attempted to evaluate their effects on the electron density at Ru by comparing the chemical shifts of their Cp proton resonances. As seen from the data in Table I, these resonances move to lower field in the order $-C{\equiv}C{-}SMe^- \approx -C(OMe){=}C(H)SMe^- > -C{\equiv}CSMe_2 > S(Me)C{\equiv}CSMe > MeSC{\equiv}CMe > {=}C(OR)CH_2SMe > {=}C{=}C(R)SMe > {=}C{=}C(R)SMe_2^+$. The trend indicates that σ-bound ligands such as acetylides and vinyl groups are the better donors, while the π-alkyne, carbene, and vinylidene ligands are the better π-acceptors. The sulfoniovinylidene ligand in $[Cp(PMe_3)_2Ru{=}C{=}C(H)(SMe_2)](BF_4)_2$ is the best π-acceptor, partly due to bonding that involves some Ru≡C carbyne character.

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Supplementary Material Available: Tables of thermal parameters, hydrogen parameters, and additional bond angles (5 pages); a table of calculated and observed structure factors (16 pages). Ordering information is given on any current masthead page.

Electrophilic and Nucleophilic Reactions of the Vinylidene Complex $[Cp(PMe_3)_2Ru{=}C{=}C(SMe)_2]BF_4$ and Its Derivatives

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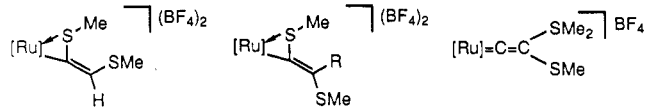
The cationic vinylidene complex $[Cp(PMe_3)_2Ru{=}C{=}C(SMe)_2]BF_4$ (1) undergoes addition of electrophiles such as $HBF_4{\cdot}Et_2O$, $[MeSSMe_2]SO_3CF_3$, and $[Me_3O]BF_4$ to give the complexes ([Ru] = $Cp(PMe_3)_2Ru$)

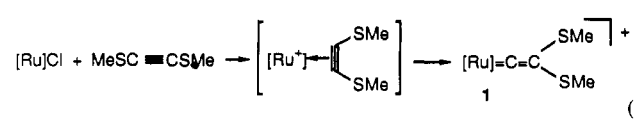


2a R = H, **2b**; SMe, **3** **4**

An X-ray diffraction investigation shows that **2a** crystallizes in space group $C2/c$ with a = 31.558 (5) Å, b = 10.492 (2) Å, c = 16.484 (5) Å, β = 100.89 (2)°, and Z = 8. The reaction of **4** with phosphines results in the cleavage of MeS^+ to form the sulfonio acetylide $[Cp(PMe_3)_2Ru{-}C{\equiv}CSMe_2]BF_4$ (**5**) and $[MeS{-}PPh_2R]^+$ (R = Me, Ph). Anionic nucleophiles such as NaSR (R = Et, Me) displace Me_2S from **4** to yield the vinylidene complexes $[Cp(PMe_3)_2Ru{=}C{=}(SR)(SMe)]BF_4$ (R = Et (**7**), R = Me (**1**)). Complex **4** also reacts with pyridines, 4-NC_5H_4R (R = H, Et, NMe_2 (DMAP)), and SEt_2 to displace Me_2S to yield the dicationic vinylidene complexes $[Cp(PMe_3)_2Ru{=}C{=}C(4\text{-}NC_5H_4R)(SMe)](BF_4)_2$ (R = H (**8**), Et (**9**), NMe_2 (**10**)) and $[Cp(PMe_3)_2Ru{=}C{=}C(SEt_2)(SMe)](BF_4)_2$ (**11**). The reactions of DMAP and SEt_2 (Nuc) with **4** in CD_3CN follow the general rate law rate = $k_1[4] + k_2[4][Nuc]$. The reaction of DMAP is dominated by the k_2 pathway, which is proposed to involve nucleophilic attack at the α-carbon of **4**. The less nucleophilic SEt_2 reacts by both nucleophilic (k_2) and dissociative (k_1) pathways.

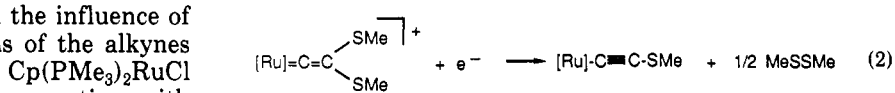
Introduction

In the previous paper,[2] we examined the influence of mercapto groups (SR) on the reactions of the alkynes MeSC≡CSMe and MeSC≡CMe with $Cp(PMe_3)_2RuCl$ (Cp = η^5-C_5H_5). We noted that the reaction with MeSC≡CSMe gave the (methylthio)vinylidene complex $[Cp(PMe_3)_2Ru{=}C{=}C(SMe)_2]BF_4$ (**1**); this presumably occurred via an η^2-alkyne intermediate that rearranged to the product by a 1,2-SMe migration (eq 1, [Ru] = Cp-



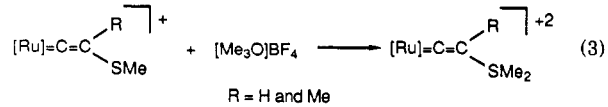
(1)

$(PMe_3)_2Ru$). Complex **1** could be reduced by $Na[HBEt_3]$ or Na/Hg to yield the (methylthio)acetylide complex Cp-$(PMe_3)_2Ru{-}C{\equiv}CSMe$ and MeSSMe (eq 2). We further



(2)

reported that the methylthio moiety of the vinylidene complexes $[Cp(PMe_3)_2Ru{=}C{=}C(R)(SMe)]BF_4$ are alkylated to give dicationic sulfoniovinylidene complexes (eq 3). In order to explore the effects of SR groups on the



(3)

R = H and Me

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(2) Miller, D. C.; Angelici, R. J. *Organometallics*, previous paper in this issue.

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Table I. ^{1}H NMR Data (ppm) for the Complexes[a]

compd (Ru = $Cp(PMe_3)_2Ru$)	Cp	PMe_3 (J_{PH}, Hz)	SMe_n (n)	other
$[Ru{=}C{=}C(SMe)_2]BF_4$ (**1**)[b]	5.48	1.47 (d, 10.56)	2.22 (1)	
$\{Ru[S(Me)C{=}C(H)SMe]\}(BF_4)_2$ (**2a**)[c,d]	5.90	1.97 (d, 10.80)	2.63 (1)	7.38 (t, H)[e]
		1.46 (d, 10.54)	2.41 (1)	
$\{Ru[S(Me)C{=}C(SMe)(H)]\}(BF_4)_2$ (**2b**)[c]	6.00	1.99 (d, 10.80)	2.62 (1)	8.34 (dd, H)[f]
		1.54 (d, 11.10)	2.43 (1)	
$\{Ru[S(Me)C{=}C(SMe)_2\}(BF_4)_2$ (**3**)[c]	6.03	1.99 (d, 10.52)	2.60 (1)	
		1.56 (d, 10.24)	2.57 (1)	
			2.49 (1)	
$[Ru{=}C{=}C(SMe_2)(SMe)](BF_4)_2$ (**4**)[c]	5.77	1.73 (d, 10.80)	2.83 (2)	
			2.43 (1)	
$[Ru{-}C{\equiv}CSMe_2]BF_4$ (**5**)[c]	4.83	1.48 (t, 9.17)	2.83 (2)	
$Ru{-}C{\equiv}CSMe$ (**6**)[b]	4.62	1.45 (t, 9.03)		1.98 (t, Me)[g]
$[Ru{=}C{=}C(SEt)(SMe)]BF_4$ (**7**)[c]	5.52	1.64 (d, 10.80)	2.22 (1)	2.65 (q, CH_2)[h]
$[Ru{=}C{=}C(NC_5H_5)(SMe)](BF_4)_2$ (**8**)[c]	5.86	1.63 (d, 10.81)	2.30 (1)	8.93 (d, o-H)[i]
				8.46 (t, p-H)[j]
				8.11 t (m-H)[k]
$[Ru{=}C{=}C(4\text{-}NC_5H_4Et)(SMe)](BF_4)_2$ (**9**)[c]	5.84	1.61 (d, 10.54)	2.29 (1)	2.98, 2.95 (2 q, CH_2)[i]
				1.33, 1.30 (2 t, CH_3)[i]
				8.74 (d, H)[l]
				7.92 (d, H)[l]
$[Ru{=}C{=}C(4\text{-}NC_5H_4NMe_2)(SMe)](BF_4)_2$ (**10**)[c]	5.76	1.56 (d, 9.67)	2.25 (1)	3.21 (NMe_2)
				8.06 (d, H)[m]
				6.94 (d, H)[n]
$[Ru(\eta^2\text{-}MeSC{\equiv}C\text{-}4\text{-}NC_5H_4NMe_2)](BF_4)_2$ (**10i**)[c]	5.55	1.65 (d, 10.20)	2.46 (1)	3.24 (NMe_2)
		1.38 (d, 9.98)		8.01 (d, H)[o]
				6.93 (d, H)[o]
$[Ru{=}C{=}C(SEt_2)(SMe)](BF_4)_2$ (**11**)[c]	5.77	1.74 (d, 10.93)	2.44 (1)	3.26 (2 q 2 q, CH_2)[p]
				1.36 (t, CH_3)[k]

[a] Abbreviations: d, doublet; t, triplet; q, quartet. [b] $CDCl_3$. [c] CD_3CN. [d] CH_3CN incorporated into solid at 2.09 ppm. [e] J_{PH} = 2.83 Hz. [f] J_{PH} = 1.68 Hz. [g] J_{PH} = 2.6 Hz. [h] J_{PH} = 7.2 Hz. [i] J_{HH} = 7.5 Hz. [j] J_{HH} = 7.8 Hz. [k] J_{HH} = 7.3 Hz. [l] J_{HH} = 6.7 Hz. [m] J_{HH} = 7.84 Hz. [n] J_{HH} = 7.93 Hz. [o] J_{HH} = 8.0 Hz. [p] J_{HH} = 7.2 Hz; J_{HH} = 7.1 Hz.

