$(PMe_3)_3$ (0.54 g, 1 mmol) in Et_2O (40 mL). The reaction mixture was stirred at ca. 10 °C for 8 h, during which time a pale red color developed. The solvent was then reduced in vacuo to 10–15 mL. After centrifugation and cooling at −10 °C $W(CH_3)(S_2CN\text{-}i\text{-}Pr_2)(CO)_2(PMe_3)_2$ was obtained as orange crystals in 80% yield.

Method II. To a red solution of an equilibrium mixture of $W(\eta^2\text{-}C(O)CH_2SiMe_3)(S_2CN\text{-}i\text{-}Pr_2)(CO)(PMe_3)_2$ and its alkyl isomer (0.65 g, 1 mmol) in acetone was added deaerated distilled water (1 drop), and the resulting solution was stirred for 1 h. Volatile components were then removed under reduced pressure, and the residue was extracted with Et_2O (15 mL). Crystallization at −10 °C afforded **8** in practically quantitative yield. From $W(CH_3)Cl(CO)_2(PMe_3)_3$ and the appropriate salts (NaS_2CNR_2, KS_2COR, and Tl(acac)) or by generation of $W(\eta^2\text{-}C(O)CH_2SiMe_3)(L\text{-}L)(CO)(PMe_3)_2$ complexes in situ and subsequent addition of 1–2 drops of H_2O, the following compounds were obtained in similar yields by using analogous procedures: $W(CH_3)(S_2CNC_5H_{10})(CO)_2(PMe_3)_2$ (**9**), $W(CH_3)(S_2COMe)(CO)_2(PMe_3)_2$ (**10**), $W(CH_3)(S_2COEt)(CO)_2(PMe_3)_2$ (**11**), $W(CH_3)(S_2CO\text{-}i\text{-}Pr)(CO)_2(PMe_3)_2$ (**12**), and $W(CH_3)(acac)(CO)_2(PMe_3)_2$ (**13**). They were isolated as yellow-orange crystalline solids by cooling Et_2O solutions of these complexes at −30 °C.

X-ray Structure Determination. A summary of the fundamental crystal data is given in Table IV. A single crystal was introduced in a glass capillary and mounted in a Kappa diffractometer. The cell dimensions were refined by least-squares fitting the values of 25 reflections. The intensities were corrected for Lorentz and polarization effects. Scattering factors for neutral atoms and anomalous dispersion corrections for W and P were taken from ref 21. The structure was solved by Patterson and Fourier methods. An empirical absorption correction[22] was applied at the end of the isotropic refinement. Final refinement with fixed isotropic factors and coordinates for H atoms gave $R_F = 0.041$ and $R(w)_F = 0.050$. Most of the calculations were carried out with the X-Ray 80 system.[23]

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Note Added in Proof. Recent work carried out in our laboratory[19] has shown that in molybdenum complexes related to the tungsten compounds described in this contribution, the agostic acetyl formulation is indeed an alternative thermodynamic structure to their isomeric η^2-acyl and alkyl carbonyl formulations.

Supplementary Material Available: Tables of H atom coordinates and thermal parameters for **13** (2 pages); a table of observed and calculated structure factors (32 pages). Ordering information is given on any current masthead page.

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Vinylidene, Acetylide, and Carbene Complexes from Reactions of 2,5-Dithiahex-3-yne ($MeSC\equiv CSMe$) with $Cp(PMe_3)_2Ru^+$

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The alkyne $MeSC\equiv CSMe$ initially displaces Cl^- in $Cp(PMe_3)_2RuCl$ at room temperature in MeOH to form the sulfur-bound alkyne complex $\{Cp(PMe_3)_2Ru[S(Me)C\equiv CSMe]\}PF_6$ (**1**). When it is warmed, **1** rearranges to the vinylidene complex $[Cp(PMe_3)_2Ru{=}C{=}C(SMe)_2]PF_6$ (**2**). Complex **2** is reduced by $Na[HBEt_3]$ or Na/Hg to give the thioacetylide $Cp(PMe_3)_2Ru{-}C\equiv CSMe$ (**5**) and MeSSMe. The vinylidene complexes $[Cp(PMe_3)_2Ru{=}C{=}C(R)(SMe)]^+$ (**6**, R = H; **7**, R = Me) are formed by electrophilic addition to the β-carbon of the thioacetylide **5**. Addition of CuCl to **5** forms $Cp(PMe_3)_2Ru(C\equiv CSMe)(CuCl)$ (**8**), in which the copper is π-bound through the $C\equiv C$ group. Reaction of **6** with methanol and ethanol yields the alkoxycarbene complexes $[Cp(PMe_3)_2Ru{=}C(OR)(CH_2SMe)]BF_4$ (**11a**, R = Me; **11b**, R = Et). Deprotonation of **11a** with NaOMe yields the vinyl complex $Cp(PMe_3)_2Ru[C(OMe){=}C(H)SMe]$ (**12**). Addition of $[Me_3O]BF_4$ to complexes **6** and **7** yields the first examples of sulfoniovinylidene dicationic complexes $[Cp(PMe_3)_2Ru{=}C{=}C(R)(SMe_2)](BF_4)_2$ (**9**, R = H; **10**, R = Me). An X-ray diffraction investigation shows that **9** crystallizes in space group $P2_1/n$ with $a = 16.641$ (2) Å, $b = 8.861$ (1) Å, $c = 18.168$ (2) Å, $\beta = 114.80$ (1)°, and $Z = 4$. Complexes **7** and **10** undergo one- and two-electron reductions, respectively, to give the acetylide $Cp(PMe_3)_2Ru{-}C\equiv CMe$ (**14**) and MeSSMe (for **7**) or SMe_2 (for **10**). Complexes **6** and **9** are readily deprotonated to give **5** and the sulfonioacetylide $[Cp(PMe_3)_2Ru{-}C\equiv CSMe_2]BF_4$ (**13**), respectively. Mechanisms of the reactions and structural features of the vinylidenes are discussed.

