornene was evidenced.

Table 4. ROCM of Norbornene Derivatives with Vinyl Chalcogenides Catalyzed by 1a or 1e[a,b]

run	norbornene derivative	ER (ER)	time (h)	product	yield[c] (%)
				[X = CH_2, Y = H]	
1		SPh	6	**2**	63 (*E*/*Z* = 63/37)
2		SCH_2Ph	89	**3**	63 (*E*/*Z* = 72/28)
3		SePh	2	**4**	92 (*E*/*Z* = 65/35)
				[X = O, Y = CO_2Me]	
4		SPh	40	**5**	98 (*E*/*Z* = 93/7)
5		$SC_6H_4Cl\text{-}p$	27	**6**	88 (*E*/*Z* = 87/13)
6		$SC_6H_4Me\text{-}p$	25	**7**	87 (*E*/*Z* = 84/16)
7		SCH_2Ph	70	**8**	85 (*E*/*Z* > 99/1)
8		SEt	164	**9**	79 (*E*/*Z* > 99/1)
9		SePh	20	**10**	99 (*E*/*Z* = 84/16)
				[X = O, Y_2 = CONMeCO]	
10		SePh	22	**11**	82 (*E*/*Z* = 72/28)

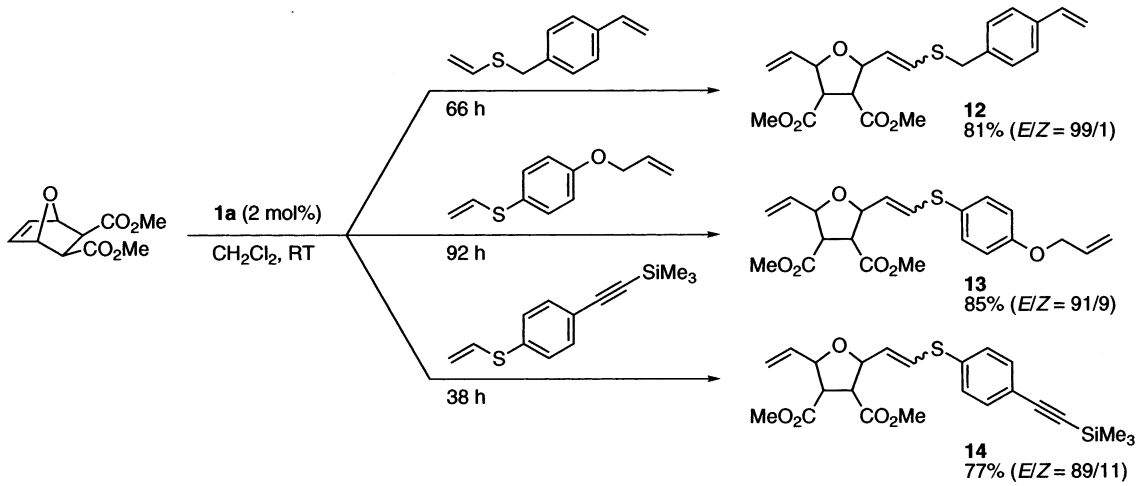
[a] All reactions were carried out in CH_2Cl_2 at room temperature. Initial concentration: [norbornene derivative] = $[CH_2{=}CHER]$ = 0.25 M, [catalyst] = 5.0 mM. The catalyst is **1a** (runs 1, 2, and 4−8) or **1e** (runs 3, 9, and 10). [b] The data for runs 1, 3, 9, and 10 were taken from a preliminary communication.[2] [c] Isolated yield. The *E*/*Z* ratio of the product was determined by ^1H NMR spectroscopy.

In summary, we found a convenient synthetic route to Fischer-type carbene complexes, starting from Ru(*p*-cymene)(cod), PCy_3, and dichloromethyl chalcogenides. The reactions of sulfides and selenides proceed cleanly at 60 °C to give the corresponding carbene complexes in high yields. The precursor complex Ru(*p*-cymene)(cod) is readily prepared and handled. The thio- and selenocarbene complexes thus prepared serve as highly efficient and selective catalysts for ring opening/cross-metathesis of norbornene derivatives with vinyl chalcogenides.

Experimental Section

General Procedure and Materials. All manipulations were performed under a nitrogen atmosphere using conventional Schlenk techniques. Nitrogen gas was purified by passing it successively through the columns of an activated copper catalyst (BASF, R3-11) and P_2O_5 (Merck, SICAPENT). NMR spectra were recorded on a Varian Mercury 300 (^1H NMR, 300.11 MHz; ^{13}C NMR, 75.46 MHz; ^{31}P NMR, 121.49 MHz) spectrometer. Chemical shifts are reported in δ (ppm), referenced to the ^1H (of residual protons) and ^{13}C signals of deuterated solvents or to the ^{31}P signal of external 85% H_3PO_4. The symbol J_{app} stands for the apparent coupling constant for a virtually coupled signal. Mass spectra were measured with a Shimadzu QP-5000 GC-mass spectrometer (EI, 70 eV).

Scheme 2



GLC analysis was performed on a Shimadzu GC-14B instrument equipped with an FID detector and a CBP-1 capillary column (25 m × 0.25 mm). Analytical TLC was carried out on Merck TLC aluminum sheets precoated with silica gel 60 F_{254}. Visualization was accomplished using UV light and/or a *p*-anisaldehyde charring solution. Flash column chromatography was performed using Merck silica gel 60 (230−400 mesh). Gel permeation chromatography was carried out on a Tosoh 8000 GPC system equipped with TSK gel columns ($G7000H_{HR}$, $G4000H_{HR}$, $G3000H_{HR}$, $G2000H_{HR}$; the molecular weight range was 2 890 000−946).

Toluene, benzene, and THF were dried over sodium benzophenone ketyl. Methanol and ethanol were dried with the corresponding magnesium alkoxides. CH_2Cl_2 was dried over CaH_2. These solvents were distilled under a nitrogen atmosphere and stored over molecular sieves (MS4A), which were activated by heating at ca. 300 °C under vacuum overnight prior to use. Acetone was dried over B_2O_3 and distilled. $CDCl_3$ was purified by passage through an alumina column, degassed by freeze−pump−thaw cycles, and stored over activated MS4A in the dark. Benzene-d_6 was dried over $LiAlH_4$ and vacuum-transferred. Norbornene was distilled from sodium prior to use. $[RuCl_2(p\text{-cymene})]_2$,[10] Cl_2CHSPh,[11] $Cl_2CHSC_6H_4Me$-*p*,[11] $Cl_2CHSC_6H_4Cl$-*p*,[11] $Cl_2CHSC_6H_4OMe$-*p*,[11] $Cl_2CHSePh$,[12] $CH_2{=}CHSPh$,[13] $CH_2{=}CHSCH_2Ph$,[5b] $CH_2{=}CHSC_6H_4Cl$-*p*,[13] $CH_2{=}CHSC_6H_4Me$-*p*,[13] $CH_2{=}CHSePh$,[14] *exo*-2,3-bis(methoxycarbonyl)-7-oxabicyclo[2.2.1]hept-5-ene,[15] *exo*-*N*-methyl-7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboximide,[16] 4-(allyloxy)phenyl bromide,[17] and bis(4-iodophenyl) disulfide[18] were synthesized according to the literature. All other chemicals were obtained from commercial suppliers and used without further purification.