Table II. ^{13}C NMR Data (ppm) for the Complexes[a]

compd	Cp	PMe_3 (J_{PC}, Hz)	SMe_n (n)	Ru–C (J_{Pc}, Hz)	β-C	other
1[b]	92.69	22.47 (t, 16.81)	18.86 (1)	326.93 (t, 16.77)	116.62	
2a[b]	96.42	20.32 (d, 35.80)	28.83 (1)	138.03 (d, 18.97)	139.99 (d)[c]	
		17.92 (d, 37.22)	18.44 (1)			
2b[b]	95.74	20.37 (d, 37.62)	30.86 (1)	141.21 (d, 18.91)	146.53 (d)[d]	
		19.54 (d, 36.73)	18.07 (1)			
3[b]	96.45	19.93 (d, 33.82)	31.33 (1)	148.23 (d, 18.50)	148.32 (d)[e]	
		19.25 (d, 33.42)	20.64 (1)			
			17.68 (1)			
4[b]	95.28	22.51 (t, 20.05)	28.02 (2)	317.01 (t, 15.20)	110.92	
			24.31 (1)			
7[f]	91.87	22.45 (t, 18.95)	17.84 (1)	[g]	113.84	28.06 (CH_2)
						14.87 (CH_3)
8[b]	94.96	22.09 (t, 19.01)	21.18 (1)	318.72 (t, 15.25)	128.57	146.41 (NC_5H_5)
						142.11
						139.79
10[b]	94.24	22.11 (t, 20.52)	20.68 (1)	324.43 (t, 15.09)	137.48	157.18 (NC_5H_4)
						141.35
						109.27
						40.53 (NMe_2)
11[b]	95.52	22.70 (t, 19.05)	23.65 (1)	313.81 (t, 12.95)	105.56	37.53 (CH_2)
						10.09 (CH_3)

[a] Abbreviations: d, doublet; t, triplet. [b] CD_3CN. [c] J_{PC} = 5.50 Hz. [d] J_{PC} = 6.09 Hz. [e] J_{PC} = 6.54 Hz. [f] $CDCl_3$. [g] Ru–C not located.

reactivity of the vinylidene ligand in **1**, we undertook a study of the reactions of $[Cp(PMe_3)_2Ru{=}C{=}C(SMe)_2]BF_4$ (**1**) and its derivatives with a number of electrophiles and nucleophiles.

Experimental Section

General Procedures. All reactions, filtrations, distillations, recrystallizations, and spectroscopic analyses were performed as described in the previous paper.[2] Acetone and chloroform were dried and stored over molecular sieves (4 Å).[3,4] The ^{31}P NMR spectra were recorded on a Bruker WM 300-MHz instrument; the ^{31}P signals that are upfield of the H_3PO_4 external reference are given as negative values. GCMS spectra were obtained on a Hewlett-Packard 5890A gas chromatograph (30 m × 0.25 mm DB5 column, TRW) interfaced to a 5970 Series mass selective detector.

The compounds $(\eta^5\text{-}C_5H_5)(PMe_3)_2RuCl$[5] ($\eta^5\text{-}C_5H_5$ = Cp), $[Cp(PMe_3)_2Ru{=}C{=}C(SMe)_2]BF_4$ (**1**),[2] $[Me_2SSMe]SO_3CF_3$ (SO_3CF_3 = Tf),[6] and NaSR[7] were prepared by using previously described procedures.

(3) Shriver, D. F.; Drezdzon, M. A. *The Manipulation of Air Sensitive Compounds*, 2nd ed.; Wiley: New York, 1986.
(4) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*, 2nd ed.; Pergamon Press: New York, 1987.
(5) (a) Treichel, P. M.; Komar, D. A. *Synth. React. Inorg. Met.-Org. Chem.* **1980**, *10*, 205. (b) Treichel, P. M.; Komar, D. A.; Vincent, P. J. *Synth. React. Inorg. Met.-Org. Chem.* **1984**, *14*, 383.
(6) Ravenscroft, M.; Roberts, R. M. G.; Tillet, J. G. *J. Chem. Soc., Perkin Trans. 2* **1982**, 1569.
(7) Kim, H. P.; Angelici, R. J. *Organometallics* **1986**, *5*, 2489.

{Cp(PMe$_3$)$_2$Ru[S(Me)C=C(H)(SMe)]}(BF$_4$)$_2$ (2a) and {Cp(PMe$_3$)$_2$Ru[S(Me)C=C(SMe)(H)]}(BF$_4$)$_2$ (2b). To a solution of complex 1 (537 mg, 1.02 mmol) in 40 mL of CH_3CN was added $HBF_4 \cdot Et_2O$ (0.30 mL, 2.0 mmol) under N_2. The resulting orange-red solution was stirred for 1 h, and the solvent was removed under vacuum. The resulting residue partially dissolved in 20 mL of acetone to give a yellow suspension; 20 mL of Et_2O was added to the acetone suspension to produce a yellow precipitate, which was collected and dried under vacuum. The yellow powder consisting of a mixture of **2a** and **2b** in a 2:1 ratio, as determined by the ^1H NMR spectrum, was collected in 98% yield (613 mg, 1.00 mmol). Complex **2a** was obtained by adding 20 mL of acetone to the above product mixture of **2a** and **2b** and placing the acetone suspension in a freezer (−20 °C) overnight. A yellow powder of **2a** was collected in 50% yield (302 mg, 0.49 mmol). Anal. Calcd for $C_{15}H_{30}B_2F_8P_2RuS_2 \cdot CH_3CN$: C, 31.31; H, 5.10. Found: C, 31.10; H, 5.06. The ^1H NMR spectrum of the sample sent for elemental analyses showed one molecule of CH_3CN per molecule of **2a**. It was not possible to isolate a pure sample of **2b**; this was due to the presence of **2a** in the solution even after several precipitations of **2a** from the acetone mixture.

{Cp(PMe$_3$)$_2$Ru[S(Me)C=C(SMe)$_2$]}(BF$_4$)$_2$ (3). A solution of complex 1 (311 mg, 0.59 mmol) and [MeSSMe$_2$]Tf (174 mg, 0.67 mmol) was stirred in 15 mL of CH_3CN for 1 h under N_2. To the solution was added NH_4BF_4 (236 mg, 2.26 mmol), and the solution was stirred for an additional 30 min. The solvent was removed under vacuum. The resulting residue was washed with CH_2Cl_2 (3 × 10 mL) and the solvent discarded. The washed residue was dissolved in acetone (3 × 10 mL), and the solution was filtered through a column of Celite (40 × 5 mm). This solution was reduced to 5 mL, and 20 mL of Et_2O was added to produce a yellow precipitate, which was collected and dried under vacuum to give a dark yellow oil of **3** in 95% yield (369 mg, 0.56 mmol). Anal. Calcd for $C_{16}H_{33}B_2F_8P_2RuS_3$: C, 29.20; H, 5.05. Found: C, 28.87; H, 4.61.

[Cp(PMe$_3$)$_2$Ru=C=C(SMe$_2$)(SMe)](BF$_4$)$_2$ (4). To a stirred solution of complex 1 (327 mg, 0.60 mmol) in 15 mL of CH_3CN was added $[Me_3O]BF_4$ (200 mg, 1.2 mmol). After it was stirred for 30 min, the solution was reduced to 3 mL under vacuum, and 20 mL of Et_2O was added to give a dark yellow oil, which was collected and dried under vacuum. A precipitate of **4** was obtained by dissolving the oil in 10 mL of acetone and adding 30 mL of Et_2O. A yellow powder of **4** was collected in 91% yield (340 mg, 0.55 mmol). The sample sent for elemental analysis was the PF_6 salt. This was obtained by adding an excess of NH_4PF_6 to a stirred acetone solution of **4** for 30 min under N_2. The acetone solution was reduced under vacuum, and Et_2O was added to produce a yellow powder of [Cp(PMe$_3$)$_2$Ru=C=C(SMe$_2$)(SMe)](PF$_6$)$_2$. Anal. Calcd for $C_{16}H_{32}F_{12}P_4RuS_2$: C, 25.92; H, 4.35. Found: C, 26.37; H, 4.50. IR (Fluorolube): ν(C=C) 1565 cm^{-1}.

Reactions of 4 with PPh$_2$R (R = Me, Ph). A 5-mm NMR tube was loaded with complex **4** (R = Me, 7.7 mg, 0.012 mmol; R = Ph, 9.3 mg, 0.015 mmol) and CD_3CN; PPh$_2$R (R = Me, 0.0032 mL, 0.015 mmol; R = Ph, 15 mg, 0.059 mmol) was added, and the tube was shaken. After 10 min a ^1H NMR spectrum showed that **4** had been completely converted to [Cp(PMe$_3$)$_2$Ru—C≡CSMe$_2$](BF$_4$) (**5**). The phosphine products were identified as [(MeS)PPh$_2$R]BF$_4$; this was achieved by preparing these salts independently. A solution of PPh$_2$R (R = Me, 0.063 mL, 0.34 mmol; R = Ph, 51 mg, 0.19 mmol) and [MeSSMe$_2$]Tf (R = Me, 89 mg, 0.34 mmol; R = Ph, 51 mg, 0.20 mmol) was stirred in 10 mL of CH_2Cl_2 for 10 min. The solution was reduced to 3 mL, and 15 mL of Et_2O was added; a colorless oil separated out of the solution. The solvent was removed, and the oil of [(MeS)PPh$_2$R]Tf (R = Me, Ph) was dried under vacuum. R = Me: ^1H NMR ($CDCl_3$) δ 7.8 (m, Ph), 2.94 (d, J_{PH} = 13.2 Hz, PMe), 2.44 (d, J_{PH} = 15.2 Hz, SMe); ^{31}P NMR ($CDCl_3$) δ 47.66 (s); MS (FAB) m/e 247 (M^+), 200 (M^+ − SMe). R = Ph: ^1H NMR ($CDCl_3$) δ 7.8 (m, Ph), 2.48 (d, J_{PH} = 15.3 Hz, SMe); ^{31}P NMR ($CDCl_3$) 46.76 (s). These spectra are the same as those observed for the phosphorus-containing products, [(MeS)PPh$_2$R]$^+$, obtained in the reaction of **4** with PPh$_2$R.

Reaction of 4 with Na/Hg. Sodium metal (50 mg, 2.2 mmol) was added to stirred mercury metal (5 mL, 68 g), followed by the addition of 10 mL of THF. To the stirred solution was added complex **4** (81 mg, 0.13 mmol) in 5 mL of THF via a syringe over a period of 5 min. The suspension was stirred for an additional 15 min and then vacuum-filtered through a bed of Celite; the Celite was washed with THF (2 × 5 mL). The solvent was removed from the filtrate under reduced pressure, and the residue was dissolved in CH_2Cl_2 (2 × 5 mL). The solution was filtered through a frit containing Celite and then evaporated under vacuum. The brownish yellow residue was redissolved in Et_2O (2 × 20 mL), and the solution was passed through a column of Celite (40 × 5 mm). The solvent was removed from the resulting yellow solution under reduced pressure to give a yellow powder of Cp(PMe$_3$)$_2$Ru—C≡CSMe (**6**) in 69% yield (35 mg, 0.089 mmol). Complex **6** has previously been characterized.[2] IR (CH_2Cl_2): ν(C≡C) 2000 cm^{-1}.

Reactions of 4 with NaSR (R = Et, Me). To a stirred solution of complex **4** (R = Et, 59 mg, 0.094 mmol; R = Me, 50 mg, 0.080 mmol) in 5 mL of CH_3CN was added NaSR (R = Et, 9.0 mg, 0.11 mmol; R = Me, 10 mg, 0.14 mmol). The resulting red solution was stirred for 4 h and the solvent removed under reduced pressure. The residue was dissolved in CH_2Cl_2 (2 × 5 mL) and filtered through a small column of Celite. The solvent was reduced to 5 mL, and 15 mL of Et_2O was added to give a red precipitate, which was collected and dried under vacuum. Red powders of [Cp(PMe$_3$)$_2$Ru=C=C(SEt)(SMe)]BF$_4$ (**7**) and **1** were obtained in 54% (28 mg, 0.051 mmol) and 50% yield (21 mg, 0.040 mmol), respectively. **7**: MS (FAB) m/e 451 (M^+), 404 (M^+ − SMe), 390 (M^+ − SEt), 319 (Cp(PMe$_3$)$_2$Ru$^+$); IR (CH_2Cl_2) ν(C=C) 1600 cm^{-1}. Anal. Calcd for $C_{16}H_{31}BF_4P_2RuS_2$: C, 35.76; H, 5.81. Found: C, 35.46; H, 5.78.