Introduction

There has been considerable experimental and theoretical interest in reactions between transition-metal centers and alkynes.[2] Alkynes, when reacted with a single ruthenium metal center, are known to give a variety of reaction products: the alkyne can form π-alkyne complexes,[3-10] it can insert into a M–H or M–C bond of metal hydride or metal alkyl complexes,[11-18] 1-alkynes form metal-bound vinylidene complexes via a 1,2-hydrogen shift,[19-31] and a variety of alkynes are known to form

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

compd	Cp	PMe_3 (J_{PH}, Hz)	SMe_n (n)	other
$\{Cp(PMe_3)_2Ru[S(Me)C\equiv CSMe]\}PF_6$ (**1**)^b	4.86	1.54 (t, 8.95)	2.79 (1)	2.44 ($\equiv$CSMe)
$[Cp(PMe_3)_2Ru{=}C{=}C(SMe)_2]PF_6$ (**2**)^b	5.48	1.47 (d, 10.56)	2.22 (1)	
$\{Cp(PMe_3)_2Ru[S(Me)C\equiv CMe]\}BF_4$ (**3a**)^b	4.86	1.55 (t, 9.00)	2.78 (1)	1.99 (Me)
$\{Cp(PMe_3)_2Ru[\eta^2\text{-}MeSC\equiv CMe]\}BF_4$ (**3b**)^b	5.14	1.60 (d, 10.80)	2.56 (1)	2.43 (Me)
$[Cp(PMe_3)_2Ru(NCCH_3)]BF_4$ (**4**)^{b,c}	4.64	1.54 (t, 9.08)		2.43 (d, Me)^d
$Cp(PMe_3)_2Ru{-}C\equiv CSMe$ (**5**)^b	4.66	1.47 (t, 8.97)	2.29 (1)	
$[Cp(PMe_3)_2Ru{=}C{=}C(H)(SMe)]BF_4$ (**6**)^b	5.51	1.69 (d, 10.21)	2.21 (1)	5.08 (H)
$[Cp(PMe_3)_2Ru{=}C{=}C(Me)(SMe)]I$ (**7**)^b	5.57	1.75 (d, 10.20)	2.20 (1)	2.08 (Me)
$Cp(PMe_3)_2Ru(CuCl)(C\equiv CSMe)$ (**8**)^b	4.84	1.52 (t, 8.87)	2.36 (1)	
$[Cp(PMe_3)_2Ru{=}C{=}C(H)(SMe_2)](BF_4)_2$ (**9**)^e	5.70	1.69 (d, 10.80)	2.87 (2)	5.22 (t, H)^f
$[Cp(PMe_3)_2Ru{=}C{=}C(Me)(SMe_2)](BF_4)_2$ (**10**)^e	5.70	1.68 (d, 10.67)	2.83 (2)	2.10 (Me)
$[Cp(PMe_3)_2Ru{=}C(OMe)(CH_2SMe)]BF_4$ (**11a**)^b	5.22	1.48 (d, 9.60)	2.25 (1)	4.28 (Me) 4.13 (CH_2)
$[Cp(PMe_3)_2Ru{=}C(OEt)(CH_2SMe)]BF_4$ (**11b**)^b	5.22	1.50 (d, 9.76)	2.24 (1)	(Me)^g 4.11 (SCH_2) 4.62 (q, CH_2)^h
$Cp(PMe_3)_2Ru[C(OMe){=}C(H)SMe]$ (**12**)^b				
isomer A	4.68	1.41 (t, 8.58)	2.10 (1)	3.47 (d, Me)^i 5.33 (br, H)^j
isomer B	4.59	1.41 (t, 8.58)	2.13 (1)	3.43 (Me) (H)^k
$[Cp(PMe_3)_2Ru{-}C\equiv CSMe_2]BF_4$ (**13**)^b	4.76	1.49 (t, 9.17)	3.00 (2)	
$Cp(PMe_3)_2Ru{-}C\equiv CMe$ (**14**)^b	4.62	1.45 (t, 9.03)		1.98 (t, Me)^l

^{a} Abbreviations: d, doublet, t, triplet; q, quartet; br, broad. ^{b} $CDCl_3$. ^{c} IR (CH_2Cl_2): $\nu(C\equiv N)$ 2260 cm^{-1}. ^{d} J_{PH} = 1.32 Hz. ^{e} CD_3CN. ^{f} J_{PH} = 1.08 Hz. ^{g} Obscured by PMe_3 resonances. ^{h} J_{HH} = 6.89 Hz. ^{i} J_{HH} = 0.62 Hz. ^{j} J_{PH} = 1.38 Hz. ^{k} Not observed. ^{l} J_{PH} = 2.6 Hz.

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

compd	Cp	PMe_3 (t)	J_{PC}, Hz	SMe_n (n)	Ru–C (t)	J_{PC}, Hz	β-C	other
1^b	82.82	21.38	16.44	36.09 (1)			88.21	91.38 (α-C) 19.57 (SMe)
2^c	92.69	22.47	16.81	18.86 (1)	326.93	16.77	116.62	
3a^c	84.01	21.82	18.10	35.85 (1)			88.61	92.41 (α-C) 4.60 (Me)
3b^c	80.45	21.28	16.50	19.57 (1)				13.33 (Me) 82.94 ($\equiv$CS) 70.66 ($\equiv$CMe)
5^b	80.60	23.00	13.30	21.47 (1)	121.58	25.25	82.02	
6^b	91.65	22.51	17.48	21.73 (1)	*d*		104.90	
7^b	90.91	22.88	18.12	18.57 (1)	331.97	15.46	113.41	12.35 (Me)
8^b	82.42	23.19	15.96	21.97 (1)	122.57	21.78	87.54	
9^c	95.21	22.58	18.93	32.01 (2)	332.64	15.03	102.58	
10^c	94.88	22.97	18.58	27.24 (2)	323.22	18.78	109.57	5.16 (Me)
11a^b	89.44	22.47	16.88	16.74 (1)	295.92	13.79		60.03 (OMe) 55.64 (CH_2)
12^b								
isomer A	81.33	23.65	13.91	19.22 (1)	190.62	17.41	102.82	54.44 (OMe)
isomer B	80.95	*e*		19.37 (1)	*e*		105.67	56.13 (OMe)
13^c	84.08	22.59	16.56	36.40 (2)	183.39	21.98	88.53	

^{a} Abbreviations: d, doublet; t, triplet. ^{b} $CDCl_3$. ^{c} CD_3CN. ^{d} Not observed. ^{e} PMe_3 and Ru–C not observed.

complexes resulting from metallacyclization and oligomerization.[32-43]

In all of the above reactions, the acetylene triple bond is the site of reactivity. It seems that mercapto groups in

