2084 *Organometallics* **2000,** *19,* 2084−2089

Ruthenium Benzylidene and Vinylidene Complexes in a Sulfur-Rich Coordination Environment

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Received January 24, 2000

Interaction of $Ru({=}CHPh)(PCy_3)_2Cl_2$ (Cy = cyclohexyl) with $K[N(PPh_2S)_2]$ affords air-stable $Ru({=}CHPh)[N(PPh_2S)_2]_2$, **1**, which has been characterized by X-ray diffraction. The $Ru{-}C_\alpha$ and average Ru−S distance for **1** are 1.88(2) and 2.377 Å, respectively. Reaction of **1** with CO gives *cis*-$Ru(CO)_2[N(PPh_2S)_2]_2$. Complex **1** undergoes metathesis with ethyl vinyl ether to give the methoxycarbene complex $Ru({=}CHOEt)[N(PPh_2S)_2]_2$, **3**. Treatment of $Ru({=}CHPh)(PCy_3)_2Cl_2$ with $K[N(PPh_2Se)_2]$ affords $Ru({=}CHPh)[PPh_2NP(Se)Ph_2]_2$, **4**, which has been characterized by X-ray crystallography. The Ru−C, average Ru−P, and average Ru−Se distances are 1.873(8), 2.383, and 2.450 Å, respectively. Reactions of $Ru({=}CHPh)(PCy_3)_2Cl_2$ with $K[P(OR)_2S_2]$ afford *cis*-$Ru({=}CHPh)(PCy_3)[P(OR)_2S_2]_2$ (R = Et (**6**) and *i*-Pr (**7**)). Reaction of $Ru({=}CHPh)(PCy_3)_2Cl_2$ with 1,4,7-trithiacyclononane ([9]aneS_3) gives $[([9]aneS_3)Ru({=}CHPh)(PCy_3)Cl]Cl$, **8**. Treatment of $Ru({=}C{=}CHPh)(PCy_3)_2Cl_2$ with $K[N(PPh_2S)_2]$ or [9]aneS_3 affords *cis*-$Ru({=}C{=}CHPh)(PCy_3)[N(PPh_2S)_2]_2$ (**9**) or $([9]aneS_3)Ru(PCy_3)Cl_2$ (**10**), respectively. The Ru−C, Ru−P, and average Ru−S distances in **9** are 1.80(1), 2.420(3), and 2.479 Å, respectively. Complexes **1** and **8** are active catalysts for ring-opening metathesis polymerization of norbornene.

Introduction

Ruthenium alkylidene (or Schrock-type carbene) complexes have attracted much attention due to their applications to ring-opening metathesis polymerization (ROMP) of cyclic olefins[1] and ring-closing metathesis of acyclic dienes.[2,3] Examples of well-defined ruthenium alkylidene species mostly contain soft π acid ligands such as phosphines, carbonyl, and nitrosyl.[1,4−6] Ruthenium alkylidene complexes supported by nitrogen donor ligands including porphyrins,[7] tetramethyldibenzotetraazaannulene,[8] and hydridotrispyrazolylborate,[9] N-heterocyclic carbene ligands,[10] and bridging halides[11] are also known. To our knowledge, there are very few examples of mononuclear ruthenium alkylidenes in sulfur- or selenium-rich coordination environments. Reaction of a ruthenium alkylidene complex with $Na[S_2CNMe_2]$ or $K[S_2COEt]$ was found to result in alkylidene−dithiocarbamate/xanthanate coupling and the formation of the corresponding metallacyle.[12] As part of our ongoing program in developing new catalysts for metathesis polymerization, we here describe the synthesis and crystal structures of ruthenium benzylidene and vinylidene complexes containing sulfur donor ligands, namely, bis(diphenylthiophosphoryl)imide $[N(PPh_2S)_2]^-$, dialkyldithiophosphate $[P(OR)_2S_2]^-$ (R = Et, *i*-Pr), and 1,4,7-trithiacyclononane ([9]aneS_3) (see below). Catalytic polymerization of norbornene with these ruthenium benzylidene complexes will be reported.

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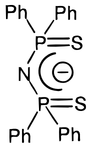
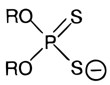
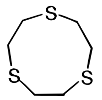
10.1021/om0000562 CCC: $19.00
Publication on Web 04/26/2000



$[N(PPh_2S)_2]^-$



$[P(OR)_2S_2]^-$
(R = Et, *i*-Pr)



[9]aneS_3

Experimental Section

General Consderations. All manipulations were carried out under nitrogen by standard Schlenk techniques. Solvents were purified, distilled, and degassed prior to use. NMR spectra were recorded on a Bruker ALX 300 spectrometer operating at 300, 75, and 121.5 MHz for ^{1}H, ^{13}C, and ^{31}P, respectively. Chemical shifts (δ, ppm) were reported with reference to $SiMe_4$ (^{1}H and ^{13}C) and H_3PO_4 (^{31}P). Infrared spectra (Nujol) were recorded on a Perkin-Elmer 16 PC FT-IR spectrophotometer. Molecular weights of poly(norbornene)s were estimated by a Waters Associates 510 gel permeation chromatograph (GPC) using 12 monodispersed polystyrenes as calibration standards. Elemental analyses were performed by Medac Ltd, Surrey, U.K.

Materials. $K[N(PPh_2Q)_2]$ (Q = S, Se),[13] $K[PS_2(OR)_2]$ (R = Et, *i*-Pr),[14] and Ru(=C=CHPh)$(PCy_3)_2Cl_2$ (Cy = cyclohexyl)[15] were prepared according to the literature methods. Ru(=CHPh)$(PCy_3)_3Cl_2$ and 1,4,7-trithiacyclononane ([9]aneS_3) were purchased from Strem Ltd and Aldrich Ltd, respectively.