Reaction of 4 with NC$_5$H$_5$. A solution of complex **4** (88 mg, 0.14 mmol) and NC$_5$H$_5$ (0.10 mL, 1.2 mmol) was refluxed in 10 mL of CH_3CN for 4 h under N_2. The solvent was removed from the resulting red solution under vacuum. The residue was extracted with CH_2Cl_2 (2 × 7 mL), and the solution was filtered through a column of Celite (40 × 5 mm), leaving undissolved [Cp(PMe$_3$)$_2$Ru=C=C(NC$_5$H$_5$)(SMe)](BF$_4$)$_2$ (**8**) on the Celite. The red CH_2Cl_2 solution was reduced to 4 mL, and 10 mL of Et_2O was added to produce a red powder of **1** in 31% yield (23 mg, 0.043 mmol). The residue that did not dissolve in CH_2Cl_2 was dissolved in CH_3CN (2 × 5 mL) and filtered through the column of Celite. The CH_3CN solution was reduced to 5 mL, and 15 mL of Et_2O was added to give a pale red powder of **8** in 57% yield (51 mg, 0.080 mmol). Anal. Calcd for $C_{19}H_{31}B_2F_8NP_2RuS$: C, 35.54; H, 4.87. Found: C, 35.68; H, 4.60. IR (CH_3CN): ν(C=C) 1620 m, 1595 s cm^{-1}.

Reaction of 4 with 4-NC$_5$H$_4$NMe$_2$ (DMAP). A solution of complex **4** (50 mg, 0.080 mmol) and DMAP (13 mg, 0.11 mmol) was refluxed in 10 mL of CH_3CN for 1 h under N_2. The solvent was removed under vacuum. The resulting red residue was washed with $CHCl_3$ (2 × 5 mL) to remove the excess DMAP, and the $CHCl_3$ solution was filtered through a column of Celite (40 × 5 mm), leaving undissolved [Cp(PMe$_3$)$_2$Ru=C=C(4-NC$_5$H$_4$NMe$_2$)(SMe)](BF$_4$)$_2$ (**10**) on the Celite. The insoluble residue that did not dissolved in $CHCl_3$ was dissolved in CH_2Cl_2 (3 × 5 mL) and filtered through the column of Celite. The CH_2Cl_2 solution was reduced to 3 mL, and 15 mL of Et_2O was added to give a pale red powder of **10** in 93% yield (51 mg, 0.074 mmol). Anal. Calcd for $C_{21}H_{36}B_2F_8N_2P_2RuS$: C, 36.81; H, 5.30. Found: C, 36.68; H, 5.60. IR (CH_3CN): ν(C=C) 1646 s, 1575 m cm^{-1}.

Reaction of 4 with SEt$_2$. A solution of complex **4** (42 mg, 0.067 mmol) and SEt$_2$ (1 mL, 9.3 mmol) was refluxed in 10 mL of CH_3CN for 5 h under N_2. The solvent was removed under vacuum. The yellow residue was dissolved in 10 mL of acetone, and 30 mL of Et_2O was added to give a yellow powder of [Cp(PMe$_3$)$_2$Ru=C=C(SEt$_2$)(SMe)](BF$_4$)$_2$ (**11**) in 64% yield (28 mg, 0.043 mmol). IR (Nujol mull): ν(C=C) 1633 cm^{-1}. Elemental analyses were not obtained because the product contained small amounts of **4** even after numerous recrystallizations.

Kinetic Measurements. The rates of reactions 10 and 11 were determined by following the disappearance of complex **4** over time by monitoring the disappearance of the Cp (for DMAP) or SMe$_2$ (for SEt$_2$) ^1H NMR resonances of **4** on a Bruker WM-200 NMR spectrometer set at a constant temperature. The instrument was programmed to automatically collect data sets consisting of 8 or 16 acquisitions at specific time intervals.

Reactions with 5-, 7-, 10-, 12-, and 15-fold excesses (Table III) of DMAP with **4** were carried out in a 5-mm ^1H NMR tube at

Table III. Pseudo-First-Order Rate Constants k_{obs} for the Reactions of $[Cp(PMe_3)_2Ru{=}C{=}C(SMe)(SMe_2)](BF_4)_2$ (4) with DMAP and SEt_2 in CD_3CN According to Eqs 9 and 10[a]

concn, M	$10^{-4}k_{obs}$, s^{-1}	concn, M	$10^{-4}k_{obs}$, s^{-1}
	DMAP (0.0 ± 0.5 °C)		
0.20	0.83 (1)	0.47	1.98 (1)
0.28	1.33 (1)	0.60	2.28 (2)
0.40	1.55 (1)		
	SEt_2 (70.0 ± 0.5 °C)		
0.36	0.83 (3)	1.05	1.20 (5)
0.54	0.95 (2)	1.44	1.33 (6)
0.75	1.10 (7)		

[a] Estimated standard deviations are given in parentheses.

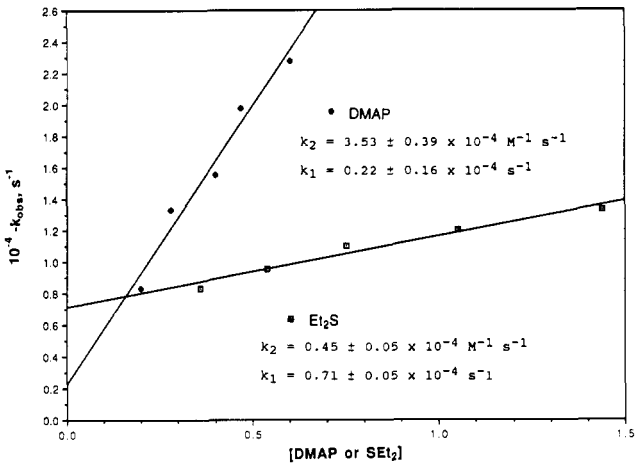


Figure 1. Plot of k_{obs} values versus the concentration of DMAP (at 0 °C) and SEt_2 (at 70 °C) for the reactions shown in eqs 10 and 11.

0 °C. The NMR tube was loaded with a solution of **4** (0.010 g, 0.016 mmol) and 0.4 mL of CD_3CN to give a 0.040 M concentration of **4**; the NMR tube was cooled inside the NMR probe for 15 min. The NMR tube was ejected, the DMAP added, and the tube shaken and then quickly placed back into the probe. The NMR-tube solution was allowed to equilibrate back to 0 °C for 5 min. The automatic collection program was set to take a series of data points consisting of two dummy scans, eight acquisitions, and a delay time between points that took a total time of 5 min. The reactions were run to approximately 90% completion.

The reactions of SEt_2 with **4** were performed in a manner similar to that for the DMAP reactions; however, the reactions were carried out at 70 °C. The NMR tube was loaded with a solution of **4** (0.009 mg, 0.014 mmol) and 0.4 mL of CD_3CN; then SEt_2 was added in 10-, 15-, 20-, 30-, or 40-fold excess (Table III). The collection of data points for the reaction of **4** with 30- and 40-fold excesses of SEt_2 was the same as that described for DMAP; data points for the reactions of 10-, 15-, and 20-fold excess of SEt_2 consist of 2 dummy scans, 16 acquisitions, and a delay time between sets to make the total time 10 min.

The data were analyzed with use of an NMRi program.[8] Pseudo-first-order rate constants, k_{obs}, were obtained from slopes of plots of the logarithms of the absolute integrals of the Cp (for DMAP) or SMe_2 (for SEt_2) ^1H NMR signals vs time (Table III). Rate constants k_1 and k_2 were obtained from the intercept and slope, respectively, of plots of k_{obs} vs concentration (M) of DMAP and SEt_2 (Figure 1).

X-ray Structure Determination of $[Cp(PMe_3)_2Ru[S(Me)C{=}C(H)SMe](BF_4)_2 \cdot {}^1/_2CH_3CN$ (2a). Orange-yellow crystals of **2a** were grown by vapor diffusion of Et_2O into an CH_3CN solution of **2a** at −20 °C. The cell constants were determined from a list of reflections found by an automated search routine. Pertinent data collection and reduction information are given in Table IV.

(8) New Methods Research, Inc. (NMRi), Syracuse, NY.

Table IV. Crystal and Data Collection Parameters for $[Cp(PMe_3)_2Ru[S(Me)C{=}C(H)(SMe)]](BF_4)_2 \cdot {}^1/_2CH_3CN$ (2a)

formula	$RuS_2P_2F_8C_{15}B_2H_{30} \cdot 0.5CH_3CN$
fw	631.67
space group	$C2/c$ (No. 15)
a, Å	31.558 (5)
b, Å	10.492 (2)
c, Å	16.484 (5)
β, deg	100.89 (2)
V, Å^3	5361 (4)
Z	8
d_{calc}, g/cm^3	1.584
cryst size, mm	0.40 × 0.25 × 0.20
μ(Mo Kα), cm^{-1}	9.01
data collection instrument	Enraf-Nonius CAD4
radiation (monochromated in incident beam)	Mo Kα (λ = 0.71073 Å)
orientation reflns: no.; range (2θ), deg	25; 18 < 2θ < 33
temp, °C	22 ± 1
scan method	θ–2θ
data collecn range, 2θ, deg	0–50
no. of unique data	
total	4714
no. with $F_o^2 > 3\sigma(F_o^2)$	2823
no. of params refined	202
transmissn factors: max, min (ψ scans)	1.00, 0.938
R^a	0.073
R_w^b	0.106
quality-of-fit indicator[c]	2.08
largest shift/esd, final cycle	<0.01
largest peak, e/Å^3	1.06

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/[\sigma^2(|F_o|) + 0.001|F_o|^2]$. [c] Quality of fit = $[\sum w(|F_o| - |F_c|)^2/(N_{observns} - N_{param})]^{1/2}$.

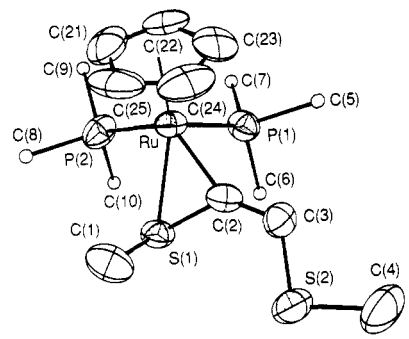


Figure 2. ORTEP drawing of $[Cp(PMe_3)_2Ru[S(Me)C{=}C(H)(SMe)]](BF_4)_2 \cdot {}^1/_2CH_3CN$ (**2a**). The phosphine methyls are shown as arbitrary spheres.

A total of 4806 reflections were collected in the $\pm h,+k,\pm l$ quadrants. An empirical absorption correction was made, on the basis of a series of ψ-scans. The agreement factors for the averaging of 125 observed reflections were 1.9% based on intensity and 1.5% based on F_o.