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the acetylene could alter this reactivity. There are only two previous reports[44] on the chemistry of mononuclear complexes of MeSC$\equiv$CSMe: CpM(MeSC$\equiv$CSMe)$_2$Cl, M(CO)(MeSC$\equiv$CSMe)$_3$ (M = Mo, W), CpMoCl(CO)(C$_9$H$_{12}$OS$_4$), M(CO)$_3$(C$_9$H$_{12}$OS$_4$) (M = Fe, Ru), W(CO)(dmpe)(MeSC$\equiv$CSMe)$_2$, and W(dmpe)(MeSC$\equiv$CSMe)$_2$. No reactions of the π-alkyne or cyclopentadienone ligands in these complexes are described, and the authors note[44] that the chemistry of MeSC$\equiv$CSMe is dominated by the triple bond. In the present paper, we examine the synthesis and reactions of a series of vinylidene, acetylide, and carbene complexes derived from reactions of MeSC$\equiv$CSMe with the Cp(PMe$_3$)$_2$Ru$^+$ group.

Experimental Section

General Procedures. All reactions, filtrations, distillations, and recrystallizations were carried out under N$_2$ with use of standard inert-atmosphere and Schlenk techniques.[45] Methylene chloride, hexane, and acetonitrile were dried over CaH$_2$ and distilled under N$_2$. Diethyl ether and tetrahydrofuran (THF) were distilled from Na/benzophenone under N$_2$. Methanol and ethanol were dried over magnesium alkoxide, which was generated from magnesium turnings and iodine in absolute alcohol, and distilled under N$_2$.[46] Reactions were carried out at room temperature unless stated otherwise. Infrared spectra were recorded on a Perkin-Elmer 681 spectrometer; the band positions were referenced to the 1601.0-cm^{-1} band of polystyrene. ^{1}H NMR spectra (Table I) were obtained with a Nicolet NT-300 (300-MHz) spectrometer, using Me$_4$Si (TMS) as the internal reference. Proton-decoupled ^{13}C NMR spectra (Table II) were recorded on Nicolet NT-300 (75.46-MHz), Bruker WM-300 (75.46-MHz), or Bruker WM-200 (50.29-MHz) instruments, using the deuteriated solvents as the internal reference. Fast atom bombardment (FAB, 3-nitrobenzyl alcohol matrix) spectra were obtained with a Kratos MS-50 spectrometer. Electron-ionization mass spectra (EIMS) were run on a Finnigan 4000 spectrometer. Elemental microanalyses were performed by Galbraith Laboratories Inc., Knoxville, TN.

The compounds (η^5-C$_5$H$_5$)(PMe$_3$)$_2$RuCl[47] (Cp = η^5-C$_5$H$_5$), MeSC$\equiv$CSMe,[48] MeSC$\equiv$CMe,[49] and (Me$_2$SSMe)SO$_3$CF$_3$[50] were prepared by using previously described procedures. All other chemicals were used as received from commercial sources.

{Cp(PMe$_3$)$_2$Ru[S(Me)C$\equiv$CSMe]}PF$_6$ (1). A solution of Cp(PMe$_3$)$_2$RuCl (50 mg, 0.14 mmol), MeSC$\equiv$CSMe (0.15 mL, 200 mg, 1.7 mmol), and NH$_4$PF$_6$ (45 mg, 0.28 mmol) in 2 mL of methanol was stirred at room temperature for 15 min under N$_2$. The solvent was removed under reduced pressure. The residue was dissolved in 5 mL of cold CH$_2$Cl$_2$ (0 °C), and the solution was filtered. The resulting yellow solution was reduced to 1 mL under vacuum, and 10 mL of Et$_2$O was added, producing a yellow precipitate that was collected and dried under vacuum. The yellow powder of 1 was collected in 27% yield (22 mg, 0.039 mmol). Anal. Calcd for C$_{15}$H$_{29}$F$_6$P$_3$RuS$_2$: C, 30.98; H, 5.03. Found: C, 31.35; H, 5.07. IR (CH$_2$Cl$_2$): ν(C$\equiv$C) 2103 cm^{-1}.

[Cp(PMe$_3$)$_2$Ru=C=C(SMe)$_2$]PF$_6$ (2). A solution of Cp(PMe$_3$)$_2$RuCl (240 mg, 0.68 mmol) and MeSC$\equiv$CSMe (0.41 mg, 3.5 mmol) in 15 mL of methanol was refluxed for 1 h under N$_2$. The heating mantle was removed from the reaction flask, and NH$_4$PF$_6$ (430 mg, 2.6 mmol) was added to the resulting red solution. The solution was cooled to room temperature, and the solvent was removed under reduced pressure. The red residue was dissolved in 10 mL of CH$_2$Cl$_2$, the resulting solution was filtered under vacuum with use of a Schlenk frit containing Celite, and the frit was washed with CH$_2$Cl$_2$ (2 × 10 mL). The filtrate solution was reduced to 5 mL, and 20 mL of Et$_2$O was added, producing a red oily residue. The solvent was removed and the residue dried under reduced pressure. Crystallization at −20 °C from CH$_2$Cl$_2$/Et$_2$O yielded red platelets of 2 in 76% yield (310 mg, 0.53 mmol). Anal. Calcd for C$_{15}$H$_{29}$F$_6$P$_3$RuS$_2$: C, 30.98; H, 5.03. Found: C, 30.79; H, 5.05. MS (FAB): *m/e* 437 (M$^+$), 319 (M$^+$ − Me$_2$S$_2$C$_2$). IR (CH$_3$CN): ν(C=C) 1603 cm^{-1}.