Preparation of Ru(=CHPh)[N(PPh$_2$S)$_2$]$_2$ (1). To a suspension of $K[N(PPh_2S)_2]$ (0.119 mg, 0.24 mmol) in THF (20 mL) was added Ru(=CHPh)$Cl_2(PCy_3)_2$ (0.1 g, 0.12 mmol), and the mixture was stirred at room temperature for 48 h. The solvent was pumped off, and the residue was recrystallized from CH_2Cl_2/Et_2O to give reddish brown crystals (yield 100 mg, 76%). ^{1}H NMR ($CDCl_3$): δ 7.07−7.85 (m, 45H, phenyl protons), 18.16 (s, 1H, H_α). ^{31}C{^{1}H} NMR ($CDCl_3$): δ 298.88 (s, C_α). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 36.59 (s). Anal. Calcd for $C_{55}H_{46}N_2P_4RuS_4$: C, 60.7; H, 4.2; N, 2.6. Found: C, 58.7; H, 4.1; N, 2.4.

Reaction of 1 with CO. To a solution of **1** (50 mg, 0.046 mmol) in CH_2Cl_2 (10 mL) was bubbled with CO for 2 min, during which time the color changed from brown to yellow. The resulting mixture was stirred at room temperature for 30 min and was evaporated to dryness. Recrystallization from CH_2Cl_2/hexane gave bright yellow crystals (yield: 34 mg, 70%), which were identified as *cis*-Ru(CO)$_2$[N(PPh$_2$S)$_2$]$_2$[18] by NMR and IR spectroscopy.

Reaction of 1 with 1-Hexene. To a solution of **1** (50 mg, 0.046 mmol) in CH_2Cl_2 with added excess 1-hexene (0.1 mL), and the mixture was stirred at room temperature for 1 day. The solvent was pumped off, and the residue was recrystallized from CH_2Cl_2/Et_2O to give a brown solid. The product was found to be a ca. 1:1 mixture of **1** and the pentylidene species Ru(=CH-*n*-Bu)[N(PPh$_2$S)$_2$]$_2$ (**2**) according to ^{1}H NMR spectroscopy. Spectroscopic data for **2**: ^{1}H NMR ($CDCl_3$): δ 0.44 (dd, 2H, CH_2), 0.60 (t, 3H, CH_3), 0.74 (dd, 2H, CH_2), 1.39 (dt, 2H, CH_2), 7.07−7.85 (m, phenyl protons, overlapped with those for **1**), 17.95 (t, J = 4 Hz, 1H, H_α). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 35.87 (s).

Preparation of Ru(=CHOEt)[N(PPh$_2$S)$_2$]$_2$ (3). To a solution of **1** (50 mg, 0.046) was added excess ethyl vinyl ether (0.1 mL), and the mixture was stirred at room temperature overnight. The solvent was pumped off, and the residue was recrystallized from CH_2Cl_2/Et_2O to give orange crystals (yield: 35 mg, 73%). ^{1}H NMR ($CDCl_3$): δ 0.66 (t, 3H, CH_3), 2.97 (q, 2H, CH_2), 7.07−7.80 (m, 20H, phenyl protons), 13.64 (s, 1H, H_α). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 36.09 (s). Anal. Calcd for $C_{51}H_{46}N_2OP_4RuS_4$: C, 58.0; H, 4.4; N, 2.7. Found: C, 57.1; H, 4.3; N, 2.6.

Reaction of Ru(=CHPh)(PCy$_3$)$_2$Cl$_2$ with K[N(PPh$_2$Se)$_2$]. To a suspension of $K[N(PPh_2Se)_2]$ (0.14 g, 0.24 mmol) in THF (20 mL) was added Ru(=CHPh)$(PCy_3)_2Cl_2$ (0.1 g, 0.12 mmol), and the mixture was stirred for 24 h. The solvent was pumped off, and the residue was washed with hexane to give a dark solid. NMR spectroscopy indicates that the dark product consists of a mixture of two ruthenium benzylidene species. Recrystallization from CH_2Cl_2/hexane afforded a dark brown crystalline solid, which was characterized as Ru(=CHPh)-[$Ph_2PNP(Se)Ph_2$]$_2$, **4** (yield: 21 mg, 15%). The other ruthenium benzylidene species, presumably Ru(=CHPh)[N(PPh$_2$Se)$_2$]$_2$ (**5**) [δ^H 16.8 (s, H_α), δ^P 22.11 (s), MS (FAB): m/z 1276 (M^+)], in the oily residue did not crystallize. Characterization data for **4**: ^{1}H NMR ($CDCl_3$): δ 7.06−7.92 (m, 20H, Ph), 15.17 (t, J_{PH} = 16.8 Hz, 1H, H_α). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 53.87 (t, J = 75 Hz, *P*Ph$_2$Se), 102.72 (t, J = 75 Hz, *P*Ph$_2$). Anal. Calcd for $C_{55}H_{46}N_2P_4RuSe_2$: C, 59.0; H, 4.1; N, 2.5. Found: C, 58.6; H, 4.2; N, 2.5.

Preparation of Ru(=CHPh)(PCy$_3$)[P(OEt)$_2$S$_2$]$_2$ (6). To a suspension of $K[P(OEt)_2S_2]$ (54 mg, 0.24 mmol) in THF (20 mL) was added Ru(=CHPh)$(PCy_3)_2Cl_2$, and the resulting mixture was stirred at room temperature for 2 h. The solvent was pumped off, and the residue was recrystallized from CH_2Cl_2/hexane to give green crystals (yield 80 mg, 78%). ^{1}H NMR ($CDCl_3$): δ 1.23−1.36 (overlapping t, 10H, CH_2CH_3), 1.52−2.45 (m, 33H, Cy protons), 4.26−4.54 (m, 10H, CH_2CH_3), 7.40−7.63 (m, 5H, C_6H_5), 20.03 (d, J = 13.8 Hz, 1H, H_α). ^{31}C{^{1}H} NMR ($CDCl_3$): δ 317.57 (d, J = 16.5 Hz, C_α). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 30.88 (t, J = 6.1 Hz, PCy_3), 102.60 (d, J = 6 Hz, $[P(OEt)_2S_2]^-$). Anal. Calcd for $C_{33}H_{59}O_4P_3RuS_4$: C, 47.1; H, 7.1. Found: C, 47.0; H, 7.2.