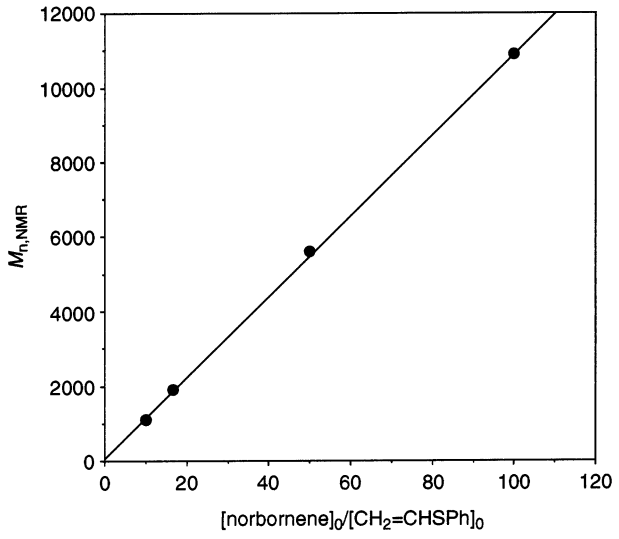


Figure 3. Plot of the $M_{n,NMR}$ values of poly(norbornene) versus the ratio of norbornene to phenyl vinyl sulfide for the polymerization using catalyst **1a** (2 mol %) in CH_2Cl_2 at room temperature.

Synthesis of Ru(*p*-cymene)(cod). The following procedure was based on the synthesis of (hexamethylbenzene)(1,3-cyclohexadiene)ruthenium.[19] A mixture of $[RuCl_2(p\text{-cymene})]_2$ (1.04 g, 1.70 mmol), anhydrous sodium carbonate (1.00 g, 9.43 mmol), 1,5-cyclooctadiene (4.0 mL, 33 mmol), and ethanol (50 mL) was refluxed at 90 °C for 2.5 h. The initially brown suspension turned to a dark brown solution. Volatile materials were thoroughly removed by pumping, and the residue was extracted with hexane (10 mL × 5). The combined extracts were concentrated to ca. 1 mL and allowed to stand at −20 °C for 1 day to give dark brown crystals of the title compound (0.95 g, 83%). Mp: 48−49 °C dec. ^1H NMR (C_6D_6): δ 4.58−4.53 (m, 4H, Ar), 3.26 (br s, 4H, =CH), 2.35 (br s, 8H, CH_2), 2.13 (septet, J = 7.0 Hz, 1H, C*H*$(CH_3)_2$), 1.85 (s, 3H, CH_3), 1.13 (d, J = 7.0 Hz, 6H, CH(C*H*$_3)_2$). $^{13}C\{^1H\}$ NMR (C_6D_6): 115.5, 104.1, 85.3, 82.7 (each s, C_6H_4), 63.0 (s, =CH), 34.5 (s, CH_2), 31.8 (s, *C*H$(CH_3)_2$), 23.6 (s, CH_3), 18.7 (s, CH(*C*H$_3)_2$). Anal. Calcd for $C_{18}H_{26}Ru$: C, 62.94; H, 7.63. Found: C, 62.56; H, 7.55.

Synthesis of Fischer-Type Ruthenium Carbene Complexes 1a−e. A typical procedure is as follows. To a solution of Ru(*p*-cymene)(cod) (84 mg, 0.24 mmol) and PCy_3 (138 mg, 0.492 mmol) in toluene (11 mL) was added Cl_2CHSPh (65 mg, 0.34 mmol). The mixture was stirred at 60 °C for 24 h. The resulting reddish brown solution was evaporated by pumping, and the residue was successively washed with acetone (3 mL

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(19) Bennett, M. A.; Huang, T.-N.; Matheson, T. W.; Smith, A. K. *Inorg. Synth.* **1982**, *21*, 74−78.

× 2) and MeOH (3 mL × 1) at −70 °C to give a purple microcrystalline solid of **1a** (168 mg, 80%). All complexes listed in eq 1 were similarly prepared. The NMR data of **1a** and **1e** were identical with those reported.[2]

$RuCl_2\{=C(H)SC_6H_4Me\text{-}p\}(PCy_3)_2$ (1b): brown solid (47%). Mp: 82−84 °C (dec). ^1H NMR ($CDCl_3$): δ 17.60 (s, 1H, Ru=CH), 7.30, 7.17 (each d, J = 1.9 Hz, 4H, C_6H_4), 2.35 (s, 3H, CH_3), 2.73−2.55, 2.06−1.88, 1.86−1.44, 1.38−1.11 (each m, 66H, Cy). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 281.5 (t, $^2J_{PC}$ = 8 Hz, Ru=C), 138.6, 137.9, 129.9, 129.2 (each s, C_6H_4), 32.4 (virtual triplet, J_{app} = 9 Hz, C^1 of Cy), 29.6 (s, $C^{3,5}$ of Cy), 27.7 (virtual triplet, J_{app} = 5 Hz, $C^{2,6}$ of Cy), 26.4 (s, C^4 of Cy), 21.2 (s, CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 30.8 (s). Anal. Calcd for $C_{44}H_{74}Cl_2P_2RuS$: C, 60.81; H, 8.58. Found: C, 61.07; H, 8.87.

$RuCl_2\{=C(H)SC_6H_4Cl\text{-}p\}(PCy_3)_2$ (1c): deep purple solid (56%). Mp: 102−105 °C dec. ^1H NMR ($CDCl_3$): δ 17.60 (s, 1H, Ru=CH), 7.35 (br s, 4H, C_6H_4), 2.72−2.56, 2.08−1.44, 1.40−1.12 (each m, 66H, Cy). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 278.8 (t, $^2J_{PC}$ = 7 Hz, Ru=C), 139.5, 134.5, 130.2, 129.4 (each s, C_6H_4), 32.4 (virtual triplet, J_{app} = 9 Hz, C^1 of Cy), 29.6 (s, $C^{3,5}$ of Cy), 27.7 (virtual triplet, J_{app} = 5 Hz, $C^{2,6}$ of Cy), 26.3 (s, C^4 of Cy). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 31.2 (s). Anal. Calcd for $C_{43}H_{71}Cl_3P_2RuS$: C, 58.06; H, 8.05. Found: C, 57.78; H, 8.23.