Structure Solution and Refinement. The position of the metal atom was taken from a Patterson map. The positions of the phosphorus and sulfur atoms were then seen in a difference Fourier synthesis. Following least-squares refinement of these atoms, the remaining carbon atoms of the complex and the two anions were located in another difference map. In a later difference map a molecule of acetonitrile was located along the crystallographic 2-fold axis.

The cyclopentadienyl ring was refined as a rigid pentagon with C–C distances of 1.420 Å. Since the BF_4^- units were not well-behaved in full-matrix refinement, the two anions were also modeled as rigid groups, having fixed B–F bond lengths of 1.37 Å and F–B–F angles of 109.5°. One of the anions (centered on atom B(2)) was later defined as two rigid BF_4 groups, with their occupancies being refined to a sum of 1.0. The two rigid BF_4 groups around B(2) were further restrained such that each group of four F atoms had a common isotropic temperature factor. In

Table V. Positional and Thermal Parameters for {Cp(PMe$_3$)$_2$Ru[S(Me)C=C(H)(SMe)]}(BF$_4$)$_2$•$^1/_2$CH$_3$CN (2a)

atom	x	y	z	B, Å^2[a]
Ru	0.11562 (3)	0.11266 (8)	0.45164 (5)	3.36 (2)
S(1)	0.1653 (1)	0.2437 (3)	0.3979 (2)	3.93 (7)
S(2)	0.2391 (1)	0.0466 (3)	0.3337 (2)	5.37 (9)
P(1)	0.1628 (1)	0.0542 (3)	0.5729 (2)	4.35 (8)
P(2)	0.0987 (1)	0.3065 (3)	0.5148 (2)	4.75 (9)
C(1)	0.1448 (5)	0.275 (1)	0.2863 (8)	6.5 (4)
C(2)	0.1703 (4)	0.080 (1)	0.4070 (7)	3.9 (3)
C(3)	0.1979 (4)	−0.004 (1)	0.3846 (7)	4.0 (3)
C(4)	0.2709 (5)	−0.095 (1)	0.342 (1)	7.8 (5)
C(5)	0.1781 (5)	−0.115 (1)	0.5781 (9)	6.1 (4)
C(6)	0.2161 (4)	0.130 (1)	0.5971 (9)	6.2 (4)
C(7)	0.1434 (5)	0.072 (2)	0.6697 (8)	6.4 (4)
C(8)	0.0738 (5)	0.424 (1)	0.4369 (9)	6.0 (4)
C(9)	0.0597 (5)	0.300 (2)	0.5835 (9)	7.0 (5)
C(10)	0.1441 (5)	0.398 (1)	0.573 (1)	7.0 (4)
C(21)	0.0433 (3)	0.1015 (9)	0.4166 (8)	6.5 (4)
C(22)	0.0595 (3)	0.0030 (9)	0.4730 (8)	5.6 (4)
C(23)	0.0862 (3)	−0.0770 (9)	0.4347 (8)	6.6 (5)
C(24)	0.0865 (3)	−0.0279 (9)	0.3546 (8)	6.8 (5)
C(25)	0.0600 (3)	0.0824 (9)	0.3434 (8)	7.2 (5)
B(1)	0.4408 (2)	0.7869 (6)	0.3823 (4)	6.5 (4)[b]
F(1)	0.4367 (2)	0.6613 (6)	0.3594 (4)	8.8 (2)[b]
F(2)	0.4692 (2)	0.7974 (6)	0.4559 (4)	11.3 (3)[b]
F(3)	0.4014 (2)	0.8339 (6)	0.3909 (4)	12.0 (3)[b]
F(4)	0.4560 (2)	0.8551 (6)	0.3229 (4)	17.1 (5)[b]
B(2)	0.1737 (4)	0.6346 (9)	0.3475 (6)	8.9 (6)[b]
F(5)	0.1890 (4)	0.6185 (9)	0.2758 (6)	13.7 (7)[b]
F(6)	0.1408 (4)	0.7222 (9)	0.3350 (6)	13.7 (7)[b]
F(7)	0.1585 (4)	0.5206 (9)	0.3707 (6)	13.7 (7)[b]
F(8)	0.2063 (4)	0.6772 (9)	0.4084 (6)	13.7 (7)[b]
F(5′)	0.1348 (4)	0.6069 (9)	0.2978 (6)	13.9 (7)[b]
F(6′)	0.1997 (4)	0.6956 (9)	0.3021 (6)	13.9 (7)[b]
F(7′)	0.1931 (4)	0.5239 (9)	0.3792 (6)	13.9 (7)[b]
F(8′)	0.1670 (4)	0.7121 (9)	0.4108 (6)	13.9 (7)[b]
N	0.500	0.672 (4)	0.750	14 (1)[b]
C(11)	0.500	0.763 (6)	0.750	15 (1)[b]
C(12)	0.500	0.897 (6)	0.750	20 (2)[b]

[a] Estimated standard deviations are given in parentheses. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $^4/_3[a^2B(11) + b^2B(22) + c^2B(33) + ab(\cos\gamma)B(12) + ac(\cos\beta)B(13) + bc(\cos\alpha)B(23)]$. [b] Atoms were refined isotropically.

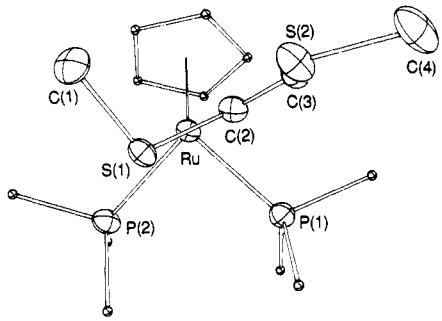


Figure 3. Another view of {Cp(PMe$_3$)$_2$Ru[S(Me)C=C(H)(SMe)]}(BF$_4$)$_2$•$^1/_2$CH$_3$CN (**2a**). The C$_5$ ring and phosphine methyls are shown as arbitrary spheres.

the final refinement, the two BF$_4$ orientations were 51 (1) and 49 (1)% occupied. The final cycle of refinement included 202 variable parameters and converged with R = 0.073 and R_w = 0.106.[9]

Refinement of the structure was carried out with use of the SHELX-76 package.[10] The final positional and thermal parameters are listed in Table V. Selected bond lengths and angles are presented in Table VI, and ORTEP drawings of the dication are given in Figures 2 and 3.

(9) Neutral-atom scattering factors and anomalous scattering corrections were taken from: *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.

(10) Sheldrick, G. M. SHELX-76. In *Computing in Crystallography*; Schenk, H., Olthof-Hazekamp, R., Van Koningsveld, H., Bassi, G. C., Eds.; Delft University Press: Delft, The Netherlands, 1978.

Table VI. Bond Distances and Angles for {Cp(PMe$_3$)$_2$Ru[S(Me)C=C(H)(SMe)]}(BF$_4$)$_2$•$^1/_2$CH$_3$CN (2a)

Bond Distances (Å)

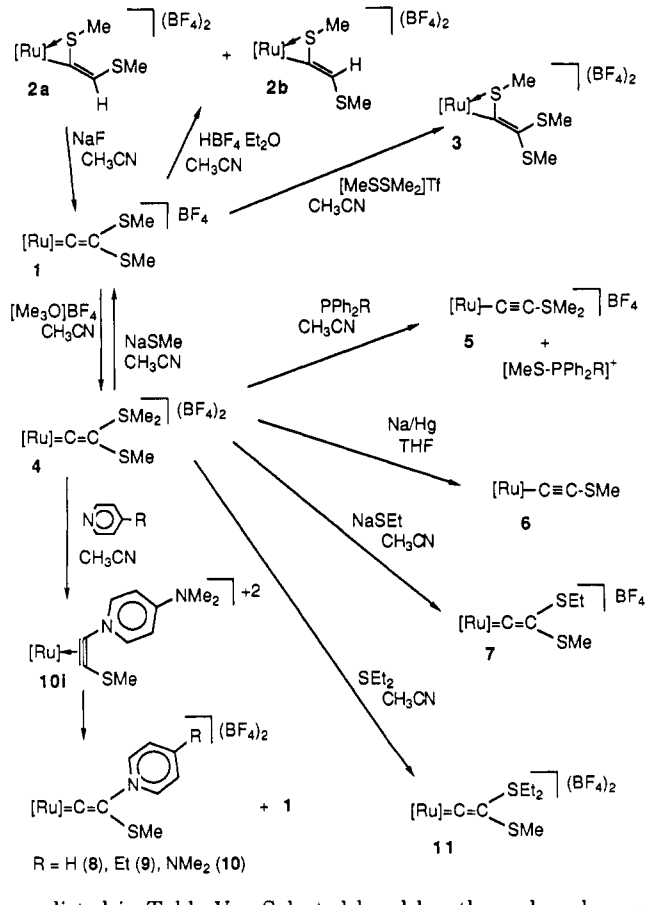
Ru-S(1)	2.380 (3)[a]	S(2)-C(3)	1.76 (1)
Ru-P(1)	2.337 (3)	S(2)-C(4)	1.78 (2)
Ru-P(2)	2.391 (4)	P(1)-C(5)	1.84 (1)
Ru-C(2)	2.03 (1)	P(1)-C(6)	1.84 (1)
Ru-C(21)	2.249 (9)	P(1)-C(7)	1.82 (1)
Ru-C(22)	2.20 (1)	P(2)-C(8)	1.84 (1)
Ru-C(23)	2.19 (1)	P(2)-C(9)	1.82 (2)
Ru-C(24)	2.24 (1)	P(2)-C(10)	1.84 (1)
Ru-C(25)	2.28 (1)	C(2)-C(3)	1.34 (2)
S(1)-C(1)	1.86 (1)	S(1)-C(2)	1.73 (1)
Ru-Centr[b]	1.876 (9)	N-C(11)	0.95 (8)[c]
C(2)-Centr	3.32 (2)	C(11)-C(12)	1.41 (9)[c]
S(1)-Centr	3.93 (1)		

Bond Angles (deg)

S(1)-Ru-P(1)	96.5 (1)	C(5)-P(1)-C(7)	100.8 (7)
S(1)-Ru-P(2)	83.6 (1)	C(6)-P(1)-C(7)	102.2 (7)
S(1)-Ru-C(2)	45.2 (3)	Ru-P(2)-C(8)	111.4 (5)
P(1)-Ru-P(2)	90.5 (1)	Ru-P(2)-C(9)	118.0 (6)
P(1)-Ru-C(2)	79.6 (3)	Ru-P(2)-C(10)	117.1 (5)
P(2)-Ru-C(2)	125.2 (3)	C(8)-P(2)-C(9)	102.2 (7)
Ru-S(1)-C(1)	109.8 (5)	C(8)-P(2)-C(10)	101.6 (6)
Ru-S(1)-C(2)	56.6 (4)	C(9)-P(2)-C(10)	104.3 (7)
C(1)-S(1)-C(2)	105.5 (6)	Ru-C(2)-S(1)	78.2 (5)
C(3)-S(2)-C(4)	99.8 (7)	Ru-C(2)-C(3)	148.3 (9)
Ru-P(1)-C(5)	114.4 (5)	S(1)-C(2)-C(3)	133 (1)
Ru-P(1)-C(6)	118.7 (4)	S(2)-C(3)-C(2)	120.6 (9)
Ru-P(1)-C(7)	117.2 (5)	C(5)-P(1)-C(6)	100.8 (7)
S(1)-Ru-Centr	134.5 (4)	N-C(11)-C(12)	180 (0)[c]
C(2)-Ru-Centr	116.3 (5)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits. [b] Centr = calculated center of the C$_5$ ring. [c] Acetonitrile molecule: N-C(11)-C(12).