Preparation of Ru(=CHPh)(PCy$_3$)[P(O-*i*-Pr)$_2$S$_2$]$_2$ (7). This was prepared similarly as for **3** using K[P(O-*i*-Pr)$_2$S$_2$] instead of $K[P(OEt)_2S_2]$ (yield: 80 mg, 73%. %). ^{1}H NMR (C_6D_6): δ 1.37−2.78 (m, 57H, cyclohexyl and $CH(CH_3)_2$), 5.03−5.37 (m, 4H, $CH(CH_3)_2$), 7.40−7.59 (m, 5H, C_6H_5), 19.94 (d, J = 14.4 Hz, 1H, H_α). ^{31}C{^{1}H} NMR (C_6D_6): δ 317.25 (d, J = 14.8 Hz, C_α). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 31.95 (m, PCy_3), 100.69 (s, [P(O-*i*-Pr)$_2$S$_2$]$^-$). Anal. Calcd for $C_{37}H_{67}O_4P_3RuS_4$: C, 49.5; H, 7.5. Found: C, 49.9; H, 7.8.

Preparation ([9]aneS$_3$)Ru(=CHPh)(PCy$_3$)Cl$_2$ (8). To a solution of Ru(=CHPh)$Cl_2(PCy_3)_2$ (0.1 g, 0.12 mmol) in CH_2Cl_2 was added 1 equiv of [9]aneS_3, and the mixture was stirred at room temperature for 1 day, during which the color changed from purple to yellow. The solvent was pumped off, and the residue was extracted with CH_2Cl_2. Recrystallization from CH_2Cl_2/hexane afforded a yellowish green powder (yield 50%). ^{1}H NMR ($CDCl_3$): δ 1.24−2.16, 2.81−3.82 (m, 45H, Cy protons and SCH_2), 7.56, 7.81, 8.59 (m, 5H, Ph protons), 17.75 (d, J_{PH} = 14.4 Hz, 1H, H_α). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 31.98 (s). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 319.2 (s br, C_α). MS (FAB): m/z 722 (M^+). Despite several attempts, we have not been obtained good carbon analysis for the compound.

Preparation of *cis*-Ru(=C=CHPh)(PCy$_3$)[N(PPh$_2$S)$_2$]$_2$ (9). To a suspension of $K[N(PPh_2S)_2]$ (0.119 mg, 0.24 mmol) in THF (20 mL) was added Ru(=C=CHPh)$Cl_2(PCy_3)_2$ (0.1 g, 0.12 mmol), and the mixture was stirred at room temperature for 48 h. The solvent was pumped off, and the residue was recrystallized from CH_2Cl_2/hexane to give orange brown crystals (yield 80 mg, 48%). ^{1}H NMR (THF-d_8): δ 0.95−2.59 (m, 33H, Cy protons), 4.02 (d, J = 3.2 Hz, 1H, Ru=C=C*H*Ph),

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Table 1. Crystallographic Data and Experimental Details for Ru(=CHPh)[N(PPh$_2$S)$_2$]$_2$ (1), Ru(=CHPh)[Ph$_2$PNP(Se)Ph$_2$]$_2$ (4), and *cis*-Ru(=C=CHPh)(PCy$_3$)[N(PPh$_2$S)$_2$]$_2$ (9)

	1	**4**	**9**
empirical formula	$C_{54}H_{46}N_2P_4RuS_4$	$C_{55}H_{46}N_2P_4RuSe_2$	$C_{74}H_{79}N_2P_5RuS_4$
fw	1088.19	1117.87	1380.66
color, habit	red, block	red, block	red, block
a, Å	10.006(1)	10.986(1)	21.573(3)
b, Å	11.213(1)	11.401(1)	14.281(3)
c, Å	13.687(1)	21.140(2)	23.245(3)
α, deg	69.54(2)	86.24(1)	
β, deg	91.40(2)	82.78(1)	107.110(9)
γ, deg	61.37(2)	69.49(1)	
V, Å^3	1241.1(4)	2459.7(4)	6844(1)
Z	1	2	4
cryst syst	triclinic	triclinic	monoclinic
space group	*P*1 (no. 1)	$P\bar{1}$ (no. 2)	$P2_1/n$ (no. 14)
D_{calc}, g cm^{-3}	1.456	1.509	1.133
T, °C	25	25	25
λ, Å	0.71073	0.71073	0.71073
scan type	*ω*	*ω*	$\omega-2\theta$
$2\theta_{\max}$, deg	50.3	55.1	49.4
μ, cm^{-1}	6.53	19.68	4.13
no. of refln measd	4469	28 673	10 584
no. of reflns obsd ($I > 1.5\sigma(I)$)	1920	5513	4622
weighting scheme	$1/[\sigma^2(F_o)+0.02F_o{}^2/4]$	$1/[\sigma^2(F_o)+0.038F_o{}^2/4]$	$1/[\sigma^2(F_o)+0.009F_o{}^2/4]$
R^a	0.069	0.062	0.084
$R_w{}^b$	0.070	0.054	0.067
F(000)	558	1124	2324
GoF^c	1.11	1.04	1.63

[a] $R = (\Sigma|F_o| - |F_c|)/\Sigma|F_o|$. [b] $R_w = [(\Sigma w|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$. [c] $\mathrm{GoF} = [(\Sigma w|F_o| - |F_c|)^2/(N_{\mathrm{obs}} - N_{\mathrm{param}}]^{1/2}$.

6.71−8.30 (m, 45H, phenyl protons). ^{31}C{^{1}H} NMR (CDCl$_3$): δ 348 (d, J_{PC}= 16.5 Hz, C$_\alpha$). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 19.81 (m), 32.75 (d), 37.54 (d), 37.81 (dd), 38.86 (dd). Anal. Calcd for $C_{74}H_{79}N_2P_5RuS_4$: C, 64.4; H, 5.8; N, 2.0. Found: C, 64.3; H, 6.0; N, 2.1.