{Cp(PMe$_3$)$_2$Ru[S(Me)C$\equiv$CMe]}BF$_4$ (3a) and [Cp(PMe$_3$)$_2$Ru(η^2-MeSC$\equiv$CMe)]BF$_4$ (3b). Similar to the procedure for the preparation of complex 2, a solution of Cp(PMe$_3$)$_2$RuCl (900 mg, 2.54 mmol) and MeSC$\equiv$CMe (0.50 mL, 750 mg, 8.7 mmol) in 30 mL of methanol was refluxed for 1 h under N$_2$. Anion exchange was accomplished with NH$_4$BF$_4$ (1.16 g, 11.0 mmol). The reaction produced a yellow powder containing isomers **3a** and **3b** (2:1 ratio, respectively) in 79% yield (969 mg, 1.97 mmol). Complex **3a** was separated by TLC (Whatman, K6 silica gel, 20 × 20 cm, layer thickness 250 μm). The mixture of **3a** and **3b** (152 mg, 0.310 mmol) was dissolved in 1 mL of CH$_2$Cl$_2$ and applied as a thin line 1 cm from the bottom of the plate. The plate was placed in a developing chamber, and the mobile phase, CH$_2$Cl$_2$, was stopped 3 cm from the top of the plate. The solvent was allowed to evaporate, and the process was repeated twice more. The top yellow band was scraped off and placed in a sintered-glass frit. Complex **3a** was collected by washing the frit with 30 mL of acetone. The acetone solution was reduced to 3 mL, and 15 mL of Et$_2$O was added to produce a yellow powder of **3a** in 28% yield (42 mg, 0.085 mmol). Anal. Calcd for C$_{15}$H$_{29}$BF$_4$P$_2$RuS: C, 36.67; H, 5.95. Found: C, 36.76; H, 5.87. MS (FAB): *m/e* 405 (M$^+$), 319 (M$^+$ − MeSC$\equiv$CMe). IR (CH$_2$Cl$_2$): ν(C$\equiv$C) 2203 cm^{-1}. Isomer **3b** decomposed on the silica gel plate; it was characterized spectroscopically (Tables I and II).

Cp(PMe$_3$)$_2$Ru—C$\equiv$CSMe (5). Sodium metal (120 mg, 5.2 mmol) was added slowly to stirred mercury metal (5 mL, 68 g), followed by the addition of 10 mL of THF. To the stirred solution was added complex 2 (310 mg, 0.53 mmol) in 15 mL of THF via a syringe over a period of 5 min. The suspension was stirred for an additional 15 min, the solution was vacuum-filtered through a bed of Celite, and the Celite was washed with THF (3 × 5 mL). The solvent was removed from the resulting solution under reduced pressure. The residue was dissolved in CH$_2$Cl$_2$ (3 × 5 mL), and the solution was filtered through a frit containing Celite. The solvent was removed under vacuum. The brownish yellow residue was dissolved in Et$_2$O and passed through a column of alumina

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(activity grade 4, 1 × 4 cm). The solvent was removed from the resulting yellow solution under reduced pressure to give a yellow powder of **5** in 87% yield (180 mg, 0.46 mmol). Anal. Calcd for $C_{14}H_{26}P_2RuS$: C, 43.18; H, 6.73. Found: C, 43.63; H, 6.92. EIMS (70 eV): *m/e* 390 (M^+), 299 [M^+ - (Me + PMe_3)], 167 ($CpRu^+$). IR (CH_2Cl_2): ν(C≡C) 2000 cm^{-1}.

[Cp(PMe_3)$_2$Ru=C=C(H)(SMe)]BF_4 (6). To a solution of **5** (28 mg, 0.072 mmol) in 10 mL of CH_2Cl_2 was added $HBF_4 \cdot Et_2O$ (0.010 mL, 11 mg, 0.068 mmol) under N_2. The resulting red solution was stirred for 10 min and filtered through a bed of Celite, and the frit was washed with CH_2Cl_2 (2 × 10 mL). The solution was reduced to 3 mL, and 20 mL of Et_2O was added, producing a red precipitate that was collected and dried under vacuum; the reddish orange powder of **6** was obtained in 85% yield (29 mg, 0.061 mmol). Anal. Calcd for $C_{14}H_{27}BF_4P_2RuS$: C, 35.23; H, 5.70. Found: C, 35.03; H, 5.85. MS (FAB): *m/e* 391 (M^+), 319 (Cp(PMe_3)$_2Ru^+$). IR (Nujol mull): ν(C=C) 1622 cm^{-1}.

[Cp(PMe_3)$_2$Ru=C=C(Me)(SMe)]I (7). Complex **5** (65 mg, 0.17 mmol) and MeI (0.053 mL, 120 mg, 0.85 mmol) were refluxed in 20 mL of CH_2Cl_2 for 4 h under N_2. The solution was cooled to room temperature and reduced to 5 mL in vacuo. The addition of 20 mL of Et_2O to the solution produced a pale reddish brown precipitate of **7** in 75% yield (68 mg, 0.13 mmol). Anal. Calcd for $C_{15}H_{29}IP_2RuS$: C, 33.91; H, 5.50. Found: C, 34.06; H, 5.64. MS (FAB): *m/e* 405 (M^+), 319 (Cp(PMe_3)$_2Ru^+$). IR (CH_2Cl_2): ν(C=C) 1667 cm^{-1}.

Cp(PMe_3)$_2$Ru(C≡CSMe)(CuCl) (8). Solid CuCl (22 mg, 0.22 mmol) was added to a solution of **5** (23 mg, 0.059 mmol) in 5 mL of CH_2Cl_2, and the mixture was stirred for 15 min. The mixture was filtered through a column of Celite (4 × 0.5 cm). The solvent was removed from the filtrate under reduced pressure, and a yellow precipitate of **8** was collected in 69% yield (20 mg, 0.041 mmol). Recrystallization from CH_2Cl_2/Et_2O gave analytically pure yellow microcrystals of **8**. Anal. Calcd for $C_{14}H_{26}ClCuP_2RuS$: C, 34.43; H, 5.37. Found: C, 34.08; H, 5.29. EIMS (70 eV): *m/e* 488 (M^+), 390 (M^+ - CuCl). IR (CH_2Cl_2): ν(C≡C) 1882 cm^{-1}.

[Cp(PMe_3)$_2$Ru=C=C(H)(SMe_2)](BF_4)$_2$ (9). To a stirred solution of complex **6** (98 mg, 0.21 mmol) in 20 mL of CH_3CN was added [Me_3O]BF_4 (100 mg, 0.68 mmol). The solution was stirred for 1 h, and the solvent was removed under reduced pressure. The insoluble residue was suspended in CH_2Cl_2 (3 × 10 mL), the suspension was filtered through Celite, and the solid remaining on the Celite was washed with Et_2O (2 × 10 mL). The solid was dissolved with acetone (3 × 10 mL). The orange-yellow acetone solution was reduced to 4 mL, and 20 mL of Et_2O was added to give a yellow powder of **9** in 72% yield (86 mg, 0.15 mmol). Anal. Calcd for $C_{15}H_{30}B_2F_8P_2RuS \cdot CH_3CN$: C, 32.93; H, 5.36. Found: C, 32.97; H, 5.06. IR (Nujol mull): ν(C=C) 1625 (s), 1577 (s) cm^{-1}. The ^1H NMR spectrum of the sample sent for elemental analysis showed one molecule of CH_3CN per molecule of **9**.