Scheme I

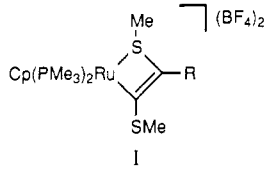


Results and Discussion

Reactions of $[Cp(PMe_3)_2Ru{=}C{=}C(SMe)_2]BF_4$ (1) with Electrophiles. The addition of $HBF_4{\cdot}Et_2O$ to $[Cp(PMe_3)_2Ru{=}C{=}C(SMe)_2]BF_4$ (1) leads to the formation of $\{Cp(PMe_3)_2Ru[C(SMe){=}C(H)SMe]\}(BF_4)_2$ as a mixture of *cis*-**2a** and *trans*-**2b** three-membered metallacyclic isomers in a 2:1 ratio (**2a:2b**) in an overall 98% yield (Scheme I). Complex **2a** was isolated as an air-stable yellow crystalline solid and was characterized by ^1H and ^{13}C NMR spectroscopy and elemental analyses, as well as an X-ray structure determination. The dark yellow residue of **2b** could not be isolated as a pure complex, so its characterization and assigned structure are based on ^1H and ^{13}C NMR data.

Complexes **2a,b** each show two SMe resonances at approximately 2.6 and 2.4 ppm (Table I); the SMe resonances at 2.6 ppm are similar to other ruthenium-coordinated sulfonium resonances observed in complexes such as $[CpRu(\eta^5\text{-}S(Me)CH{=}CHCH{=}CH_2]BF_4$[11] at 2.73 ppm and $\{Cp(PMe_3)_2Ru[S(Me)C{\equiv}CSMe]\}BF_4$[2] at 2.79 ppm. The β-vinyl proton of **2a**, assigned in the cis position with respect to the metal, is observed as a triplet at 7.38 ppm with J_{PH} = 2.83 Hz. In the complexes $Cp[P(OMe)_3]_3Mo[(E)\text{-}C(H){=}C(H)\text{-}t\text{-}Bu]$[12] and $Cp(dppe)Ru[(E)\text{-}C(CO_2Me){=}C(H)(CO_2Me)]$,[13] for which *E* isomer structures (proton cis to the metal center) were established by X-ray diffraction, the ^1H NMR β-vinyl proton resonances are observed as a triplet at 5.40 ppm with J_{PH} = 2.0 Hz and a singlet at 4.29 ppm, respectively. The β-vinyl proton resonance of **2b** is observed downfield with respect to the β-vinyl proton of **2a** as a doublet of doublets at 8.34 ppm with J_{PH} = 1.68 Hz. On the basis of a structural determination of $Cp(CO)(PPh_3)Ru[(Z)\text{-}C(CO_2Me){=}C(H)CO_2Me]$[13] the β-vinyl proton trans to the metal center was assigned as a doublet at 6.60 ppm with J_{PH} = 2.0 Hz; the trans β-vinyl proton chelate $Cp(PPh_3)Ru[C(CO_2Me){=}C(H)C(O)OMe]$[13] also is observed downfield, with respect to the cis complexes, as a doublet at 6.20 ppm with J_{PH} = 2.5 Hz. Likewise, the β-vinyl proton is further downfield when it is trans (6.815 ppm) to the Rh than cis (5.566 ppm) to the Rh in $(C_5Me_5)(PMe_3)(3,5\text{-xylyl})Rh[\text{-}C(CO_2Me){=}C(H)(CO_2Me)]$, on the basis of X-ray-determined structures of both isomers;[14a] the splitting patterns of the β-vinyl protons in these isomers are the same as in **2a,b**.

Another possible structure for **2b** is a four-membered metallacyclic complex as shown in structure I; however, this seems less likely because of steric congestion about the ruthenium center.



I

Complex **3** is prepared by the reaction of $[MeSSMe_2]Tf$ and $[Cp(PMe_3)_2Ru{=}C{=}C(SMe)_2]BF_4$ (1) (Scheme I). The resulting air-stable dark yellow residue was characterized by its ^1H and ^{13}C NMR spectra and elemental analysis. A number of attempts to grow crystals of **3** for X-ray determination were not successful. The ^1H NMR spectrum of **3** was found to be similar to the spectra of **2a,b** (Table I).

The ^{13}C NMR spectra of **2a,b** and **3** show the β-carbon resonances to be very similar, appearing as doublets at 139.99, 146.53, and 148.32 ppm, respectively, with $J_{PC} \approx 6$ Hz (Table II); the α-carbon resonances are also similar, appearing as doublets at 138.03, 141.21, and 148.23 ppm with J_{PH} = 18–19 Hz (Table II). The α- and β-carbon resonances of **2a,b** and **3** are similar to those of the *E* and *Z* isomers of the vinyl complex $Cp(CO)[P(OPh)_3]Fe[C(Me){=}C(Me)Ph]$;[14b] the ^{13}C NMR α- and β-carbon resonances are found at 137.7 (J_{PC} = 34.2 Hz) and 149.1 ppm (J_{PC} = 3.1 Hz) for the *E* isomer and 136.5 (J_{PC} = 37.2 Hz) and 152.4 ppm for the *Z* isomer. In contrast to a triplet that is observed for the α-carbon in many of the other complexes reported in Table II, the doublet observed for the α-carbon of **2a,b** and **3** may be due to the lack of coupling to the cis PMe_3.

The two PMe_3 methyl resonances in the ^1H and ^{13}C NMR spectra of **2a,b** and **3** occur as true doublets with J_{PH} and J_{PC} ranging from approximately 1.5 to 1.9 ppm and 18 to 20 ppm, respectively, for each of the inequivalent PMe_3 ligands (Tables I and II). Inequivalent PMe_3 resonances were also observed in the allene complex $[Cp(PMe_3)_2Ru(\eta^2\text{-}CH_2{=}C{=}CMe_2)]PF_6$,[15] for which the ^1H NMR spectra show PMe_3 resonances as doublets at 1.72 and 1.32 ppm ($J_{PH} \approx 9$ Hz) and the ^{13}C NMR resonances occur as doublets at 20.57 and 21.00 ppm ($J_{PC} \approx 32$ Hz). The appearances of inequivalent PMe_3 resonances in the ^1H and ^{13}C NMR spectra of **2a,b** and **3** are in contrast to the equivalent PMe_3 resonances observed for complexes 4–11 (Tables I and II). The inequivalent PMe_3 groups in the ^1H and ^{13}C NMR spectra are supported by an X-ray study of **2a**.

A slow reaction (88 h, 23 °C) of complex **2a** and an excess of NaF in CH_3CN gives the deprotonated vinylidene product **1** in 47% yield (Scheme I); however, under the same conditions no reaction was observed with **2b**, as established by ^1H NMR spectroscopy. Bases such as $Na[HBEt_3]$, NaOMe, and Na/Hg when reacted with **2a** and/or **2b** afford only decomposition products.

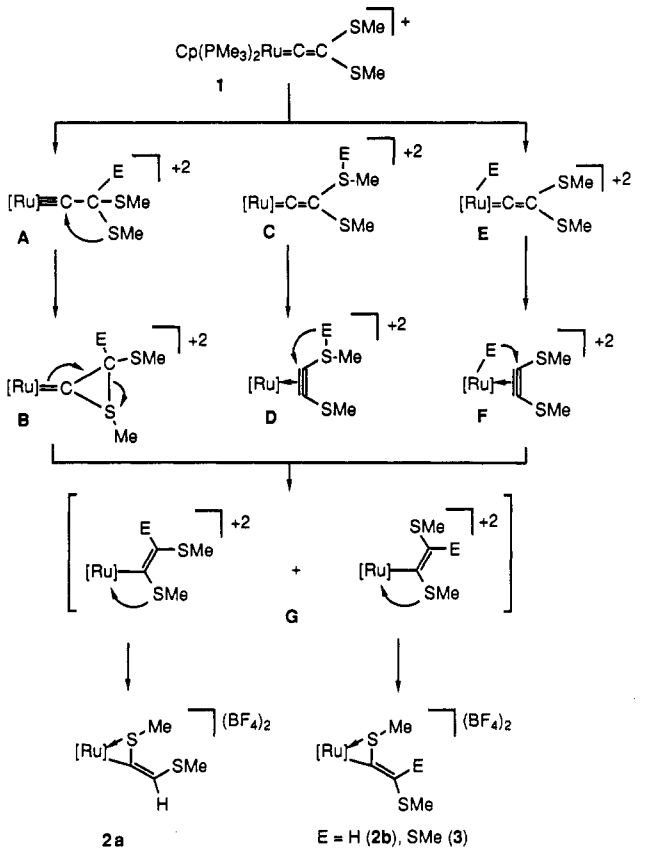
The addition of $[Me_3O]BF_4$ to $[Cp(PMe_3)_2Ru{=}C{=}C(SMe)_2]BF_4$ (1) gives the sulfoniovinylidene $[Cp(PMe_3)_2Ru{=}C{=}C(SMe_2)(SMe)](BF_4)_2$ (**4**) in 91% yield (Scheme I). Complex **4** was isolated as an air-stable yellow powder and was characterized by its ^1H and ^{13}C NMR and IR spectra and elemental analyses. Its ^{13}C NMR spectrum shows a vinylidene α-carbon resonance as a triplet at 317.01 ppm and a β-carbon resonance as a singlet at 110.92 ppm (Table II). The α- and β-carbon resonances are characteristic of other vinylidene complexes such as $[Cp(PMe_3)_2Ru{=}C{=}C(SMe_2)(Me)](BF_4)_2$,[2] where the α-carbon is observed as a triplet at 323.22 ppm with J_{PC} = 18.78 Hz and the β-carbon is a singlet at 109.57 ppm. Further characterization and discussion of a variety of both mono- and dicationic vinylidene complexes of $[Cp(PMe_3)_2Ru{=}C{=}C(R)SMe_n](BF_4)_n$ (R = H, Me; n = 1, 2) have been presented previously.[2]

Mechanisms for the Formation of the Sulfur-Coordinated Vinyl Complexes 2a,b and 3. For the formation of the sulfur-coordinated vinyl complexes **2a,b** and **3**, one may consider the three mechanisms shown in Scheme II.