$RuCl_2\{=C(H)SC_6H_4OMe\text{-}p\}(PCy_3)_2$ (1d): brown solid (77%). Mp: 77−80 °C dec. ^1H NMR ($CDCl_3$): δ 17.52 (s, 1H, Ru=CH), 7.34−7.31 (m, 2H, C_6H_4), 6.90−6.87 (m, 2H, C_6H_4), 3.82 (s, 3H, OCH_3), 2.73−2.56, 1.97−1.49, 1.34−1.20 (each m, 66H, Cy). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 282.5 (s, Ru=C), 159.7, 132.3, 131.0, 114.5 (each s, C_6H_4), 55.4 (s, OCH_3), 32.5 (virtual triplet, J_{app} = 9 Hz, C^1 of Cy), 29.7 (s, $C^{3,5}$ of Cy), 27.7 (virtual triplet, J_{app} = 5 Hz, $C^{2,6}$ of Cy), 26.5 (s, C^4 of Cy). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 30.7 (s). Anal. Calcd for $C_{44}H_{74}Cl_2OP_2RuS$: C, 59.71; H, 8.43. Found: C, 59.45; H, 8.66.

X-ray Crystallographic Studies. A single crystal of **1b** for X-ray diffraction study was obtained by cooling of the saturated solutions in CH_2Cl_2/MeOH. The crystal of **1e** was grown by slow diffusion of EtOH into the CH_2Cl_2 solution at room temperature. These crystals were mounted on a glass fiber and fixed with an epoxy resin adhesive. The crystal data and details of the data collection and structure refinement are summarized in Table 5.

(a) Data Collection. All measurements were made on a Rigaku RAXIS-RAPID imaging plate diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 69 Å). The camera radius was 127.40 mm. Indexing was performed from two oscillations which were exposed for 5.0 min (for **1b**) or 10.0 min (for **1e**). Diffraction data were collected at 20 ± 1 °C to a maximum 2θ value of 55°. The exposure time was 2.5 min/deg (for **1b**) or 3.0 min/deg (for **1e**). The readout was performed in the 0.100 mm pixel mode. The data were processed by the PROCESS-AUTO program package and corrected for Lorentz and polarization effects. A symmetry-related absorption correction using the program ABSCOR was applied.[20]

(b) Structure Solution. All calculations were performed with the Texsan Crystal Structure Analysis Package provided by Rigaku Corp., Tokyo, Japan.[21] The scattering factors were taken from ref 22. The structures were solved by heavy-atom Patterson methods (PATTY)[23] and expanded using Fourier techniques (DIRDIF94).[24] Each structure was refined by full-matrix least squares with anisotropic thermal parameters for all non-hydrogen atoms. In the final cycles of refinement, hydrogen atoms were located at idealized positions (d(C−H) = 0.95 Å) with isotropic temperature factors (B_{iso} = $1.20B_{bonded\ atom}$) and were included in the calculation without refinement of their parameters. The function minimized in least squares was $\sum w(F_o^2 - F_c^2)^2$ ($w = 1/[\sigma^2(F_o^2)]$).

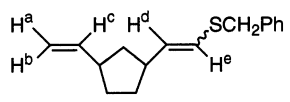
Table 5. Crystallographic Data and Structure Refinement Details for 1b and 1e

	1b	1e
formula	$C_{44}H_{74}Cl_2P_2RuS$	$C_{43}H_{72}Cl_2P_2RuSe$
fw	869.05	986.86
cryst size, mm	0.20 × 0.10 × 0.10	0.20 × 0.20 × 0.05
cryst syst	triclinic	triclinic
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a, Å	12.5582(7)	9.2716(2)
b, Å	19.085(1)	11.1768(3)
c, Å	11.0898(6)	21.3181(5)
α, deg	105.711(2)	84.502(1)
β, deg	114.406(2)	86.667(1)
γ, deg	71.787(2)	83.1874(7)
V, Å^3	2268.2(2)	2180.98(9)
Z	2	2
d_{calcd}, g cm^{-3}	1.272	1.373
diffractometer	Rigaku RAXIS-RAPID	
μ(Mo Kα), cm^{-1}	6.08	14.18
F(000)	924	944
2θ max, deg	55.0	54.9
temp, K	293	293
transmission factors	0.843−0.941	0.711−0.932
no. of rflns collcd	13932	20347
no. of unique rflns	10 268 (R_{int} = 0.030)	9752 (R_{int} = 0.039)
no. of obsd rflns	4248 ($I \geq 3\sigma(I)$)	7791 ($I \geq 3\sigma(I)$)
no. of variables	451	442
R1[a]	0.052	0.039
R[b]	0.066	0.057
R_w[c]	0.109	0.121
GOF[d]	1.20	1.57
max Δ/σ in final cycle	0.00	0.00
max and min peak, e Å^{-3}	0.61, −0.49	0.72, −0.46

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R = \sum(F_o^2 - F_c^2)/\sum F_o^2$. [c] $R_w = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$, $w = 1/[\sigma^2(F_o^2)]$. [d] GOF = $[\sum w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$, where N_o is the number of observations and N_v the number of variables.

ROCM of Norbornene Derivatives with Vinyl Chalcogenides. A typical procedure (Table 4, run 9) is as follows. To a solution of phenyl vinyl selenide (284 mg, 1.55 mmol) and *exo*-2,3-bis(methoxycarbonyl)-7-oxabicyclo[2.2.1]hept-5-ene (328 mg, 1.55 mmol) in CH_2Cl_2 (6.2 mL) was added solid **1e** (28.1 mg, 31.2 μmol), and the resulting brown solution was stirred at room temperature. The reaction progress was followed by GLC. After 20 h, the solvent was removed by pumping to give a brown oil, which was subjected to flash column chromatography. Elution with hexane/AcOEt (20/1) gave a purple fraction containing **1e** (28.0 mg), and further elution with hexane/AcOEt (5/1) afforded a colorless fraction. Evaporation of the latter eluate gave the coupling product **10** (609 mg, 99% yield) as a colorless oil. All the reactions listed in Table 4 and Scheme 2 were similarly carried out. In runs 1 and 2 in Table 4, polymeric products were removed by pouring the reaction mixtures into a large amount of methanol (ca. 100 mL) followed by filtration. The identification data of compounds **2**, **4**, **10**, and **11** were reported in our previous communication.[2]

Compound 3.