[Cp(PMe_3)$_2$Ru=C=C(Me)(SMe_2)](BF_4)$_2$ (10). A solution of **7** (68 mg, 0.13 mmol) and [Me_3O]BF_4 (45 mg, 0.30 mmol) in 20 mL of CH_3CN was stirred for 1 h under N_2, yielding a dark yellow solution. To the solution was added NH_4BF_4 (140 mg, 1.3 mmol). After the solution was stirred for an additional 30 min, the solvent was removed under reduced pressure, leaving a dark yellow residue. The residue was washed with CH_2Cl_2 (2 × 10 mL) and then partially dissolved in 20 mL of acetone; the resulting acetone suspension was treated with 30 mL of Et_2O to give a dark yellow precipitate of **10** in 55% yield (42 mg, 0.071 mmol). Anal. Calcd for $C_{16}H_{32}B_2F_8P_2RuS$: C, 32.40; H, 5.44. Found: C, 32.50; H, 5.49. IR (CH_3CN): ν(C=C) 1624 cm^{-1}.

[Cp(PMe_3)$_2$Ru=C(OMe)(CH_2SMe)]BF_4 (11a) and [Cp(PMe_3)$_2$Ru=C(OEt)(CH_2SMe)]BF_4 (11b). Complex **6** (11 mg, 0.023 mmol, for **11a**; 8.7 mg, 0.018 mmol, for **11b**) was stirred in 20 mL of MeOH or EtOH for 10 h under N_2. The solvent was removed from the resulting yellow solution under reduced pressure. The resulting yellow oil was dissolved in 3 mL of CH_2Cl_2, and 20 mL of Et_2O was added to give a yellow precipitate. The solvent was removed and the product dried under reduced pressure to give a yellow powder of **11a** in 78% yield (9.1 mg, 0.018 mmol). The percent yield for **11b**, based on the amount of reacted **6** as determined by ^1H NMR spectroscopy, was 60%. Anal. Calcd for **11a**, $C_{15}H_{31}BF_4OP_2RuS$: C, 35.38; H, 6.14. Found: C, 35.12; H, 6.02. MS for **11a** (FAB): *m/e* 423 (M^+), 319 (Cp(PMe_3)$_2Ru^+$).

Table III. Crystal and Data Collection Parameters for [Cp(PMe_3)$_2$Ru=C=C(H)(SMe_2)](BF_4)$_2$ (9)

formula	$RuSP_2F_8C_{15}B_2H_{30}$
fw	579.10
space group	$P2_1/n$
a, Å	16.641 (2)
b, Å	8.861 (1)
c, Å	18.168 (2)
β, deg	114.80 (1)
V, Å^3	2432 (2)
Z	4
d_{calc}, g/cm^3	1.582
cryst size, mm	0.30 × 0.36 × 0.15
μ(Mo Kα), cm^{-1}	9.036
data collection instrument	Enraf-Nonius CAD4
radiation (monochromated in incident beam)	Mo Kα (λ = 0.71073 Å)
orientation rflns: no.; range (2θ), deg	25; $18 < 2\theta < 30$
temp, °C	22 ± 1
scan method	θ–2θ
data collecn range, 2θ, deg	0–45
no. of unique data	
total	4276
no. with $F_o^2 > 3\sigma(F_o^2)$	3200
no. of params refined	207
transmission factors: max, min (ψ scans)	0.999, 0.940
R^a	0.051
$R_w{}^b$	0.074
quality-of-fit indicator^c	1.914
largest shift/esd, final cycle	0.09
largest peak, e/Å^3	0.819

[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 $= [\sum w(|F_o| - |F_c|)^2/(N_{observns} - N_{params})]^{1/2}$.

Cp(PMe_3)$_2$Ru[C(OMe)=C(H)SMe] (12). To a stirred solution of **11a** (33 mg, 0.065 mmol) in 10 mL of MeOH was added 1.3 mL of a 0.10 M solution of NaOMe (0.13 mmol) under N_2. The solution was stirred for 30 min; then the solvent was removed under reduced pressure. The resulting pale yellow oil was extracted with Et_2O (3 × 2 mL), and the resulting solution was filtered through a bed of Celite. The solvent was removed under reduced pressure, producing a pale yellow powder of **12** in 84% yield (23 mg, 0.056 mmol). EIMS (70 eV): *m/e* 422 (M^+), 390 (M^+ - MeOH), 319 (Cp(PMe_3)$_2Ru^+$). Elemental analyses were not obtained due to noticeable thermal decomposition of the product within a few days at room temperature.

[Cp(PMe_3)$_2$Ru—C≡CSMe_2]BF_4 (13). To a stirred solution of complex **9** (86 mg, 0.15 mmol) in 15 mL of methanol was added 1 mL of a 0.16 M methanolic solution of NaOMe (0.16 mmol). The resulting red solution was stirred for 10 min, and the solvent was removed under reduced pressure. The resulting residue was dissolved in 5 mL of CH_2Cl_2. The solution was filtered under vacuum through a bed of Celite, and the frit was washed with CH_2Cl_2 (2 × 5 mL). The volume of the filtered solution was reduced to 5 mL under vacuum, and 20 mL of Et_2O was added to produce a red precipitate of **13**, which was collected in 94% yield (66 mg, 0.13 mmol). IR (CH_2Cl_2): ν(C≡C) 1960 cm^{-1}. Elemental analyses were not obtained due to noticeable thermal decomposition of the product in 12 h at room temperature.

Cp(PMe_3)$_2$Ru—C≡CMe (14). The preparation of this complex from the reaction of Na/Hg (10 mg, 0.43 mmol/3 mL, 41 g) with complex **7** (10 mg, 0.019 mmol) in 10 mL of THF proceeded analogously to the synthesis of **5**. A yellow oil of **14** was collected in over 80% yield (5.5 mg, 0.015 mmol). IR (CH_2Cl_2): ν(C≡C) 2095 cm^{-1}. Complex **14** has been previously characterized by Bruce and co-workers.[24]

X-ray Structure Determination of [Cp(PMe_3)$_2$Ru=C=C(H)(SMe_2)](BF_4)$_2$ (9). Yellow crystals of **9** were grown by vapor diffusion of Et_2O into an acetone solution of **9** 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 is given in Table III.