The first mechanism involves initial addition of the H^+ and MeS^+ (from $[MeSSMe_2]^+$) electrophiles to the β-vinylidene carbon of **1** to form a carbyne (A). This addition

(11) Hachgenei, J. W.; Angelici, R. J. *J. Organomet. Chem.* **1988**, *355*, 359.
(12) Bottrill, M.; Green, M. *J. Am. Chem. Soc.* **1977**, *99*, 5795.
(13) Bruce, M. I.; Catlow, A.; Humphrey, M. G.; Koutsantonis, G. A.; Snow, M. R.; Tiekink, R. T. *J. Organomet. Chem.* **1988**, *338*, 59.
(14) (a) Jones, W. D.; Chandler, V. L.; Feher, F. J. *Organometallics* **1990**, *9*, 164. (b) Reger, D. L.; Belmore, K. A.; Mintz, E.; Charles, N. G.; Griffith, E. A. H.; Amma, E. L. *Organometallics* **1983**, *2*, 101.
(15) Bruce, M. I.; Hambley, T. W.; Rodgers, J. R.; Snow, M. R.; Wong, F. S. *Aust. J. Chem.* **1982**, *35*, 1323.

Scheme II



of electrophiles (such as H^+) to β-vinylidene carbons is known for molybdenum and tungsten compounds[16] to give complexes such as $(dppe)(CO)_3W(\equiv CCH_2Ph)$[16b] and $Cp[P(OMe)_3]_2Mo[\equiv CC(H)(t\text{-}Bu)(SMe)]$.[16c] However, such additions to the β-carbon of ruthenium vinylidene complexes have not been reported previously. Further rearrangement of the carbyne intermediate (A) could proceed by attack of a lone pair of electrons on one of the SMe groups on the carbyne carbon to form a thiiranium–carbene intermediate (B). A related thiiranium compound[17] was observed at −60 °C following the ionization of 2,3-dimethyl-3-(methylthio)-2-chlorobutane in SO_2 (eq 4).

(4)

Further rearrangement of B could form either the cis- or trans-vinyl complex G; these 16-electron intermediates would then go on to form **2a,b** or **3** by coordination of an α-sulfur (Scheme II).

A second possible mechanism may involve initial addition of H^+ and MeS^+ to a sulfur in **1** to give the sulfoniovinylidene intermediate C, similar to the products shown in eq 3. Rearrangement of C to D by a 1,2-SMe migration, for which there is evidence in reactions of 1,[2] could be followed by the migration of H^+ of MeS^+ to give the isomers of G. Coordination of a sulfur in G would give the isomeric products (**2** and **3**).

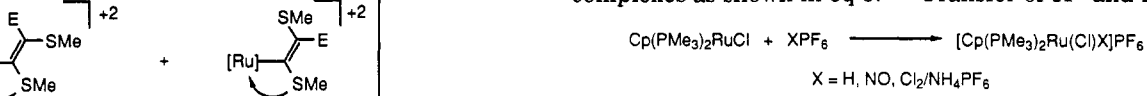
(16) (a) Kim, H. P.; Angelici, R. J. *Adv. Organomet. Chem.* **1987**, *27*, 51. (b) Birdwhistell, K. R.; Burgmayer, S. J. N.; Templeton, J. L. *J. Am. Chem. Soc.* **1983**, *105*, 7789. (c) Beevor, R. G.; Freeman, M. J.; Green, M.; Morton, C. E.; Orpen, A. G. *J. Chem. Soc., Chem. Commun.* **1985**, 68.

(17) Lucchini, V.; Modena, G.; Zaupa, T.; Capozzi, G. *J. Org. Chem.* **1982**, *47*, 590.

Table VII. Selected Bond Lengths (Å) in Metal–Carbon–Sulfur Three-Membered Metallacyclic Complexes

compd	M–S	M–C	C–S
$\{Cp(PMe_3)_2Ru[S(Me)C{=}C(H)SMe]\}(BF_4)_2$ (**2a**)	2.380 (3)	2.03 (1)	1.73 (1)
$Cp(CO)_2Mo[S(Me)CH_2]$[25]	2.442 (3)	2.24 (1)	1.78 (1)
$[Me_2Ga(N_2C_3H_3)(OCH_2CH_2NMe_2)](CO)_2Mo[S(Me)CH_2]$[26]	2.475 (6)	2.202 (3)	1.744 (3)
$(HBPz_3)(CO)_2W[S(Me)C(H)PPh_2]$[24]	2.440 (9)	2.22 (3)	1.80 (3)
$(PPh_3)ClPd[S(Me)CH_2]$[27]	2.362 (1)	2.042 (9)	1.726 (9)
$\{(PPh_3)_2Pd[S(Me)CH_2]\}PF_6$[21]	2.367 (8)	2.06 (4)	1.77 (4)

A third possible mechanism involves initial addition of H^+ or MeS^+ to the ruthenium center to form the ruthenium–hydride or ruthenium–sulfide intermediate E (Scheme II). In a related system, $Cp(PMe_3)_2RuCl$ reacts with HPF_6, $(NO)PF_6$, or Cl_2 to give 7-coordinate cationic complexes as shown in eq 5.[18] Transfer of H^+ and MeS^+



(5)

to the carbon of the π-alkyne complex F would give G, which could then go on to form **2a,b** and **3** (Scheme II). All three mechanisms have plausible features, and there is no evidence that strongly favors one over the others.

X-ray Crystal Structure of $\{Cp(PMe_3)_2Ru[S(Me)C{=}C(H)SMe]\}(BF_4)_2 \cdot {}^1/_2CH_3CN$ (2a). The geometry about the ruthenium is a 7-coordinate, distorted capped octahedron as shown in Figure 2. The orientation (Figure 3) of the η^2-S(Me)C=C(H)SMe ligand is defined by the angle (22.3 (2)°) between the S(1)–C(2)–C(3) plane and the Ru–P(2) bond vector. Perhaps crowding by the η^2 ligand causes the P(1)–Ru–P(2) angle at 90.5 (1)° to be the smallest angle reported for $Cp(PMe_3)_2RuX$-type compounds: X = Cl,[19] 95.0 (2)°; X = $(=C{=}C(Me)_2)PF_6$,[20] 94.08 (8)°; X = $[=C{=}C(H)(SMe_2)](BF_4)_2$,[2] 93.08 (7)°; X = $(\eta^2\text{-}CH_2{=}C{=}CH_2)PF_6$,[15] 91.9 (1)°. Although the P(1), P(2), S(1), and C(2) atoms (Figure 2) are not arranged in a square, the longer Ru–P(2) distance (2.391 (4) Å) is very roughly trans to the carbon and the shorter Ru–P(1) distance (2.337 (3) Å) is approximately trans to the sulfur. The differences are comparable to those in the complex $\{(PPh_3)_2Pd[S(Me)CH_2]\}PF_6$,[21] in which the Pd–P bond trans to the carbon is longer (2.350 (5) Å) than the Pd–P bond trans to the sulfur (2.271 (6) Å). These differences were interpreted in terms of a stronger trans influence for carbon than for sulfur.[22,23]

The Ru–C(2)–S(1) system is a three-membered metallacycle with Ru–C(2), Ru–S(1), and C(2)–S(1) distances that are similar to those of other three-membered metallacyclic complexes (Table VII) in which the η^2-carbon–sulfur ligand is a three-electron donor. The Ru–C(sp^2) distance is expected to be slightly shorter than the M–C(sp^3) distances shown in Table VII; however, the distance is still much longer than the M=C(carbene) distance of

(18) Bruce, M. I.; Tomkins, I. B.; Wong, F. S.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1982**, 687.

(19) Bruce, M. I.; Wong, F. S.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1981**, 1398.

(20) Bruce, M. I.; Wong, F. S.; Skelton, B. W. *J. Chem. Soc., Dalton Trans.* **1982**, 2203.

(21) Miki, K.; Kai, Y.; Yasuoka, N.; Kasai, N. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 3639.

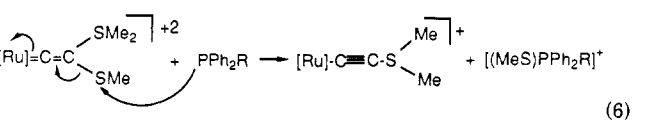
(22) Appleton, T. G.; Clark, H. C.; Manzer, L. E. *Coord. Chem. Rev.* **1973**, *10*, 335.

(23) McWeeny, R.; Mason, R.; Towl, A. D. C. *Discuss. Faraday Soc.* **1969**, *47*, 20.

1.93 (2) Å in the metallacyclic carbene $\{(HBPz_3)(CO)_2W[\eta^2\text{-}CH(SMe)]\}$.[24] The C(2)–C(3) distance at 1.34 (2) Å and S(1)–C(2)–C(3) angle at 133 (1)° is similar to the vinyl C–C distance at 1.31 (3) Å and S–C–C angle at 138.1 (18)° for the complex $Cp[P(i\text{-}Pr)_3]Rh[C(S)=CH_2]$.[28] The C(2)–C(3)–S(2) angle (120.6 (9)°) is typical of $C(sp^2)$ centers. The C(3)–S(2) distance at 1.76 (1) Å is similar to $C(sp^2)$–S single-bond distances found in $[(PPh_3)_2(CO)_3Mn{=}C{=}C(NMe_2)(SMe)]BF_4$[29] (1.784 (16) Å) and $Cp(PPh_3)(CO)W(\equiv CSPh)$[30] (1.768 (12) Å). The angle between the C(2)–C(3)–S(2) plane and the Cp plane is 43.0 (9)° with C(2) at 3.32 (2) Å and S(1) at 3.93 (1) Å from the centroid of the Cp ring. The S(1), C(4), and Ru atoms lie out of the C(2)–C(3)–S(2) plane by −0.020 (3), −0.38 (2), and 0.169 (1) Å, respectively, indicating that the vinyl ligand is not entirely planar.

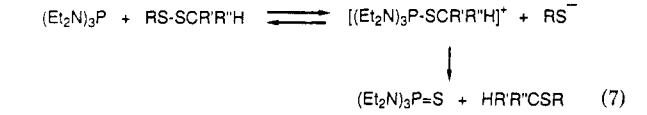
Reactions of 4 with Phosphines and Reducing Agents. The reaction of **4** with PPh_2R (R = Me, Ph; Scheme I) gives $[Cp(PMe_3)_2Ru{-}C{\equiv}CSMe_2]BF_4$ (**5**) and $[(MeS)PPh_2R]BF_4$ in quantitative conversion according to ^1H NMR spectra of the reaction solutions. Complex **5** has previously been characterized,[2] and its ^1H NMR data are given in Table I. The phosphonium salts were characterized by preparing them independently in reactions of $[MeSSMe_2]Tf$ with PPh_2R in CH_2Cl_2. The resulting colorless oils of $[(MeS)PPh_2R]Tf$ were characterized by ^1H and ^{31}P NMR spectroscopy and when R = Me, a FAB mass spectrum was also obtained. The $[(MeS)PPh_3]ClO_4$ compound was reported[31] previously as exhibiting a ^1H NMR methyl resonance at 2.47 ppm (d, J_{PH} = 15 Hz), which is identical with that obtained in our studies (see Experimental Section). The $[(MeS)PPh_2Me]Tf$ compound has not been reported previously. During the reactions of **4** with the phosphines, it was observed that the resonances for $[(MeS)PPh_2R]^+$ disappeared with time and new peaks appeared. The new resonances were identified as $[MePPh_2R]Tf$ and $S{=}PPh_2R$ by an independent reaction; a solution of $[(MeS)PPh_2Me]Tf$ and excess PPh_2Me in CH_2Cl_2 was refluxed for 1 h, and the solution was concentrated under reduced pressure; Et_2O was added to precipitate $[Me_2PPh_2]Tf$ and $S{=}PPh_2Me$. The compounds were characterized by ^1H NMR and GCMS spectroscopy.[32]

Although vinylidene ligands in cationic complexes often undergo nucleophilic attack at the α-carbon to give vinyl derivatives,[33] this does not occur in the reaction of **4** with phosphines, probably due to congestion at the ruthenium center. Instead, the MeS^+ group is displaced by the phosphine, presumably by nucleophilic attack at the sulfur (eq 6). Harpp and Gleason[34] observed similar phosphine



(6)

products in the reaction of PR_3 and a disulfide, which gave in the first step (alkylthio)triaminophosphonium and RS^- ions (eq 7). RS^- subsequently attacks the carbon adjacent



(7)

to the sulfur of the phosphonium salt, giving thioether and phosphine sulfide products.