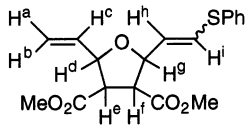


^1H NMR ($CDCl_3$): δ 7.33−7.21(m, *E*- and *Z*-Ph), 5.90 (dd, J =

(20) Higashi, T. Program for Absorption Correction; Rigaku Corp., Tokyo, Japan, 1995.
(21) TEXSAN Structure Analysis Package, Molecular Structure Corp., 1985 and 1992.
(22) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*, Kynoch Press: Birmingham, U.K., 1974; Vol. IV.
(23) Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; Garcia-Granda, S.; Gould, R. O.; Smits, J. M. M.; Smykalla, C. The PATTY and DIRDIF Program System; Technical Report of the Crystallographic Laboratory; University of Nijmegen, Nijmegen, The Netherlands, 1992.
(24) Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; de Gelder, R.; Israel, R.; Smits, J. M. M. The DIRDIF-94 Program System; Technical Report of the Crystallographic Laboratory; University of Nijmegen, Nijmegen, The Netherlands, 1994.

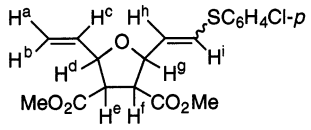
15.0, 0.9 Hz, *E*-H^{e}), 5.84 (dd, *J* = 9.4, 0.9 Hz, *Z*-H^{e}), 5.79 (ddd, *J* = 17.2, 10.1, 2.7 Hz, *Z*-H^{c}), 5.76 (ddd, *J* = 17.2, 10.1, 2.7 Hz, *E*-H^{c}), 5.65 (dd, *J* = 15.0, 7.9 Hz, *E*-H^{d}), 5.51 (dd, *J* = 9.4, 9.2 Hz, *Z*-H^{d}), 4.96 (ddd, *J* = 17.2, 1.6, 0.9 Hz, *E*- and *Z*-H^{b}), 4.87 (ddd, *J* = 10.1, 1.8, 0.9 Hz, *E*- and *Z*-H^{a}), 3.85 (s, *Z*-SCH_2), 3.84 (s, *E*-SCH_2), 2.92−2.80, 2.58−2.43, 2.00−1.73, 1.55−1.26, 1.16−1.00 (each m, *E*- and *Z*-CH_2, CH). $^{13}C\{^1H\}$ NMR ($CDCl_3$): *δ* 143.1, 137.7, 136.5, 128.8, 128.8, 128.5, 127.1, 127.1, 122.4, 120.4, 120.2, 112.5, 112.4, 44.3, 44.0, 43.8, 40.3, 40.1, 40.1, 38.0, 37.6, 31.9, 31.7, 31.5. MS (*m*/*z* (relative intensity, %)): *E* isomer 153 (31), 92 (11), 91 (100), 65 (17); *Z* isomer 153 (33), 97 (10), 92 (11), 91 (100), 65 (17). Anal. Calcd for $C_{16}H_{20}S$: C, 78.63; H, 8.25. Found: C, 79.21; H, 8.46.

Compound 5.



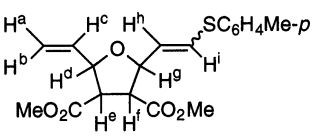
^1H NMR ($CDCl_3$): *δ* 7.39−7.22 (m, *E*- and *Z*-Ph), 6.76 (dd, *J* = 9.6, 1.0 Hz, *Z*-H^{i}), 6.60 (dd, *J* = 15.0, 1.1 Hz, *E*-H^{i}), 5.93 (ddd, *J* = 16.5, 10.5, 6.0 Hz, *Z*-H^{c}), 5.88 (ddd, *J* = 16.5, 10.4, 6.0 Hz, *E*-H^{c}), 5.80 (dd, *J* = 15.0, 6.6 Hz, *E*-H^{h}), 5.80 (dd, *J* = 9.6, 8.1 Hz, *Z*-H^{h}), 5.44 (ddd, *J* = 16.5, 1.3, 1.3 Hz, *Z*-H^{b}), 5.40 (ddd, *J* = 16.5, 1.3, 1.3 Hz, *E*-H^{b}), 5.24 (ddd, *J* = 10.5, 1.3, 1.3 Hz, *Z*-H^{a}), 5.22 (ddd, *J* = 10.4, 1.1, 1.1 Hz, 1H, *E*-H^{a}), 4.83−4.78, 4.72−4.67 (each m, *E*- and *Z*-H^{d,g}), 3.73, 3.72, 3.70 (s, *E*- and *Z*-CO_2Me), 3.25−3.06 (m, *E*- and *Z*-H^{e,f}). $^{13}C\{^1H\}$ NMR ($CDCl_3$): *δ* 171.1, 171.0, 170.8, 136.3, 135.5, 134.2, 130.1, 129.6, 129.3, 129.1, 129.0, 128.8, 127.8, 127.1, 126.8, 117.6, 117.5, 81.6, 80.9, 77.7, 52.4, 52.3, 52.2, 52.0. MS (*m*/*z* (relative intensity, %)): *E* and *Z* isomers 348 (M^+, 1), 239 (19), 207 (17), 163 (22), 135 (11), 127 (100), 121 (12), 111 (20), 109 (18), 91 (10), 65 (19), 59 (38), 55 (56). Anal. Calcd for $C_{18}H_{20}O_5S$: C, 62.05; H, 5.79. Found: C, 61.88; H, 5.71.

Compound 6.



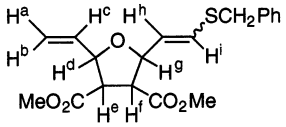
^1H NMR ($CDCl_3$): *δ* 7.29−7.26 (m, *E*- and *Z*-Ar), 6.55 (dd, *J* = 15.0, 1.1 Hz, *E*-H^{i}), 6.41 (dd, *J* = 9.5, 0.9 Hz, *Z*-H^{i}), 5.92 (ddd, *J* = 17.0, 10.4, 6.0 Hz, *Z*-H^{c}), 5.88 (ddd, *J* = 17.0, 10.4, 6.0 Hz, *E*-H^{c}), 5.82 (dd, *J* = 15.0, 6.6 Hz, *E*-H^{h}), 5.83 (dd, *J* = 9.5, 7.5 Hz, *Z*-H^{h}), 5.39 (ddd, *J* = 17.0, 1.5, 1.3 Hz, *Z*-H^{b}), 5.39 (ddd, *J* = 17.0, 1.4, 1.0 Hz, *E*-H^{b}), 5.25 (ddd, *J* = 10.4, 1.5, 1.1 Hz, *Z*-H^{a}), 5.23 (ddd, *J* = 10.4, 1.4, 1.1 Hz, 1H, *E*-H^{a}), 4.83−4.66 (m, *E*- and *Z*-H^{d,g}), 3.71, 3.72, 3.73 (each s, *E*- and *Z*-CO_2Me), 3.22−3.05 (m, *E*- and *Z*-H^{e,f}). $^{13}C\{^1H\}$ NMR ($CDCl_3$): *δ* 171.4, 170.8, 136.3, 132.8, 131.4, 130.9, 130.0, 129.7, 129.3, 129.2, 128.7, 127.2, 117.7, 81.8, 81.6, 80.8, 78.4, 52.4, 52.3, 52.0. MS (*m*/*z* (relative intensity, %)): *E* and *Z* isomers 382 (M^+, 1), 239 (18), 207 (25), 197 (15), 150 (10), 143 (18), 127 (100), 125 (11), 121 (11), 111 (21), 108 (12), 97 (13), 93 (12), 86 (12), 81 (11), 79 (11), 77 (11), 67 (12), 66 (14), 65 (19), 59 (59), 55 (68), 53 (24). Anal. Calcd for $C_{18}H_{19}ClO_5S$: C, 56.47; H, 5.00. Found: C, 56.91; H, 4.90.