A total of 4434 reflections were collected in the $+h,+k,\pm l$ quadrant. An empirical absorption correction was made, on the basis of a series of ψ-scans. The agreement factors for the av-

Table IV. Positional and Thermal Parameters for $[Cp(PMe_3)_2Ru{=}C{=}C(H)(SMe_2)](BF_4)_2$ (9)

atom	x	y	z	B, Å^2 [a]
Ru	0.76300 (3)	0.14873 (6)	0.47919 (3)	3.14 (1)
S	0.6393 (2)	0.1836 (2)	0.6432 (1)	5.31 (6)
P(1)	0.7190 (1)	0.3544 (2)	0.3908 (1)	4.18 (5)
P(2)	0.8670 (1)	0.2874 (2)	0.5820 (1)	4.46 (5)
C(1)	0.6833 (4)	0.1953 (7)	0.5180 (4)	3.7 (2)
C(2)	0.6213 (5)	0.2305 (9)	0.5456 (4)	5.0 (2)
C(3)	0.6353 (8)	0.358 (1)	0.6902 (7)	8.6 (5)
C(4)	0.5315 (7)	0.106 (1)	0.6270 (7)	8.1 (4)
C(5)	0.6366 (6)	0.477 (1)	0.4009 (6)	6.8 (3)
C(6)	0.6665 (8)	0.298 (1)	0.2864 (5)	8.0 (3)
C(7)	0.8005 (6)	0.485 (1)	0.3862 (6)	7.4 (3)
C(8)	0.9716 (5)	0.312 (1)	0.5739 (5)	6.1 (3)
C(9)	0.8374 (6)	0.474 (1)	0.6039 (6)	7.4 (3)
C(10)	0.9012 (6)	0.190 (1)	0.6786 (5)	7.9 (3)
C(21)	0.8113 (7)	−0.0905 (8)	0.5173 (4)	7.8 (4)
C(22)	0.8681 (7)	−0.0221 (8)	0.4865 (4)	8.9 (4)
C(23)	0.8168 (7)	0.0140 (8)	0.4038 (4)	8.3 (5)
C(24)	0.7283 (7)	−0.0321 (8)	0.3834 (4)	7.9 (4)
C(25)	0.7249 (7)	−0.0967 (8)	0.4536 (4)	7.5 (4)
B(1)	−0.0466 (3)	0.2596 (5)	0.3059 (3)	4.3 (2)[b]
F(1)	−0.1283 (3)	0.1935 (5)	0.2680 (3)	8.08 (9)[b]
F(2)	−0.0504 (3)	0.4045 (5)	0.2784 (3)	8.08 (9)[b]
F(3)	−0.0220 (3)	0.2614 (5)	0.3880 (3)	8.08 (9)[b]
F(4)	0.0141 (3)	0.1790 (5)	0.2894 (3)	8.08 (9)[b]
B(1′)	−0.049 (1)	0.236 (2)	0.311 (1)	4.3 (2)[b]
F(1′)	−0.032 (1)	0.085 (2)	0.326 (1)	10.9 (5)[b]
F(2′)	−0.017 (1)	0.312 (2)	0.383 (1)	10.9 (5)[b]
F(3′)	−0.139 (1)	0.257 (2)	0.272 (1)	10.9 (5)[b]
F(4′)	−0.010 (1)	0.289 (2)	0.263 (1)	10.9 (5)[b]
B(2)	0.1386 (6)	0.770 (1)	0.1136 (5)	6.3 (2)[b]
F(5)	0.2071 (6)	0.835 (1)	0.1777 (5)	8.2 (2)[b]
F(6)	0.0651 (6)	0.765 (1)	0.1294 (5)	8.2 (2)[b]
F(7)	0.1620 (6)	0.626 (1)	0.1025 (5)	8.2 (2)[b]
F(8)	0.1205 (6)	0.853 (1)	0.0449 (5)	8.2 (2)[b]
B(2′)	0.1236 (7)	0.770 (1)	0.1013 (6)	6.3 (2)[b]
F(5′)	0.2115 (7)	0.804 (1)	0.1438 (6)	8.8 (2)[b]
F(6′)	0.1154 (7)	0.639 (1)	0.0587 (6)	8.8 (2)[b]
F(7′)	0.0851 (7)	0.752 (1)	0.1542 (6)	8.8 (2)[b]
F(8′)	0.0825 (7)	0.885 (1)	0.0486 (6)	8.8 (2)[b]
B(2″)	0.128 (1)	0.763 (2)	0.113 (1)	6.3 (2)[b]
F(5″)	0.101 (1)	0.669 (2)	0.047 (1)	10.7 (5)[b]
F(6″)	0.171 (1)	0.681 (2)	0.182 (1)	10.7 (5)[b]
F(7″)	0.183 (1)	0.872 (2)	0.107 (1)	10.7 (5)[b]
F(8″)	0.055 (1)	0.831 (2)	0.116 (1)	10.7 (5)[b]
H(1)	0.5612 (5)	0.2880 (9)	0.5067 (4)	5 (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.

Table V. Bond Distances (Å) and Angles (deg) for $[Cp(PMe_3)_2Ru{=}C{=}C(H)(SMe_2)](BF_4)_2$ (9)

	Bond Distances (Å)		
Ru–P(1)	2.334 (2)[a]	P(1)–C(6)	1.796 (8)
Ru–P(2)	2.298 (2)	P(1)–C(7)	1.81 (1)
Ru–C(1)	1.792 (8)	P(2)–C(8)	1.820 (9)
S–C(2)	1.719 (9)	P(2)–C(9)	1.82 (1)
S–C(3)	1.78 (1)	P(2)–C(10)	1.82 (1)
S–C(4)	1.83 (1)	C(1)–C(2)	1.36 (1)
P(1)–C(5)	1.82 (1)	C(2)–H(1)	1.08 (1)[b]
Ru–C(21)	2.270 (7)	Ru–C(24)	2.256 (7)
Ru–C(22)	2.27 (1)	Ru–C(25)	2.258 (7)
Ru–C(23)	2.27 (1)		
	Bond Angles (deg)		
P(1)–Ru–P(2)	93.08 (7)	C(6)–P(1)–C(7)	99.9 (5)
P(1)–Ru–C(1)	91.1 (2)	Ru–P(2)–C(8)	114.8 (3)
P(2)–Ru–C(1)	89.3 (2)	Ru–P(2)–C(9)	118.9 (3)
C(2)–S–C(3)	104.9 (5)	Ru–P(2)–C(10)	110.8 (4)
C(2)–S–C(4)	101.0 (4)	C(8)–P(2)–C(9)	105.3 (5)
C(3)–S–C(4)	99.8 (6)	C(8)–P(2)–C(10)	102.3 (4)
Ru–P(1)–C(5)	115.5 (3)	C(9)–P(2)–C(10)	102.8 (5)
Ru–P(1)–C(6)	112.4 (3)	Ru–C(1)–C(2)	178.7 (5)
Ru–P(1)–C(7)	120.4 (3)	S–C(2)–C(1)	119.6 (5)
C(5)–P(1)–C(7)	103.4 (5)	C(5)–P(1)–C(6)	102.8 (5)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits. [b] Fixed.