Ruthenium vinylidene complexes such as $[Cp(PMe_3)_2Ru{=}C{=}C(SMe_n)(Me)](BF_4)_n$ (n = 1, 2) undergo one- (n = 1) or two-electron (n = 2) reductions to give $Cp(PMe_3)_2Ru{-}C{\equiv}CMe$. The reactions and mechanisms have been discussed in the previous paper.[2] Similarly, the reduction of **4** with Na/Hg amalgam gives $Cp(PMe_3)_2Ru{-}C{\equiv}CSMe$ (**6**) in 69% yield as the only isolated ruthenium-containing product (Scheme I). Complex **6** was previously characterized (Table I). Complex **4** reacts with the reducing agent $Na[HBEt_3]$ to give both complexes **5** and **6**. A 5-mm NMR tube containing **4** in CD_3CN was treated with three $^1/_2$-equiv aliquots of $Na[HBEt_3]$. The ^1H NMR spectra of the solution showed that complexes **5** and **6** were present in equal ratios after each addition of $Na[HBEt_3]$. The equal distribution between **5** and **6** suggests that this reduction does not favor the one-electron reduction over the two-electron reduction.

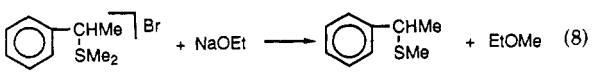
Reactions of $[Cp(PMe_3)_2Ru{=}C{=}C(SMe_2)(SMe)](BF_4)_2$ (4) with Nucleophiles. Unlike the reactions of phosphines and reducing agents, other nucleophiles react with **4** to displace the SMe_2 group from the vinylidene ligand. Thus, the addition of 1 equiv of NaSR (R = Me, Et) to **4** gives products **1** and $[Cp(PMe_3)_2Ru{=}C{=}C(SEt)(SMe)]BF_4$ (**7**), which are isolated in 50% and 54% yields, respectively (Scheme I). Complex **7** was isolated as a red powder and was characterized by ^1H and ^{13}C NMR (Tables I and II), IR, and FAB mass spectra and elemental analyses. In the ^1H and ^{13}C NMR spectra of **7** the vinylidene resonances are similar to those of **1** and are discussed in detail in the previous paper.[2] Mercaptides, NaSR, can also act as reducing agents in the reaction with **4**. In reactions with an excess (over 2 equiv) of NaSR, the acetylides $Cp(PMe_3)_2Ru{-}C{\equiv}CX$ (X = SMe (**5**) for R = Me; X = SMe (**5**), SEt for R = Et) were observed as side products in the ^1H NMR spectra. The (ethylthio)acetylide $Cp(PMe_3)_2Ru{-}C{\equiv}CSEt$ was identified in the ^1H NMR spectrum; however, the complex was not successfully separated from **5**, which was also present in the reaction mixture.

The reactions of $4\text{-}NC_5H_4R$ (R = H, Et, NMe_2) and SEt_2 with **4** give the dicationic vinylidene complexes **8**–**11** (Scheme I). The ^1H NMR spectra of the reaction mixtures show the presence of free SMe_2 when the reactions are performed in a 5-mm NMR tube. The ^{13}C NMR spectra of **8**, **10**, and **11** show α-carbon resonances as a triplet ranging from 313.81 to 324.43 ppm ($J_{PC} \approx 15$ Hz) and β-carbon resonances ranging from 105.56 to 128.57 ppm (Table II). The α- and β-carbon resonances are similar to those of other dicationic vinylidene complexes such as $[Cp(PMe_3)_2Ru{=}C{=}C(SMe_2)(R)](BF_4)_2$:[2] 323.22 and 109.57 ppm for R = Me; 332.64 and 102.58 ppm for R = H.

A refluxing solution of pyridine and complex **4** in CH_3CN gives a yellow powder of $[Cp(PMe_3)_2Ru{=}C{=}C$-

(24) (a) Kim, H. P.; Kim, S.; Jacobson, R. A.; Angelici, R. J. *Organometallics* **1984**, *3*, 1124. (b) Kim, H. P.; Kim, S.; Jacobson, R. J.; Angelici, R. J. *Organometallics* **1986**, *5*, 2481.
(25) de Gil, E. R.; Dahl, L. F. *J. Am. Chem. Soc.* **1969**, *91*, 3751.
(26) Chong, K. S.; Rettig, S. J.; Storr, A.; Trotter, J. *Can. J. Chem.* **1980**, *58*, 1080.
(27) Miki, K.; Kai, Y.; Yasuoka, N.; Kasai, N. *J. Organomet. Chem.* **1977**, *135*, 53.
(28) Werner, H.; Wolf, J.; Zolk, R.; Schubert, U. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 981.
(29) Clark, G. R.; Marsden, K.; Roper, W. R.; Wright, L. J. *J. Am. Chem. Soc.* **1980**, *102*, 6570.
(30) Greaves, W. W.; Angelici, R. J.; Helland, B. J.; Klima, R.; Jacobson, R. A. *J. Am. Chem. Soc.* **1979**, *101*, 7618.
(31) Ohmori, H.; Maeda, H.; Konomoto, K.; Sakai, K.; Masui, M. *Chem. Pharm. Bull.* **1987**, *35*, 4473.
(32) $[PPh_2Me_2]Tf$: ^1H NMR ($CDCl_3$) δ 7.79 (m, 10 H), 2.45 (d, J_{PH} = 14.1 Hz, 6 H). $S{=}PPh_2Me$: ^1H NMR ($CDCl_3$) δ 7.84 (m, 10 H), 2.94 (d, J_{PH} = 13.2 Hz, 3 H); GCMS m/e 232 (M^+), 217 (M^+ – Me), 200 (M^+ – S).
(33) Bruce, M. I.; Swincer, A. G. *Adv. Organomet. Chem.* **1983**, *22*, 59.
(34) Harpp, D. N.; Gleason, J. G. *J. Am. Chem. Soc.* **1971**, *93*, 2437.

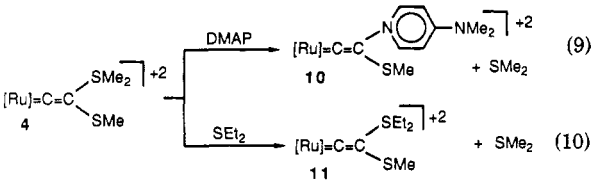
$(NC_5H_5)(SMe)](BF_4)_2$ (8) and a red powder of 1 collected in 57% and 31% yields, respectively (Scheme I). The formation of 1 and $[Me\text{-}NC_5H_5]BF_4$ presumably occurs by attack of the pyridine on one of the sulfonium methyl groups of 4. Saunders and co-workers[35] have reported that EtO^- attacks a sulfonium methyl group as shown in eq 8



(8)

to give a thioether compound. The identification of $[Me\text{-}NC_5H_5]^+$ as a product of the reaction of 4 with pyridine was made by comparing the ^1H NMR spectrum of this reaction mixture run in CD_3CN in an NMR tube with the spectrum of $[Me\text{-}NC_5H_5]Tf$[36] prepared from the reaction of $MeSO_3CF_3$ with pyridine in a 5-mm NMR tube with CD_3CN. Similar products were observed when a 5-mm NMR tube was charged with complex 4 (5 mg, 0.008 mmol) and 4-NC_5H_4Et (0.001 mL, 0.009 mmol) in CD_3CN and heated to 70 °C for 20 h. The ^1H NMR spectrum of this reaction mixture showed the presence of $[Cp(PMe_3)_2Ru{=}C{=}C(4\text{-}NC_5H_4\text{-}Et)(SMe)](BF_4)_2$ (9) and 1 in a 3:1 ratio. However, a refluxing solution of DMAP with 4 in CH_3CN for 1 h gave $[Cp(PMe_3)_2Ru{=}C{=}C(4\text{-}NC_5H_4NMe_2)(SMe)](BF_4)_2$ (10) as the only ruthenium product as a pale red powder in 93% yield (Scheme I). When 4 and the sterically hindered 2,6-dimethylpyridine were refluxed in CH_3CN for 70 h, there was no reaction.

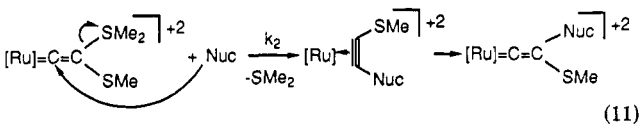
Kinetics and Mechanisms of the Reaction of 4 with DMAP and SEt_2. Kinetic studies of the reactions of DMAP and SEt_2 with 4 were undertaken to determine if reactions 9 and 10 proceed by either a nucleophilic attack or a dissociative mechanism. Nucleophilic attack would



(9)

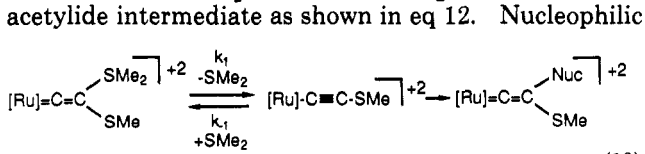
(10)

presumably proceed by initial addition of the nucleophile at the α-carbon of the vinylidene followed by loss of SMe_2 to give the intermediate $[Cp(PMe_3)_2Ru(\eta_2\text{-}MeSC{\equiv}CNuc)](BF_4)_2$ as shown in eq 11. This η^2-acetylene complex could then rearrange via a 1,2-SMe migration to the vinylidene product 10 or 11. Evidence for such 1,2-SMe migration has been obtained for 1, and mechanisms for this rearrangement have been discussed in the previous paper.[2]



(11)

A dissociative mechanism for reactions 9 and 10 would involve initial SMe_2 dissociation to give a 16-electron acetylide intermediate as shown in eq 12. Nucleophilic addition of the nucleophile to the β-carbon of the acetylide intermediate would give the observed vinylidene complex.