Compound 7.



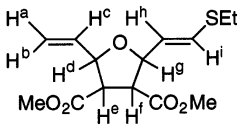
^1H NMR ($CDCl_3$): *δ* 7.29−7.26 (m, *E*- and *Z*-Ar), 6.56 (dd, *J* = 15.0, 1.1 Hz, *E*-H^{i}), 6.44 (dd, *J* = 9.5, 1.1 Hz, *Z*-H^{i}), 5.93 (ddd, *J* = 17.0, 10.4, 6.0 Hz, *Z*-H^{c}), 5.87 (ddd, *J* = 17.0, 10.4, 6.0 Hz, *E*-H^{c}), 5.70 (dd, *J* = 15.0, 6.8 Hz, *E*-H^{h}), 5.74 (dd, *J* = 9.5, 8.2 Hz, *Z*-H^{h}), 5.44 (ddd, *J* = 17.0, 1.3, 1.3 Hz, *Z*-H^{b}), 5.39 (ddd, *J* = 17.0, 1.3, 1.3 Hz, *E*-H^{b}), 5.24 (ddd, *J* = 10.4, 1.3, 1.3 Hz, *Z*-H^{a}), 5.22 (ddd, *J* = 10.4, 1.3, 1.3 Hz, 1H, *E*-H^{a}), 4.80−4.68 (m, *E*- and *Z*-H^{d,g}), 3.70, 3.72, 3.73 (each s, *E*- and *Z*-CO_2Me), 3.23−3.05 (m, *E*- and *Z*-H^{e,f}), 2.34 (s, *E*-$C_6H_4CH_3$), 2.33 (s, *Z*-$C_6H_4CH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): *δ* 171.2, 170.9, 137.5, 136.3, 131.0, 130.1, 130.0, 129.8, 128.9, 127.8, 117.7, 81.5, 81.1, 52.2, 52.1, 21.1. MS (*m*/*z* (relative intensity, %)): *E* and *Z* isomers 362 (M^+, 3), 250 (4), 239 (17), 207 (25), 179 (13), 177 (22), 147 (12), 136 (12), 135 (12), 127 (100), 125 (10), 124 (16), 123 (27), 121 (14), 111 (23), 97 (13), 93 (15), 91 (24), 79 (17), 77 (11), 67 (10), 66 (12), 65 (27), 59 (54), 55 (73), 53 (21). Anal. Calcd for $C_{19}H_{22}O_5S$: C, 62.96; H, 6.12. Found: C, 63.14; H, 5.92.

Compound 8.



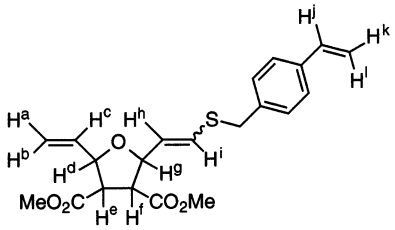
^1H NMR ($CDCl_3$): *δ* 7.33−7.25 (m, 5H, Ph), 6.41 (dd, *J* = 15.0, 1.1 Hz, 1H, H^{i}), 5.84 (ddd, *J* = 17.0, 10.3, 6.0 Hz, 1H, H^{c}), 5.58 (dd, *J* = 15.0, 6.8 Hz, 1H, H^{h}), 5.37 (ddd, *J* = 17.0, 1.5, 1.3 Hz, 1H, H^{b}), 5.21 (ddd, *J* = 10.3, 1.3, 1.3 Hz, 1H, H^{a}), 4.74−4.64 (m, 2H, H^{d,g}), 3.91 (s, 2H, SCH_2), 3.69, 3.67 (each s, 6 H, CO_2-Me), 3.10−2.99 (m, 2H, H^{e,f}). ^{13}C NMR ($CDCl_3$): *δ* 171.1, 171.0, 136.8, 136.3, 128.8, 128.6, 128.4, 127.3, 125.4, 117.6, 81.3, 81.3, 52.2, 52.0, 36.8. MS (*m*/*z* (relative intensity, %)): 271 (14), 239 (14), 159 (25), 127 (15), 91 (100), 87 (13), 65 (22), 59 (22), 55 (22). Anal. Calcd for $C_{19}H_{22}O_5S$: C, 62.96; H, 6.12. Found: C, 63.88; H, 6.33.

Compound 9.



^1H NMR ($CDCl_3$): *δ* 6.42 (d, *J* = 15.2 Hz, H^{i}), 5.89 (ddd, *J* = 17.0, 10.3, 6.0 Hz, H^{c}), 5.53 (dd, *J* = 15.2, 7.1 Hz, H^{h}), 5.40 (dd, *J* = 17.0, 1.3 Hz, H^{b}), 5.23 (dd, *J* = 10.3, 1.3 Hz, 1H, H^{a}), 4.77−4.66 (m, H^{d,g}), 3.70, 3.69 (each s, CO_2Me), 3.15−3.05 (m, H^{e,f}), 2.72 (q, *J* = 7.5 Hz, CH_2CH_3), 1.30 (t, *J* = 7.5 Hz, CH_2CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): *δ* 171.2, 171.0, 136.4, 129.1, 124.2, 117.6, 81.5, 81.3, 52.3, 52.2, 26.1, 14.3. MS (*m*/*z* (relative intensity, %)): 300 (M^+, 1), 239 (20), 207 (15), 188 (12), 159 (16), 153 (12), 127 (100), 125 (17), 121 (14), 115 (27), 111 (21), 97 (21), 93 (17), 87 (27), 81 (12), 71 (13), 67 (11), 66 (13), 65 (21), 60 (18), 59 (78), 55 (71), 53 (23). Anal. Calcd for $C_{14}H_{20}O_5S$: C, 55.98; H, 6.71. Found: C, 56.10; H, 6.54.