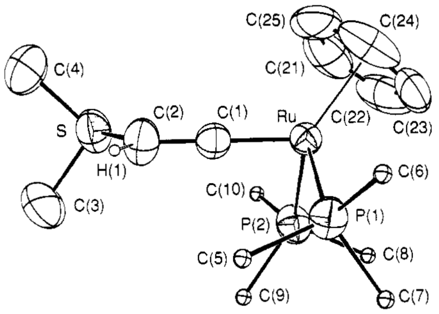

Figure 1. ORTEP drawing of $[Cp(PMe_3)_2Ru{=}C{=}C(H)(SMe_2)](BF_4)_2$ (9). The phosphine carbons are shown as arbitrary spheres. The vinylidene hydrogen is shown for clarity.

eraging of 222 observed reflections were 1.3% based on intensity and 1.2% based on F_o.

Structure Solution and Refinement. The positions of the Ru, S, and P atoms and one of the BF_4 anions were located by direct methods.[51] Following three cycles of least-squares refinement, a difference Fourier map indicated the positions of the remainder of the carbon atoms and the other BF_4 ion; disorder in the anions also became evident.

The position of the vinylic hydrogen atom bound to C(2) was also seen in a difference map. However, only the isotropic temperature factor for the hydrogen atom was refined, while the idealized position was held fixed. All other hydrogen atoms were placed in idealized positions, riding 1.08 Å from the carbon atoms. The alkyl hydrogen atoms were given a common temperature factor, as were the hydrogen atoms of the Cp ring. The Cp ring itself was refined as a rigid pentagon (C–C distance fixed at 1.42 Å); the carbon atoms of the ring were refined with anisotropic temperature factors in the final refinement cycles.

While the cationic complex was refined smoothly, the disordered anions posed some problems. In the final model, one of the anions was refined as two superimposed BF_4 units and the other as three superimposed units. Each BF_4 unit was refined as a rigid group having B–F bond lengths of exactly 1.37 Å and bond angles of 109.5°. The occupancy of each rigid group was refined independently until the final set of least-squares cycles, in which the occupancies were slightly adjusted and fixed to make the total occupancy at each site 1.0. The groups centered on B(1) and B(1′) were 78 (1) and 22 (1)% occupied; those on B(2), B(2′), and B(2″) were 40 (2), 37 (2), and 23 (1)% occupied. All B and F atoms were refined with isotropic temperature factors. A common temperature factor was refined for the four F atoms in each group. The final cycle of refinement included 207 variable parameters and converged to $R = 0.051$ and $R_w = 0.074$.[52]

Refinement of the structure was carried out with the SHELX-76 package.[53] The final positional and thermal parameters are listed in Table IV. Selected bond lengths and angles are presented in Table V, and an ORTEP drawing of the cation is given in Figure 1.

Results and Discussion

Reactions of MeSC≡CSMe and MeSC≡CMe with $Cp(PMe_3)_2RuCl$. The sulfur-bound alkyne complexes $\{Cp(PMe_3)_2Ru[S(Me)C{\equiv}CR]\}^+$ (R = SMe (1), Me (3a)) are formed in room-temperature reactions of $Cp(PMe_3)_2RuCl$

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

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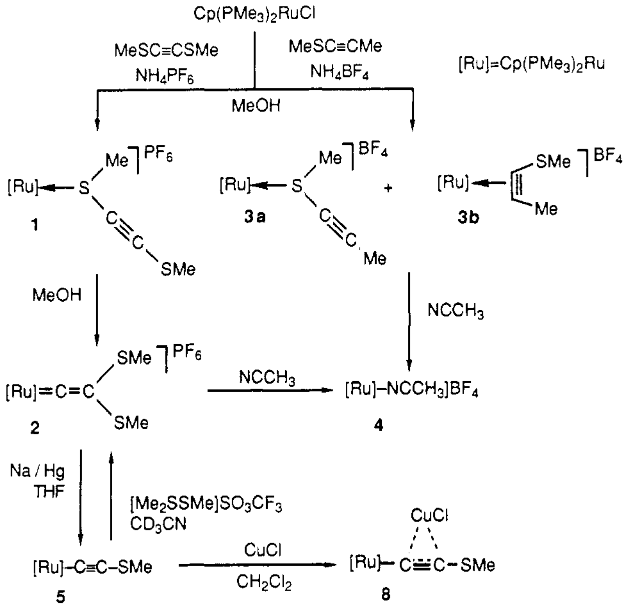
Scheme I



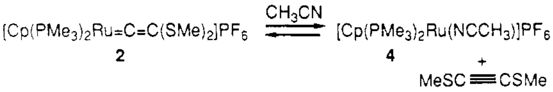
with excess alkyne and either NH_4PF_6 or NH_4BF_4 to produce air-stable yellow powders of complexes **1** and **3a** (Scheme I). Complexes **1** and **3a** show characteristic IR ν(C≡C) bands at 2103 and 2203 cm^{-1}, respectively. The ^1H NMR spectra of **1** and **3a** show a downfield methyl resonance at 2.79 and 2.78 ppm, respectively, due to the methyl on the coordinated sulfur; these chemical shifts are similar to those of the sulfonio methyl groups in complexes **9** and **10** (Table I). In the ^{13}C NMR spectrum of complex **1**, the alkyne carbon resonances occur at 91.38 and 88.21 ppm; the same carbons in **3a** occur at 92.41 and 88.61 ppm. These ^{13}C alkyne resonances are slightly downfield of those of the free alkynes MeSC≡CSMe (87.17 ppm) and MeSC≡CMe (88.55 and 68.89 ppm). Heating complex **1** in CD_3CN at 40 °C for 4 h gives the vinylidene complex **2** in quantitative yield; heating complex **3a** in MeOH at 40 °C for 4 h gives a mixture of **3a** and the π-alkyne **3b** (discussed later) in a 2:1 ratio.