Preparation of ([9]aneS$_3$)Ru(PCy$_3$)Cl$_2$ (10). To a solution of Ru(=C=CHPh)Cl$_2$(PCy$_3$)$_2$ (0.1 g, 0.12 mmol) in CH$_2$Cl$_2$ (20 mL) was added 1 equiv of [9]aneS$_3$ (22 mg, 0.12 mmol), and the mixture was stirred at room temperature overnight. The solvent was pumped off, and the residue washed with hexane. Recrystallization from CH$_2$Cl$_2$ afforded yellow crystals (yield: 40 mg, 56%). ^{1}H NMR (CDCl$_3$): δ 0.84−3.21 (m, Cy protons and SCH$_2$). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 25.81 (s). MS (FAB): *m/z* 632 (M$^+$). Anal. Calcd for $C_{24}H_{45}Cl_2PRuS_3 \cdot CH_2Cl_2$: C, 41.8; H, 6.6. Found: C, 43.0; H, 6.5.

Catalytic Polymerization of Norbornene. This was performed according to Grubbs' procedure.[1a] Typically, to a solution of norbornene (150 mg) in CH$_2$Cl$_2$ (5 mL) was added ruthenium catalyst (10 mg). The mixture was stirred at room temperature for 2 h and was treated with small amounts of 2,6-di-*tert*-butyl-4-methylphenol and ethyl vinyl ether in CH$_2$Cl$_2$. The solution was stirred for a further 20 min and filtered, and excess methanol was added. The polymer obtained was collected, washed with methanol, recrystallized from THF/methanol, and analyzed by GPC. The trans ratio of the poly(norbornene) was estimated by NMR spectroscopy.[16]

X-ray Diffraction Measurements. A summary of crystallographic data and experimental details for complexes **1**, **4**, and **9** are listed in Table 1. Intensity data were collected on a MAR-Research image-plate diffractometer (for **1**), a Bruker SMART CCD diffractometer (for **4**), and a Rigaku AFC7R diffractometer (for **9**) using graphite-monochromated Mo Kα radiation. All intensity data were corrected for Lorentz and polarization and absorption effects (with inter-image scaling for **1** and **4**). The structures were solved by direct methods and refined on *F* by full-matrix least-squares analyses. Hydrogen atoms were placed at the idealized positions (C−H = 0.95 Å). All calculations were performed using the TEXSAN[17] crystallographic software package. Selected bond lengths and angles for **1**, **4**, and **9** are listed in Tables 3−5, respectively. Final atomic coordinates are given in the Supporting Information.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Ru(=CHPh)[N(PPh$_2$S)$_2$]$_2$ (1)

Ru(1)−S(1)	2.338(7)	Ru(1)−S(2)	2.399(8)
Ru(1)−S(3)	2.395(7)	Ru(1)−S(4)	2.376(8)
Ru(1)−C(49)	1.88(2)		

S(1)−Ru(1)−S(2)	99.8(2)	S(1)−Ru(1)−S(3)	167.3(2)
S(1)−Ru(1)−S(4)	80.2(2)	S(1)−Ru(1)−C(49)	98.2(6)
S(2)−Ru(1)−S(3)	78.4(2)	S(2)−Ru(1)−S(4)	165.2(2)
S(2)−Ru(1)−C(49)	94.3(6)	S(3)−Ru(1)−S(4)	98.3(3)
S(3)−Ru(1)−C(49)	94.5(6)	S(4)−Ru(1)−C(49)	100.3(6)
Ru(1)−C(49)−C(50)	132(1)		

Table 3. Selected Bond Lengths (Å) and Angles (deg) for Ru(=CHPh)[Ph$_2$PNP(Se)Ph$_2$]$_2$ (4)

Ru(1)−Se(1)	2.471(1)	Ru(1)−Se(2)	2.428(1)
Ru(1)−P(1)	2.382(2)	Ru(1)−P(3)	2.383(2)
Ru(1)−C(1)	1.873(8)	Se(1)−P(2)	2.213(2)
Se(2)−P(4)	2.228(2)	P(1)−N(1)	1.647(6)
P(2)−N(1)	1.568(6)	P(3)−N(2)	1.647(6)
P(4)−N(2)	1.555(6)		

Se(1)−Ru(1)−Se(2)	150.28(4)	Se(1)−Ru(1)−P(1)	88.76(6)
Se(1)−Ru(1)−P(3)	88.14(6)	Se(1)−Ru(1)−C(1)	103.2(2)
Se(2)−Ru(1)−P(1)	89.68(6)	Se(2)−Ru(1)−P(3)	89.69(6)
Se(2)−Ru(1)−C(1)	106.4(2)	P(1)−Ru(1)−P(3)	172.61(8)
P(1)−Ru(1)−C(1)	88.0(3)	P(3)−Ru(1)−C(1)	99.2(3)
Ru(1)−Se(1)−P(2)	94.68(6)	Ru(1)−Se(2)−P(4)	99.73(6)
Ru(1)−P(1)−N(1)	114.0(2)	Ru(1)−P(3)−N(2)	114.3(2)
Se(1)−P(2)−N(1)	113.5(2)	Se(2)−P(4)−N(2)	113.6(3)
P(1)−N(1)−P(2)	117.8(4)	P(3)−N(2)−P(4)	121.9(9)

Results and Discussion

Ruthenium Benzylidene Complexes. The synthesis of ruthenium benzylidene complexes from Ru(=CHPh)(PCy$_3$)$_2$Cl$_2$ is summarized in Scheme 1.