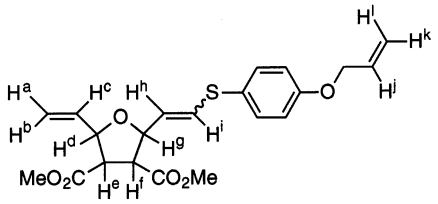
Compound 12.



^1H NMR ($CDCl_3$): *δ* 7.37−7.26 (m, 4H, C_6H_4), 6.69 (dd, *J* = 17.8, 11.0 Hz, 1H, H^{j}), 6.40 (dd, *J* = 15.0, 1.1 Hz, 1H, H^{i}), 5.84 (ddd, *J* = 16.4, 10.4, 6.0 Hz, 1H, H^{c}), 5.73 (dd, *J* = 17.8, 0.9 Hz, 1H, H^{l}), 5.59 (dd, *J* = 15.0, 6.8 Hz, 1H, H^{h}), 5.37 (ddd, *J* = 16.4, 1.4, 1.4 Hz, 1H, H^{b}), 5.24 (dd, *J* = 11.0, 0.9 Hz, 1H,

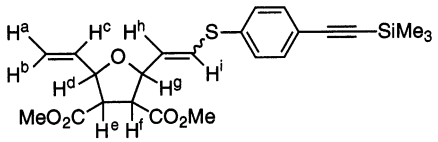
H^k), 5.20 (ddd, J = 10.4, 1.4, 1.4 Hz, 1H, H^a), 4.73−4.64 (m, 2H, $H^{d,g}$), 3.89 (s, 2H, SCH_2), 3.69, 3.67 (each s, 6H, CO_2Me), 3.10−2.99 (m, 2H, $H^{e,f}$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 171.1, 170.9, 136.7, 136.4, 136.3, 129.0, 128.3, 126.4, 125.6, 117.5, 113.9, 81.3, 81.2, 52.2, 52.0, 36.6. MS (*m*/*z* (relative intensity, %)): 388 (M^+, 0.25), 271 (13), 239 (11), 159 (12), 117 (100), 91 (11), 59 (14), 55 (15). Anal. Calcd for $C_{21}H_{24}O_5S$: C, 64.93; H, 6.23. Found: C, 64.67; H, 6.51.

Compound 13.



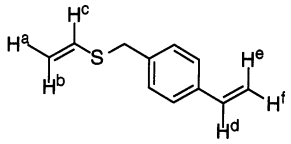
^1H NMR ($CDCl_3$): δ 7.36−7.30, 6.92−6.85 (each m, *E*- and *Z*-Ar), 6.52 (dd, J = 15.0, 1.1 Hz, *E*-H^i), 6.38 (dd, J = 9.5, 0.9 Hz, *Z*-H^i), 6.05 (ddt, J = 17.2, 10.4, 5.3 Hz, *E*-H^j), 6.04 (ddt, J = 17.2, 10.4, 5.3 Hz, *Z*-H^j), 5.92 (ddd, J = 17.0, 10.4, 6.1 Hz, *Z*-H^c), 5.86 (ddd, J = 17.0, 10.4, 6.1 Hz, *E*-H^c), 5.68 (dd, J = 9.5, 8.2 Hz, *Z*-H^h), 5.54 (dd, J = 15.0, 6.8 Hz, *E*-H^h), 5.42 (ddt, J = 17.2, 2.7, 1.5 Hz, *E*- and *Z*-H^l), 5.38 (ddd, J = 17.0, 1.3, 1.3 Hz, *E*- and *Z*-H^b), 5.30 (ddt, J = 10.4, 2.7, 1.5 Hz, *E*- and *Z*-H^k), 5.21 (ddd, J = 10.4, 1.5, 1.3 Hz, 1H, *E*- and *Z*-H^a), 4.77−4.72, 4.69−4.64 (each m, *E*- and *Z*-$H^{d,g}$), 4.54 (ddd, J = 5.3, 1.5, 1.5 Hz, *E*- and *Z*-OCH_2), 3.69 (s, *E*- and *Z*-CO_2Me), 3.21−3.02 (m, *E*- and *Z*-$H^{e,f}$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 171.1, 171.0, 158.6, 136.3, 133.8, 132.9, 130.1, 126.3, 123.8, 118.0, 117.7, 115.6, 81.4, 81.1, 68.9, 52.2, 52.2, 52.1. MS (*m*/*z* (relative intensity, %)): *E* and *Z* isomers 404 (M^+, 11), 260 (18), 239 (18), 219 (25), 207 (31), 179 (37), 175 (19), 166 (22), 165 (14), 153 (11), 151 (27), 147 (16), 133 (12), 127 (79), 125 (28), 121 (22), 111 (26), 109 (11), 107 (10), 97 (15), 93 (19), 91 (11), 81 (13), 79 (18), 71 (19), 67 (14), 66 (14), 65 (28), 59 (74), 55 (100), 53 (22). Anal. Calcd for $C_{21}H_{24}O_6S$: C, 62.36; H, 5.98. Found: C, 61.99; H, 5.91.

Compound 14.



^1H NMR ($CDCl_3$): δ 7.42−7.38, 7.27−7.24 (m, *E*- and *Z*-Ar), 6.59 (dd, J = 15.0, 1.1 Hz, *E*-H^i), 6.46 (dd, J = 9.5, 1.1 Hz, *Z*-H^i), 5.89 (dd, J = 15.0, 6.6 Hz, *E*-H^h), 5.88 (ddd, J = 17.0, 10.4, 6.0 Hz, *E*-H^c), 5.40 (ddd, J = 17.0, 1.5, 1.3 Hz, *E*-H^b), 5.24 (ddd, J = 10.4, 1.3, 1.3 Hz, *E*-H^a), 4.85−4.80, 4.72−4.68 (each m, *E*- and *Z*-$H^{d,g}$), 3.72, 3.71 (each s, *E*- and *Z*-CO_2Me), 3.19−3.06 (m, *E*- and *Z*-$H^{e,f}$), 0.25 (s, *E*- and *Z*-$SiMe_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 171.2, 170.8, 136.3, 135.5, 132.5, 132.4, 130.9, 130.2, 129.0, 128.6, 128.0, 126.5, 121.5, 117.7, 113.4, 104.4, 95.2, 81.7, 81.6, 80.8, 77.6, 77.2, 52.3, 52.0, 0.1. MS (*m*/*z* (relative intensity, %)): *E* and *Z* isomerd 444 (M^+, 2), 259 (10), 239 (23), 207 (26), 179 (11), 175 (12), 127 (100), 121 (14), 115 (12), 111 (17), 93 (10), 73 (18), 59 (38), 55 (50), 53 (10), 44 (17), 41 (12). Anal. Calcd for $C_{23}H_{28}O_5SSi$: C, 62.13; H, 6.35. Found: C, 62.01; H, 6.19.