(12)

Rates of reactions 9 and 10 were determined under pseudo-first-order conditions, where DMAP and SEt_2 were present in large excess.[37] The DMAP concentrations were between 5 (0.20 M) and 15 (0.60 M) times as large as that of 4 (Table III). It was not possible to use DMAP concentrations greater than 0.60 M, because the DMAP precipitates from solution at 0 °C. The SEt_2 concentrations were varied between 10 (0.36 M) and 40 (1.44 M) times as large as that of 4 (Table III). Pseudo-first-order rate constants, k_{obs}, for reactions 10 and 11 are given in Table III. Plots (Figure 1) of k_{obs} vs [Nuc] give k_1 and k_2 values from the intercept and slope, respectively, and show that the reactions follow the rate law $-d[4]/dt = k_1[4] + k_2[4][Nuc]$, where $k_{obs} = k_1 + k_2[Nuc]$.

The plot of k_{obs} vs concentration for DMAP (Figure 1) gives a k_2 value of $(3.53 \pm 0.39) \times 10^{-4}$ M^{-1} s^{-1} at 0 °C with a marginally significant k_1 value of $(0.22 \pm 0.16) \times 10^{-4}$ s^{-1}; for SEt_2 (Figure 1) the plot gives $k_2 = (0.45 \pm 0.05) \times 10^{-4}$ M^{-1} s^{-1} and $k_1 = (0.71 \pm 0.05) \times 10^{-4}$ s^{-1} at 70 °C. While the reaction of DMAP appears to occur almost completely by the k_2 nucleophilic attack pathway, the reaction with the less nucleophilic Et_2S occurs to a significant extent by both the k_2 and k_1 (dissociative) pathways.

Supporting a nucleophilic attack mechanism (eq 11) for the reaction with DMAP is the observation of an intermediate, which we propose to be the η^2-acetylene complex $[Cp(PMe_3)_2Ru(\eta^2\text{-}MeSC{\equiv}C\text{-}4\text{-}NC_5H_4NMe_2)](BF_4)_2$ (**10i**), during kinetic studies of the reaction of DMAP and 4 in CD_3CN at 0 °C (Scheme I). The ^1H NMR resonances of the intermediate are significantly different from those of the vinylidene product **10**; the Cp resonance at 5.55 ppm is upfield of that (5.76 ppm) in **10**. Bullock[38] has reported a similar upfield shift of the ^1H NMR Cp resonance in the η^2-acetylene complex $[Cp(PMe_3)_2Ru(\eta^2\text{-}MeC{\equiv}CH)]PF_6$ (5.02 ppm) as compared to that (5.41 ppm) in the vinylidene $[Cp(PMe_3)_2Ru{=}C{=}C(H)(Me)]PF_6$. The methyl groups of the inequivalent PMe_3 ligands in **10i** are observed as doublets at 1.65 and 1.38 ppm with $J_{PH} \approx 10$ Hz (Table I), whereas the equivalent PMe_3 ligands in **10** give rise to a pseudodoublet for the methyl groups at 1.56 ppm. Complexes with unsymmetrical ligands as in **10i** generally show inequivalent PMe_3 resonances; this also occurs in complexes **2a,b** and **3** (Table I) and in $[Cp(PMe_3)_2Ru(\eta^2\text{-}CH_2{=}C{=}CMe_2)]PF_6$,[15] for which the PMe_3 resonances occur at 1.72 and 1.32 ppm (d, $J_{PH} \approx 9$ Hz). The intermediate **10i** partially rearranges to **10** and partially gives $[Cp(PMe_3)_2Ru(NCCD_3)]BF_4$ (previously characterized by Treichel and Komar)[5] upon warming the NMR tube from the 0 °C of the reaction to room temperature. The acetonitrile complex was observed in increasing amounts with respect to **10** as the concentration of DMAP was increased. This suggests that the DMAP somehow promotes the displacement of the η^2-alkyne from **10i** to give more $[Cp(PMe_3)_2Ru(NCCD_3)]BF_4$.

Conclusions

Electrophiles generally add to non-sulfur-containing vinylidene complexes at the β-carbon to give carbyne complexes such as $(dppe)(CO)_3W(\equiv CCH_2Ph)$[16b] or at the metal center to give metal hydride or alkyl complexes. In contrast the (methylthio)vinylidene $[Cp(PMe_3)_2Ru{=}C{=}C(SMe)_2]BF_4$ (1) reacts with electrophiles either at a sulfur to give the sulfoniovinylidene complex 4 (Scheme I) or at a vinylidene carbon to give a sulfur-coordinated vinyl

(35) Saunders, W. H., Jr.; Bonadies, S. D.; Braunstein, M.; Borchardt, J. K.; Hangreaves, R. T. *Tetrahedron* **1977**, *33*, 1570.
(36) ^1H NMR (CD_3CN): δ 8.66 (d, J_{HH} = 5.9 Hz, 2-H), 8.49 (t, J_{HH} = 7.8 Hz, 4-H), 8.01 (t, J_{HH} = 6.6 Hz, 3-H), 4.31 (s, Me).
(37) Espenson, J. H. *Chemical Kinetics and Reaction Mechanisms*; McGraw-Hill: St. Louis, MO, 1981; p 12.
(38) Bullock, R. M. *J. Chem. Soc., Chem. Commun.* **1989**, 165.

complex as in **2a,b** and **3** (Scheme II).

While nucleophiles primarily add to the α-carbon of non-sulfur-containing vinylidenes to afford vinyl complexes, nucleophilic addition to the sulfoniovinylidene complex $[Cp(PMe_3)_2Ru{=}C{=}C(SMe_2)SMe](BF_4)_2$ (**4**) occurs in several ways: (1) Phosphines displace an MeS^+ group to give $[Cp(PMe_3)_2Ru{-}C{\equiv}CSMe_2]BF_4$ (**5**). (2) Pyridines displace a methyl from the sulfonium group, forming $[Cp(PMe_3)_2Ru{=}C{=}C(SMe)_2]BF_4$ (**1**). (3) Pyridines, mercaptides, and sulfides displace the SMe_2 group. The observation of the π-alkyne intermediate **10i** in mechanistic studies of **4** with SEt_2 and DMAP supports the proposal that the latter reactions proceed by nucleophilic attack at the α-carbon of **4** to form a π-alkyne, which rearranges to the vinylidene product. It is clear from these and previous studies[2] that the presence of MeS groups has a major influence on the reactivity of the vinylidene ligand.

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Supplementary Material Available: Tables of thermal parameters, additional bond angles, and least-squares planes (4 pages); a table of calculated and observed structure factors (15 pages). Ordering information is given on any current masthead page.

Studies on Rare-Earth Allyl Compounds. 6. Syntheses and Structures of the Novel Trinuclear Complexes $(\eta^3\text{-}C_3H_5)_2Ln(\mu_2\text{-}Cl)_2(\mu_3\text{-}Cl)_2Mg(tmed)(\mu_2\text{-}Cl)Mg(tmed)$

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A series of new allyllanthanide complexes, $(\eta^3\text{-}C_3H_5)_2LnCl_5Mg_2(tmed)_2$ (where Ln = La, Ce, Pr, Nd, Sm; and tmed = tetramethylethylenediamine), have been prepared by the reaction of anhydrous $LnCl_3$ with allyl Grignard reagents and tmed in THF at 0 °C. They are air- and moisture-sensitive and show the characteristic reactions of allyl metallic compounds with CO_2, H_2O, acetone, etc. The five compounds were characterized by elemental analyses, infrared spectra, mass spectra, and molar conductivities. The structures of three complexes have been determined by X-ray analysis: $(\eta^3\text{-}C_3H_5)_2Ce(\mu_2\text{-}Cl)_2(\mu_3\text{-}Cl)_2Mg(tmed)(\mu_2\text{-}Cl)Mg(tmed)$, orthorhombic, space group $P2_12_12_1$, a = 11.245 (2) Å, b = 15.053 (1) Å, c = 18.206 (1) Å, Z = 4, R = 0.043 for 2371 observed reflections; $(\eta^3\text{-}C_3H_5)_2Ce(\mu_2\text{-}Br)_2(\mu_3\text{-}Br)_2Mg(ether)_2(\mu_2\text{-}Br)Mg(ether)_2$, monoclinic, space group $C2/c$, a = 20.223 (3) Å, b = 11.333 (2) Å, c = 18.917 (3) Å, β = 122.58 (2)°, Z = 4, R = 0.088 for 1663 observed reflections; $(\eta^3\text{-}C_3H_5)_2Nd(\mu_2\text{-}Br)_2(\mu_3\text{-}Br)_2Mg(ether)_2(\mu_2\text{-}Br)Mg(ether)_2$, monoclinic, space group $C2/c$, a = 20.203 (3) Å, b = 11.286 (3) Å, c = 18.925 (4) Å, β = 122.58 (2)°, Z = 4, R = 0.072 for 1904 observed reflections. The complexes have trianglar metallic skeletons bonded together by three bridging and two capping halide atoms. The two allyl groups in the structures are η^3-bonded to the lanthanide ions.

Introduction

During the last three decades, allylnickel and allylpalladium complexes, among others, have been widely used in organic syntheses for the formation of C–C bonds. The success of these complexes in synthetic work mainly depends on their high reactivities.[1] In contrast, allyllanthanide complexes are less known and studied, probably owing to the difficulty of their preparation. However, these complexes may show activities[2] just as high as those of allyl transition-metal complexes.

Earlier we reported the structure of $[Li_2(\mu\text{-}C_3H_5)(C_4H_8O_2)_3][Ce(\eta^3\text{-}C_3H_5)_4]$,[3] the first structure of an allyllanthanide complex. Here we report the syntheses, structural studies, and some properties of a novel series of trinuclear allyllanthanide complexes.

Tsutsui[4] used allyl Grignard reagents to synthesize allyllanthanide compounds, but no further developments have been reported since. Three years ago, when lanthanide chlorides were treated with allylmagnesium bromide in ether at 0–5 °C, we found that beautiful crystals grew in these systems, which were characterized as $(\eta^3\text{-}C_3H_5)_2LnX_5Mg_2(Et_2O)_4$ (where Ln = Ce, Nd) by X-ray analysis. However, some difficulties arose in the determinations: these new compounds were mixed together with the white solid $LnCl_3$. Besides, they were difficult to isolate and analyze due to the weakly coordinating Et_2O. There was also the problem that the halide atoms in these crystals might be Cl, Br, or both, which was difficult to determine by routine analysis. Therefore, with allylmagnesium chloride instead of allylmagnesium bromide as the initial material, THF instead of ether as the

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(1) Chiusoli, G. P.; Salerno, G. In *The Chemistry of the Metal-Carbon Bond*; Hartley, F. R., Patai, S., Eds.; Wiley: New York, 1985; Vol. 3, p 143.
(2) Mazzei, A. In *Organometallics of the f-Elements*; Marks, T. J., Fischer, R. D., Eds.; D. Reidel: Dordrecht, The Netherlands, 1979; p 388.
(3) Huang, Z. E.; Chen, M. Q.; Qiu, W. J.; Wu, W. L. *Inorg. Chim. Acta* **1987**, *139*, 203.
(4) Tsutsui, M.; Ely, N. *J. Am. Chem. Soc.* **1975**, *97*, 3551.

0276-7333/91/2310-0098$02.50/0