Interaction of Ru(=CHPh)(PCy$_3$)$_2$Cl$_2$ with 2 equiv of K[N(PPh$_2$S)$_2$] afforded five-coordinate Ru(=CHPh)[N(PPh$_2$S)$_2$]$_2$, **1**, isolated as air-stable reddish brown crystals. Unlike the vinylidene analogue (see later section), the octahedral phosphine adduct Ru(=CHPh)(PCy$_3$)[N(PPh$_2$S)$_2$]$_2$ was not formed apparently due to steric reasons. The H$_\alpha$ of **1** appears as a singlet at δ

Table 4. Selected Bond Lengths (Å) and Angles (deg) for *cis*-Ru(=C=CHPh)(PCy$_3$)[N(PPh$_2$S)$_2$]$_2$ (9)

Ru(1)−S(1)	2.595(3)	Ru(1)−S(2)	2.424(3)
Ru(1)−S(3)	2.456(3)	Ru(1)−S(4)	2.439(3)
Ru(1)−P(5)	2.420(3)	Ru(1)−C(49)	1.80(1)
C(49)−C(50)	1.32(1)		
S(1)−Ru(1)−S(2)	88.4(1)	S(1)−Ru(1)−S(3)	87.3(1)
S(1)−Ru(1)−S(4)	83.0(1)	S(1)−Ru(1)−P(5)	88.9(1)
S(1)−Ru(1)−C(49)	175.8(3)	S(2)−Ru(1)−S(3)	90.2(1)
S(2)−Ru(1)−S(4)	171.3(1)	S(2)−Ru(1)−P(5)	87.9(1)
S(2)−Ru(1)−C(49)	92.4(4)	S(3)−Ru(1)−S(4)	90.0(1)
S(3)−Ru(1)−P(5)	175.9(1)	S(3)−Ru(1)−C(49)	88.6(3)
S(4)−Ru(1)−P(5)	91.3(1)	S(4)−Ru(1)−C(49)	96.3(4)
P(5)−Ru(1)−C(49)	95.2(3)	Ru(1)−C(49)−C(50)	172.4(9)
C(49)−C(50)−C(51)	128(1)		

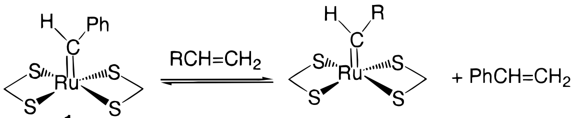
Table 5. Ru-Catalyzed Polymerization of Norbornene[a]

catalyst	% yield of poly(norbornene)	M_n	PDI[b]	% trans[c]
1	50	7.0×10^5	1.7	81
7	<5	1.5×10^4	5.1	86
8	92	2.7×10^5	3.5	87
10	trace	nd[d]	nd	nd

[a] Carried out under nitrogen at room temperature in 5 mL of CH$_2$Cl$_2$ for 2 h; [norbornene] = 0.32 M, [catalyst] = 0.002 M. [b] PDI = M_w/M_n. [c] Determined by NMR (ref 16). [d] Not determined.

18.57, which is slightly more upfield than that for Ru(=CHPh)(PCy$_3$)$_2$Cl$_2$ (δ 20.02).[1a] The resonant signal for C$_\alpha$ was found at δ 298.88, which is similar to that for Ru(=CHPh)(PCy$_3$)$_2$Cl$_2$ (δ 294.72).[1a] Complex **1** has been unambiguously characterized by X-ray diffraction. To our knowledge, **1** is the first example of ruthenium alkylidene in a sulfur-only coordination environment. Figure 1 shows a perspective view of **1**; selected bond lengths and angles are listed in Table 2. The geometry around Ru is square pyramidal with the benzylidene occupying the apical position. The Ru−C distance of 1.88(2) Å is typical for ruthenium alkylidenes. The benzylidene ligand lies on a symmetry plane between the two [N(PPh$_2$S)$_2$] ligands in order to minimize nonbonding repulsion among the phenyl rings. The average Ru−S distance (2.377 Å) is comparable to that for the related phosphine complex Ru(PPh$_3$)[N(PPh$_2$S)$_2$]$_2$, which also has a square pyramidal structure.[18]

Although complex **1** is a formally 16e complex, it does not react with Lewis bases such as pyridine and PPh$_3$ to give octahedral adducts. Reaction of **1** with CO led to formation of a yellow product, which displays intense ν_{CO} bands at 1980 and 2040 cm^{-1}. According to NMR and IR spectroscopy, this yellow compound was identified as Ru(CO)$_2$[N(PPh$_2$S)$_2$]$_2$, which has been prepared directly from [Ru(CO)$_2$Cl$_2$]$_x$ and K[N(PPh$_2$S)$_2$].[18] Like Ru(=CHPh)(PCy$_3$)$_2$Cl$_2$,[1b] complex **1** undergoes metathesis reaction of terminal olefins to give styrene and ruthenium carbenes. For example, reaction of **1** with 1 equiv of 1-hexene in CDCl$_3$ led to formation of a ca. 1:1 mixture of **1** and pentylidene complex Ru(=CH-*n*-Bu)[N(PPh$_2$S)$_2$]$_2$, **2**, characterized by NMR spectroscopy [δ 17.95 (t, $^2J_{HH}$ = 4 Hz, H$_\alpha$)] (eq 1). The crude product of **2** was found to be contaminated with **1**, which could not be separated by fractional recrystallization. However, reaction of **1** with CH(OEt)=CH$_2$ led to almost quantitative formation of the ethoxycarbene species Ru(=CHOEt)[N(PPh$_2$S)$_2$]$_2$, **3**, isolated as orange crystals after recrystallization from CH$_2$Cl$_2$/hexane. The H$_\alpha$ of **3** appears as a singlet at δ 13.64, which is more upfield than the alkylidene analogues.