Preparation of 4-Vinylbenzyl Vinyl Sulfide. To a white suspension of lithium ethenethiolate (3.8 mmol), which was prepared from lithium wire (47 mg, 6.8 mmol), ethyl vinyl sulfide (0.39 mL, 3.8 mmol), and ammonium chloride (0.20 g, 3.8 mmol) in liquid ammonia (ca. 5 mL) according to the literature,[25] was added dropwise a solution of 4-vinylbenzyl chloride (0.48 mL, 3.4 mmol) in THF (2.5 mL) over 5 min at −70 °C. The mixture was kept at room temperature with stirring to remove ammonia. Then the resulting suspension was stirred at 40 °C for 30 min. To this reaction mixture was carefully added water (5 mL) at room temperature. The crude product was extracted with ether (5 mL × 3), and the combined extracts were washed with brine and dried over anhydrous Na_2SO_4. The solution was filtered and evaporated to give a yellow oil, which was purified by flash column chromatography with hexane as eluent. Evaporation of the eluate gave the title compound (220 mg, 32% yield) as a yellow oil.

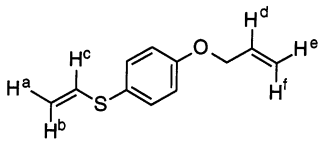


^1H NMR ($CDCl_3$): δ 7.42−7.28 (m, 4H, C_6H_4), 6.71 (dd, J = 17.6, 10.8 Hz, 1H, H^d), 6.36 (dd, J = 16.7, 10.1 Hz, 1H, H^c), 5.74 (dd, J = 17.6, 0.9 Hz, 1H, H^e), 5.25 (dd, J = 10.8, 0.9 Hz, 1H, H^f), 5.21 (dd, J = 10.1, 0.6 Hz, 1H, H^a), 5.17 (dd, J = 16.7, 0.6 Hz, 1H, H^b), 3.91 (s, 2H, SCH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 136.7, 136.6 (each s, C_6H_4), 136.3 (s, $C_6H_4CH{=}CH_2$), 131.8 (s, $SCH{=}CH_2$), 129.0, 126.4 (each s, C_6H_4), 113.9 (s, $C_6H_4CH{=}CH_2$), 111.7 (s, $SCH{=}CH_2$), 35.9 (s, SCH_2). MS (*m*/*z* (relative intensity, %)): 176 (M^+, 16), 117 (100), 115 (37), 91 (19), 65 (11), 51 (11). Anal. Calcd for $C_{11}H_{12}S$: C, 74.95; H, 6.86. Found: C, 74.69; H, 6.82.

Preparation of 4-(Allyloxy)benzenethiol. To a solution of (4-(allyloxy)phenyl)magnesium bromide, which was prepared from 4-(allyloxy)phenyl bromide (5.43 mg, 25.5 mmol) and magnesium (0.690 g, 28.4 mmol) in THF (26 mL), was slowly added sulfur (0.736 g, 22.9 mmol) at room temperature. The mixture was stirred at room temperature for 3 h and then quenched with water. After the mixture was acidified with 5% HCl, the organic layer was separated. The aqueous layer was extracted with ether (100 mL × 3). The combined organic layers were washed with brine and dried over anhydrous $MgSO_4$. The solution was filtered and evaporated to give a yellow oil, which was purified by distillation under reduced pressure (0.14 mmHg, 60 °C). The title compound was obtained as a colorless oil (2.27 g, 59%). ^1H NMR ($CDCl_3$): δ 7.28−7.23, 6.84−6.80 (m, 4H, C_6H_4), 6.04 (ddt, J = 17.2, 10.4, 5.3 Hz, 1H, $CH{=}CH_2$), 5.40 (ddt, 17.2, 1.7, 1.5 Hz, 1H, $CH{=}CH_2$), 5.29 (ddt, J = 10.4, 1.5, 1.5 Hz, 1H, $CH{=}CH_2$), 4.51 (ddd, J = 5.3, 1.7, 1.5 Hz, 2H, OCH_2), 3.36 (s, 1H, SH). ^{13}C NMR ($CDCl_3$): δ 157.4 (s, Ar), 133.0 (s, $CH{=}CH_2$), 132.3 (s, Ar), 120.1 (s, Ar), 117.8 (s, $CH{=}CH_2$), 115.5 (s, Ar), 68.9 (s, OCH_2). MS (*m*/*z* (relative intensity, %)): 166 (M^+, 46), 125 (100), 97 (31), 69 (11), 53 (15). Anal. Calcd for $C_9H_{10}OS$: C, 65.03; H, 6.06. Found: C, 65.32; H, 6.19.

Preparation of 4-(Allyloxy)phenyl Vinyl Sulfide. 4-(Allyloxy)benzenethiol (1.49 g, 9.00 mmol) was added dropwise to a solution of NaOEt (prepared by dissolving 0.21 g (9.0 mmol) of sodium in 3.6 mL of EtOH) over 10 min at room temperature. The resulting solution was then added dropwise to 1,2-dibromoethane (2.37 g, 12.6 mmol) over 20 min at room temperature. After the mixture was stirred for 1 h, a solution of NaOEt (prepared by dissolving 0.36 g (16 mmol) of sodium in 7.2 mL of EtOH) was added dropwise over 30 min. The reaction mixture was heated to reflux overnight. The resulting yellow suspension was cooled to room temperature and then poured into 50 mL of water. The mixture was extracted with ether (50 mL × 3). The combined organic layers were washed with brine and dried over anhydrous $MgSO_4$. The solution was filtered and evaporated to give a yellow oil, which was purified by flash column chromatography with hexane/CH_2Cl_2 (4:1) as eluent. Evaporation of the eluate gave the title compound (0.86 g, 49% yield) as a colorless oil.

(25) Wijers, H. E.; Boelens, H.; van der Gen, A.; Brandsma, L. *Recl. Trav. Chim. Pays-Bas* **1969**, *88*, 519−529.



^{1}H NMR ($CDCl_3$): δ 7.38−7.33, 6.93−6.88 (each m, 4H, Ar), 6.47 (dd, J = 16.5, 9.7 Hz, 1H, H^c), 6.05 (ddt, J = 17.6, 10.6, 5.3 Hz, 1H, H^d), 5.42 (ddt, J = 17.6, 3.1, 1.5 Hz, 1H, H^f), 5.30 (ddt, J = 10.6, 3.1, 1.5 Hz, 1H, H^e), 5.22 (d, J = 9.7 Hz, 1H, H^a), 5.10 (d, J = 16.5 Hz, 1H, H^b), 4.54 (ddd, J = 5.3, 1.5, 1.5 Hz, 2H, OCH_2). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 158.6 (s, Ar), 134.0 (s, $OCH_2CH{=}CH_2$), 133.6 (s, Ar), 132.9 (s, $SCH{=}CH_2$), 123.7 (s, Ar), 117.9 (s, $OCH_2CH{=}CH_2$), 115.6 (s, Ar), 112.7 (s, $SCH{=}CH_2$), 68.7 (s, OCH_2). MS (*m*/*z* (relative intensity, %)): 192 (M^+, 61), 152 (10), 151 (97), 123 (20), 108 (10), 107 (100), 97 (10), 79 (18), 77 (14), 69 (12), 63 (12), 53 (13). Anal. Calcd for $C_{11}H_{12}OS$: C, 68.71; H, 6.29. Found: C, 69.05; H, 6.16.