(1)

R = *n*-Bu (**2**), OEt (**3**)

In an attempt to prepare ruthenium benzylidene complexes with selenium ligands, reaction of Ru(=CHPh)(PCy$_3$)$_2$Cl$_2$ with K[N(PPh$_2$Se)$_2$] was attempted. Treatment of Ru(=CHPh)(PCy$_3$)$_2$Cl$_2$ with 2 equiv of K[N(PPh$_2$Se)$_2$] led to formation of a brown solid. According to NMR spectroscopy, this brown crude product was found to consist of two ruthenium benzylidene species, presumably Ru(=CHPh)[Ph$_2$PNP(Se)Ph$_2$]$_2$ (**4**) and Ru(=CHPh)[N(PPh$_2$Se)$_2$]$_2$ (**5**). Recrystallization from CH$_2$Cl$_2$/hexane afforded dark red crystals of **4**, which are suitable for X-ray crystallography. We have not been able to obtain **5** in a pure form. It should be noted that metal-centered dechalcogenization of [N(PPh$_2$Q)$_2$]$^-$ ligands (Q = S, Se) and subsequent formation of the resulting M[Ph$_2$PNP(Q)Ph] or M[N(PPh$_2$)$_2$] metallacycles is well documented.[19] The finding that [N(PPh$_2$Se)$_2$]$^-$ was dechalcogenized by Ru while [N(PPh$_2$S)$_2$]$^-$ remained intact is perhaps a reflection of the weaker P=Se bond strength compared with that for P=S. The fate of the displaced selenium was not determined. The H$_\alpha$ of **4** was found to be coupled with the two PPh$_2$ groups and appears as a triplet at δ 15.17 Hz (J_{PH} = 16.8 Hz). The observation of two triplets at δ 53.87 and 102.72 (J_{PP} = 75 Hz), assignable to *P*(Se)Ph$_2$ and *P*Ph$_2$, respectively, in the ^{31}P {^{1}H} NMR spectrum is indicative of the 2-fold symmetry of the molecule shown below.

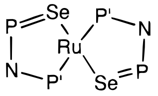


Figure 2 shows the molecular structure of **4**; selected bond lengths and angles are listed in Table 3. Like complex **1**, the geometry around Ru in **4** is square pyramidal with the apical benzylidene lying on a plane bisecting the two [Ph$_2$PNP(Se)Ph$_2$] chelates. The two bulky PPh$_2$ groups are situated mutually trans apparently due to steric reasons. The Ru−C bond of 1.873(8) Å is similar to that in **1**. The average Ru−Se and Ru−P distances are 2.450 and 2.383 Å, respectively. As expected the P(Se)−N bonds in the [Ph$_2$PNP(Se)Ph$_2$] chelates are shorter than those between N and trivalent P. The average C−Ru−Se angle (104.8°) is larger than the average C−Ru−P angle (93.6°) despite the expectation that the PPh$_2$ group is more sterically demanding than the Se=PPh$_2$ group. The large C−Ru−Se angles may be rationalized in terms of the π interaction between the Se donor and the electron density of alkylidene, as suggested in a theoretical study on tungsten alkylidyne complexes.[20]

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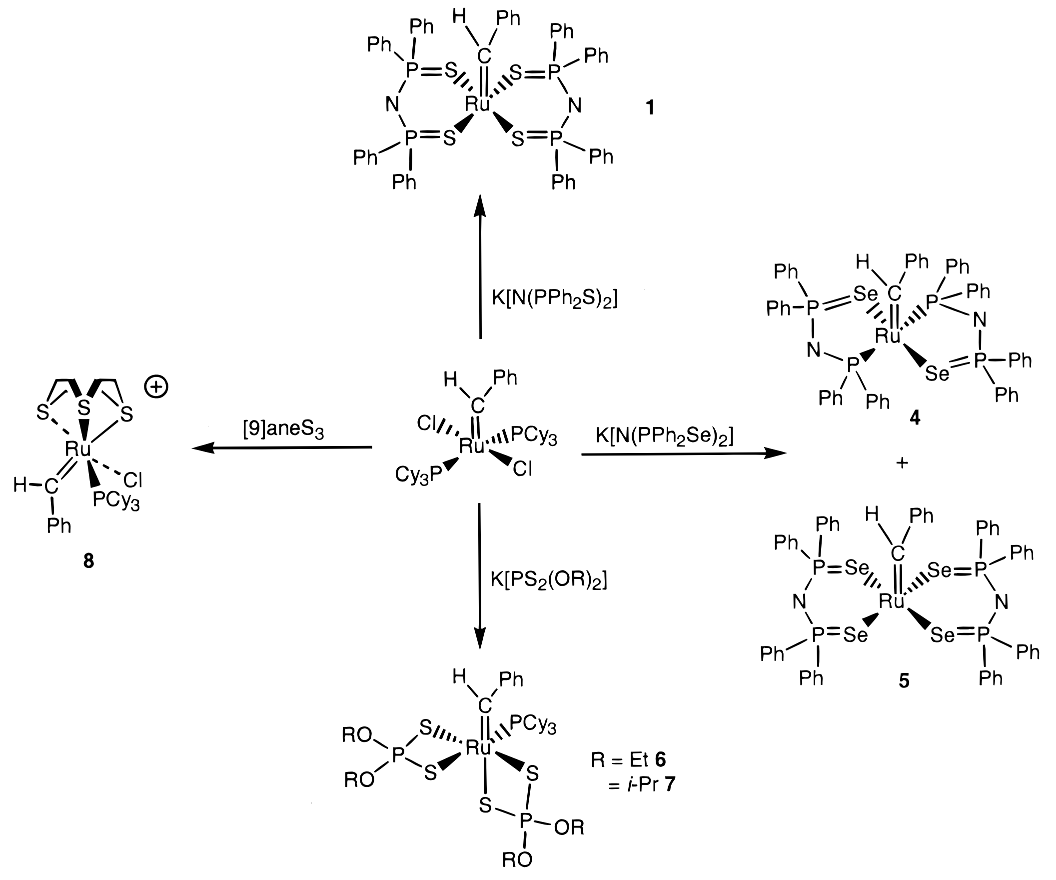
[19] (a) Rossi, R.; Marchi, A.; Marvelli, L.; Castellato, U., Tamburini, S.; Graziani, R. *J. Chem. Soc., Dalton Trans.* **1991**, 263. (b) Rossi, R.; Marchi, A.; Marvelli, L. Magor, L.; Peruzzini, M.; Castellato, U.; Graziani, *J. Chem. Soc., Dalton Trans.* **1993**, 723. (c) Slawin, A. M. Z.; Smith, M. B.; Woollins, *J. D. J. Chem. Soc., Dalton Trans.* **1997**, 1877.

[20] Choi, S.-H.; Lin, Z.; Xue, Z. *Organometallics* **1999**, *18*, 5488.

Scheme 1



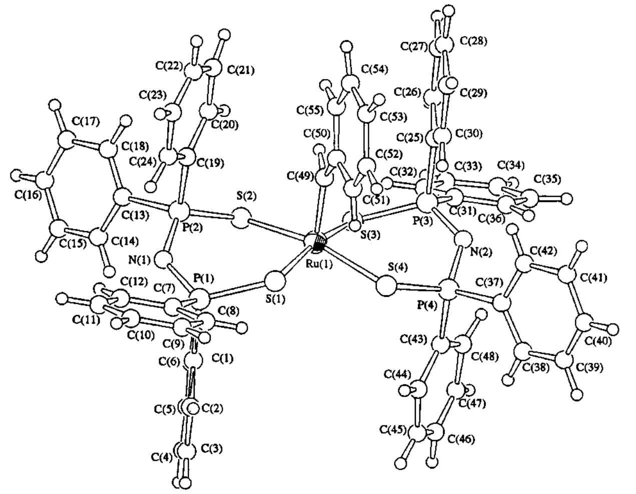


Figure 1. Perspective view of Ru(=CHPh)[N(PPh$_2$S)$_2$]$_2$, **1**.

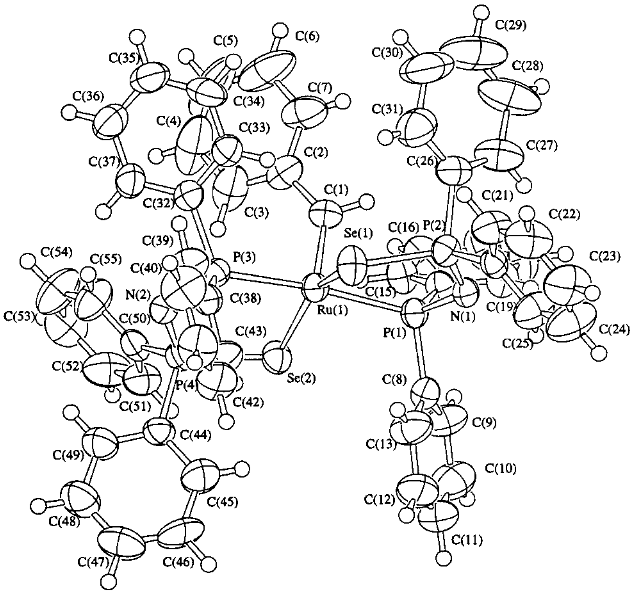


Figure 2. Perspective view of Ru(=CHPh)[Ph$_2$PNP(Se)Ph$_2$]$_2$, **4**.

Reaction of Ru(=CHPh)(PCy$_3$)$_2$Cl$_2$ with 2 equiv of K[P(OR)$_2$S$_2$] afforded the corresponding Ru benzylidene complexes Ru(=CHPh)(PCy$_3$)[P(OR)$_2$S$_2$]$_2$ (R = Et **6**, *i*-Pr **7**). Unlike **1**, complexes **6** and **7** are six-coordinate, suggesting that [P(OR)$_2$S$_2$]$^-$ are less bulky than [N(PPh$_2$S)$_2$]$^-$. The benzylidene and PCy$_3$ ligands in these complexes are presumably mutually cis. The H$_\alpha$ for **6** and **7** appear as doublets at δ 20.3 and 19.94 with $^3J_{PH}$ of 13.8 and 14.8 Hz, respectively. The C$_\alpha$ signals (δ 317 and 315, respectively) for these complexes are more downfield than that for **1**.

Reaction of Ru(=CHPh)(PCy$_3$)$_2$Cl$_2$ with [9]aneS$_3$ led to isolation of a yellowish green solid **8**. The observation of a doublet at ca. δ 17.75 with $^3J_{PH}$ of 14.4 Hz suggests that **8** is a Ru benzylidene species. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at δ 31.98 assignable to the coordinated PCy$_3$. Addition of Ag(CF$_3$SO$_3$) to a CH$_2$Cl$_2$ solution of **8** led to formation of AgCl precipitate, suggesting that **8** contains a labile chloride ligand or chloride counteranion. The FAB mass spectrum shows the parent ion assignable to [([9]aneS$_3$)Ru(=CHPh)(PCy$_3$)Cl]$^+$. Compound **8** is therefore tentatively formulated as [([9]aneS$_3$)Ru(=CHPh)(PCy$_3$)Cl]Cl. It may be

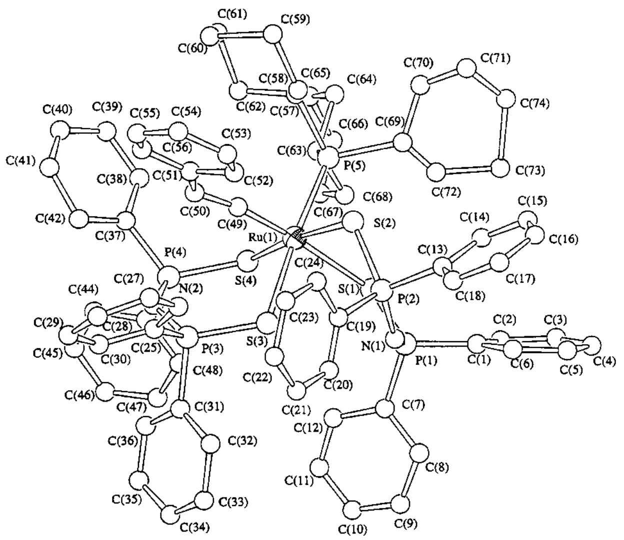


Figure 3. Perspective view of *cis*-Ru(=C=CHPh)(PCy$_3$)[N(PPh$_2$S)$_2$]$_2$, **9**.

noted that a similar cationic half-sandwich ruthenium allenylidene species has been isolated by Hill and coworkers.[9b] Unfortunately we have not been able to obtain good analytical results for **8** possibly due to contamination with [([9]aneS$_3$)Ru(PCy$_3$)Cl$_2$] (see later section).