Preparation of 4-Iodophenyl Vinyl Sulfide. Ethylene gas was gently bubbled into a solution of bis(4-iodophenyl) disulfide (2.67 g, 5.68 mmol) in CH_2Cl_2 (56 mL). A solution of bromine (1.0 g, 6.3 mmol) in CH_2Cl_2 (4 mL) was slowly added over 10 min at room temperature. Ethylene was added continuously until the color of bromine disappeared. DBU (1.80 g, 11.8 mmol) was added at room temperature, and the reaction mixture was refluxed for 27 h. The reaction mixture was cooled to room temperature and then quenched with 1.0 M aqueous ammonia (10 mL). The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (50 mL × 2). The combined organic layers were washed with water and dried over anhydrous $MgSO_4$. After the drying agent was filtered off, the solution was concentrated to dryness to give a brown liquid. The crude product was purified by flash column chromatography with hexane as eluent to give the title compound as a colorless oil (1.91 g, 64% yield). ^{1}H NMR ($CDCl_3$): δ 7.66−7.62, 7.12−7.08 (each m, 4H, C_6H_4), 6.49 (dd, J = 16.5, 9.5 Hz, 1H, $SCH{=}CH_2$), 5.41 (d, J = 9.5 Hz, 1H, $SCH{=}CH_2$), 5.39 (d, J = 16.5 Hz, 1H, $SCH{=}CH_2$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 138.1, 134.5 (each s, C_6H_4), 131.8 (s, $SCH{=}CH_2$), 130.8 (s, C_6H_4), 116.9 (s, $SCH{=}CH_2$), 92.1 (s, C_6H_4). MS (*m*/*z* (relative intensity, %)): 262 (M^+, 94), 217 (13), 136 (11), 135 (98), 134 (41), 109 (15), 108 (34), 91 (100), 90 (11), 82 (14), 76 (19), 75 (11), 74 (15), 69 (31), 65 (21), 63 (23), 59 (16), 58 (24), 51 (17), 50 (51). Anal. Calcd for C_8H_7IS: C, 36.66; H, 2.69. Found: C, 36.95; H, 2.89.

Preparation of 4-((Trimethylsilyl)ethynyl)phenyl Vinyl Sulfide. A mixture of 4-iodophenyl vinyl sulfide (1.49 g, 5.68 mmol), (trimethylsilyl)acetylene (0.67 g, 6.9 mmol), $PdCl_2(PPh_3)_2$ (222 mg, 0.230 mmol), CuI (11 mg, 0.057 mmol), and diethylamine (24 mL) was stirred at room temperature for 5 h. Volatile materials were removed by pumping, and the residue was poured into water. The mixture was extracted with ether (100 mL × 3). The combined organic extracts were washed with brine and dried over anhydrous $MgSO_4$. The solution was filtered and evaporated to give a brown solid. The crude product was purified by flash column chromatography with hexane as eluent to give the title compound as a yellow crystals (0.97 g, 92% yield). ^{1}H NMR ($CDCl_3$): δ 7.42−7.38, 7.29−7.24 (m, 4H, C_6H_4), 6.52 (dd, J = 16.7, 9.5 Hz, 1H, $SCH{=}CH_2$), 5.43 (d, J = 9.5 Hz, 1H, $SCH{=}CH_2$), 5.43 (d, J = 16.7 Hz, 1H, $CH{=}CH_2$), 0.25 (s, 9H, $SiMe_3$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 135.5 (s, Ar), 132.5 (s, $SCH{=}CH_2$), 130.6, 129.2, 121.5 (each s, Ar), 117.2 (s, $SCH{=}CH_2$), 104.4, 95.1 (each s, C≡C), 0.1 (s, $SiMe_3$). MS (*m*/*z* (relative intensity, %)): 232 (M^+, 51), 219 (11), 218 (23), 217 (15), 115 (13), 108 (23), 43 (16). Anal. Calcd for $C_{13}H_{16}SSi$: C, 67.18; H, 6.94. Found: C, 67.00; H, 6.79.

Table 6. ROMP of Norbornene (NBE) Catalyzed by 1a in the Presence of Phenyl Vinyl Sulfide (PVS)[a]

run	NBE/PVS (molar ratio)	yield (%)[b]	$M_{n,theor}$[c]	$M_{n,NMR}$	$M_{n,GPC}$[d]	PDI[d]
1	100/1	98	9600	10900	21600	2.12
2	100/2	95	4800	5600	12200	1.99
3	100/6	89	1700	1900	3600	1.97
4	100/10	91	1100	1100	2500	1.71

[a] All reactions were carried out in CH_2Cl_2 at room temperature for 30 min. Initial concentration: $[NBE]_0$ = 0.10 M, $[\mathbf{1a}]_0$ = 2.0 mM. [b] Isolated yield based on the total amount of NBE and phenyl vinyl sulfide employed. [c] $M_{n,theor} = M_w(NBE) \times$ (molar ratio) + $M_w(PVS)$. [d] Determined by GPC on the basis of polystyrene standards.

ROMP of Norbornene in the Presence of Phenyl Vinyl Sulfide (Figure 3). A typical procedure (Table 6, run 2) is as follows. To a solution of norbornene (180 mg, 1.91 mmol) and phenyl vinyl sulfide (5.2 mg, 38 μmol) in CH_2Cl_2 (19 mL) was added **1a** (32 mg, 37 μmol) at room temperature. The mixture was stirred for 10 min. GLC analysis revealed the complete consumption of norbornene and phenyl vinyl sulfide. The resulting solution was concentrated to ca. 5 mL and then slowly added to a vigorously stirred MeOH to give a white suspension. The precipitate was collected by filtration, washed with MeOH, and dried under vacuum (176 mg, 95%). The ^{1}H NMR data was identical with those previously reported.[1] The results of polymerization at four different ratios of norbornene (NBE) to phenyl vinyl sulfide (PVS) are listed in Table 6.

Supporting Information Available: Details of the structure determinations of **1b** and **1e**, including figures giving the atomic numbering schemes and tables of atomic coordinates, thermal parameters, and all bond distances and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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