Reaction of Ru(=CHPh)(PCy$_3$)$_2$Cl$_2$ with other dithiol ligands such as sodium diethyldithiocarbamate and disodium salt of 3-toluenedithiol led to formation of intractable dark materials, which have yet to be characterized.

Ruthenium Vinylidene Complexes. Treatment of Ru(=C=CHPh)Cl$_2$(PCy$_3$)$_2$ with 2 equiv of K[N(PPh$_2$S)$_2$] afforded *cis*-Ru(=C=CHPh)(PCy$_3$)[N(PPh$_2$S)$_2$]$_2$, **9**, isolated as red crystals. Complex **9** is air stable both in the solid state and in solution. No nucleophilic attack on the vinylidene was found when **9** was refluxed with methanol. The H$_\beta$ of the vinylidene ligand appears as a doublet at δ 4.02 with $^4J_{PH}$ of 3.2 Hz. Consistent with cis geometry of the molecule, five ill-resolved ^{31}P resonant signals were observed. Similar ^{31}P NMR spectral patterns were found for the related complexes such as *cis*-Ru(SO$_2$)(PPh$_3$)[N(PPh$_2$S)$_2$]$_2$.[18] The C$_\alpha$ resonant signal for **9** appears as a doublet at δ 348 ($^2J_{PC}$ = 16.5 Hz), which is similar to that for Ru(=C=CHPh)Cl$_2$(PCy$_3$)$_2$ (δ 342.1).[15] The solid-state structure of **9** has been unambiguously established by X-ray diffraction. Figure 3 shows the molecular structure of **9**; selected bond lengths and angles are listed in Table 4. The geometry around Ru is octahedral, with PCy$_3$ adjacent to the vinylidene. Complex **9** was isolated as a phosphine adduct, while **1** is five-coordinate, suggesting that the vinylidene ligand is less sterically demanding than benzylidene. The Ru−P distance of 2.420(3) Å is similar to that in Ru(=C=CHPh)(PCy$_3$)$_2$Cl$_2$ (2.4161 Å).[16] The Ru−S(trans to C) bond (of 2.595(3) Å) is considerably longer than the Ru−S(cis to C) bonds (average 2.440 Å), indicative of trans influence of the vinylidene ligand. The Ru−C$_\alpha$ (1.80(1) Å) and C$_\alpha$−C$_\beta$ (1.32(1) Å) distances are typical for ruthenium vinylidene compounds.[21] The Ru−C$_\alpha$−C$_\beta$ (172.4(9)°) and C$_\alpha$−C$_\beta$−C(Ph) (128(1)°) angles are consistent with the sp and sp^2 hybridization of C$_\alpha$ and C$_\beta$, respectively.

Treatment of Ru(=C=CHPh)Cl$_2$(PCy$_3$)$_2$ with [9]aneS$_3$ led to substitution of vinylidene and formation of ([9]aneS$_3$)Ru(PCy$_3$)Cl$_2$, **10**. The fate of the vinylidene moiety is not clear. The observation of vinylidene substitution is in contrast with the reactions of [9]aneS$_3$ with the ruthenium benzylidene and allenylidene analogues, which yielded the corresponding half-sandwich ruthenium benzylidene and allenylidene[9b] products.

Catalytic Polymerization of Norbornene. The ruthenium benzylidene complexes were found to be active catalysts for ROMP of norbornene, and the results are summarized in Table 5. For example, treatment of norbornene with **1** led to isolation of a poly(norbornene), which is ca. 81% trans, in 50% yield. The molecular weight (M_n) was determined to be ca. 7.0 × 10^5, which is higher than that obtained for Ru(=CHPh)(PCy$_3$)$_2$Cl$_2$ under similar conditions (M_n = 3.45 × 10^4).[1] The polydispersity index of 1.7 is higher than that for the Grubbs' catalyst (1.2[1]). Coordinately saturated complex **7** was found to be a poor ROMP catalyst apparently due to lack of a vacant site on ruthenium. By contrast, half-sandwich complex **8** can catalyze polymerization of norbornene to give a poly(norbornene) in 92% yield with a lower polydispersity (3.5). It seems probable that ligand dissociation has occurred for **8** before olefin coordination and metathesis take place. The related dichloride compound **10** did not show any reactivity toward norbornene polymerization, demonstrating that the alkylidene group is essential for the ROMP activity of the ruthenium catalyst.

In summary, we have isolated and structurally characterized the first ruthenium benzylidene and vinylidene complexes in a sulfur-rich coordination environment. Ru(=CHPh)[N(PPh$_2$S)$_2$]$_2$ was found to undergo metathesis with terminal olefins to give ruthenium carbene complexes. Both Ru(=CHPh)[N(PPh$_2$S)$_2$]$_2$ and [([9]aneS$_3$)Ru(=CHPh)(PCy$_3$)Cl]Cl are active catalysts for ROMP of norbornene. The study of other reactivity of these sulfur-rich ruthenium benzylidene and vinylidene complexes is underway.

Acknowledgment. We thank The Hong Kong University of Science and Technology and The Hong Kong Research Grants Council for support.

Supporting Information Available: Tables of crystal and intensity collection data, positional and displacement parameters, and complete bond lengths and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0000562

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[21] (a) Bruce, M. I.; Swincer, A. G. *Adv. Organomet. Chem.* **1983**, *22*, 59. (b) Bruce, M. I. *Chem. Rev.* **1991**, *91*, 197.