Refluxing a solution of $Cp(PMe_3)_2RuCl$ with an excess of MeSC≡CSMe in dry methanol produces air-stable, red platelets of **2** in 76% yield (Scheme I). The ^1H NMR spectrum of **2** shows a Cp resonance at 5.48 ppm, which is downfield approximately 1 ppm from that for the neutral complex $Cp(PMe_3)_2RuCl$ (4.44 ppm). The 5.48 ppm value compares with those for the similar complexes $[Cp(PMe_3)_2Ru{=}C{=}C(H)(R)]PF_6$[19] (R = Me, 5.41 ppm; R = H, 5.43 ppm). The ^1H NMR methyl resonance of the PMe_3 group is at 1.68 ppm for **2** and appears as an apparent doublet (J_{PH} = 10.56 Hz). Table I shows that the PMe_3 resonances for all the complexes, both neutral and cationic, fall in the range 1.41–1.75 ppm with coupling constants ranging from 8.58 to 10.67 Hz. The J_{PH} coupling pattern is characteristic of an $A_9XX'A'_9$ system.[54,55] The doublet pattern often appears in the cationic complexes (Table I) to have fine structure between the two outer lines. In other cases, such as neutral $Cp(PMe_3)_2RuR$ (R = Cl, –C≡CSMe (**5**), –C≡CMe (**14**)) compounds, the doublet is almost filled in and may or may not have what appears to be another resonance rising between the outer resonances. Coupling constants (J_{PH}) of both apparent doublets and triplets are measured between the two outer peaks. A more detailed discussion of the ^1H NMR spectra of complexes with two PMe_3 ligands has been reported by others.[7,8]

The ^{13}C NMR spectrum of **2** shows a Cp resonance at 92.86 ppm, which is similar to the Cp resonances reported for the complexes $[Cp(PMe_3)_2Ru{=}C{=}C(H)(R)]PF_6$[19] (R = Me, 91.7 ppm; R = H, 92.7 ppm). The carbon resonances of PMe_3 appear as an apparent triplet (J_{PC} = 18.33 Hz) at 22.52 ppm. The triplet is part of an $A_3XX'A'_3$ pattern, and the J_{PC} values are measured from the middle peak to an outer peak. Table II shows that the resonances do not change significantly for the neutral and cationic species, all of which fall in the range 22.47–23.65 ppm with coupling constants ranging from 13.30 to 18.93 ppm. The key observation that establishes the presence of the vinylidene ligand is a far downfield triplet in the ^{13}C NMR spectrum for the carbon bound to ruthenium (α-carbon). This ^{13}C NMR α-carbon resonance in complex **2** appears at 326.93 ppm and is split into a triplet (J_{PC} = 16.81 Hz) by the phosphorus; the β-carbon occurs as a singlet at 116.62 ppm. The α-carbon and β-carbon resonances are characteristic of the related vinylidene complexes $[Cp(PMe_3)_2Ru{=}C{=}C(H)(Me)]PF_6$[19] (347.9 and 103.4 ppm), $[Cp\{(MeO)_3P\}_2Mo{=}C{=}C(H)(t\text{-}Bu)]Li$[56] (322.8 and 121.8 ppm), and $[Cp(PPh_3)(NO)Re{=}C{=}C(H)(Me)]CF_3SO_3$[57] (328.5 and 126.0 ppm).

Unlike the reaction of $Cp(PMe_3)_2RuCl$ with MeSC≡CSMe to give **1** and **2**, under similar conditions $Cp(PMe_3)_2RuCl$ reacts with MeSC≡CMe to give a 2:1 ratio of the sulfur-bound (**3a**) and π-bound (**3b**) complexes, which are collected in 79% total yield. Although pure **3a** was isolated, **3b** could not be separated completely from **3a**. Refluxing a solution of pure **3a** in MeOH for 30 min or warming **3a** in CD_3OD at 40 °C for 4 h again gave a 2:1 ratio of **3a** to **3b**. Complex **3b** was characterized by its ^1H NMR Cp resonance at 5.14 ppm, which is similar to the Cp resonances reported for the complexes $[Cp(PMe_3)_2Ru(\eta^2\text{-alkyne})]PF_6$ (HC≡CMe, 5.02 ppm;[19] HC≡CH, 5.02 ppm;[19] EtC≡CEt, 5.25 ppm[7]). The ^{13}C NMR resonances for the alkyne carbons in **3b** occur at 82.94 and 70.66 ppm as singlets. In similar compounds, the alkyne resonances occur as singlets at 73.0 and 53.6 ppm for $[Cp(PMe_3)_2Ru(\eta^2\text{-MeC}{\equiv}CH)]PF_6$[19] and at 54.29 for $[Cp(PMe_3)_2Ru(\eta^2\text{-CF}_3C{\equiv}CCF_3)]PF_6$.[7]

When the mixture of isomers **3a** and **3b** was refluxed in CH_3CN for 9 h under N_2, the pale yellow powder $[Cp(PMe_3)_2Ru(NCCH_3)]BF_4$ (**4**) was isolated in quantitative yield (Scheme I). Complex **4** was previously characterized by Treichel and Komar,[47a] and its ^1H NMR and IR data are given in Table I. Complex **2** reacts slowly and partially with CH_3CN at 95 °C to liberate MeSC≡CSMe and form complex **4** (eq 1); an equilibrium mixture of complexes **2**



$$\underset{\textbf{2}}{[Cp(PMe_3)_2Ru{=}C{=}C(SMe)_2]PF_6} \xrightleftharpoons{CH_3CN} \underset{\textbf{4}}{[Cp(PMe_3)_2Ru(NCCH_3)]PF_6} + MeSC{\equiv}CSMe \qquad (1)$$

and **4** (1.25:1 ratio) is established after 72 h. The reaction of the vinylidene complex **2** with CH_3CN to generate free MeSC≡CSMe must result from a facile 1,2-migration of SMe from one carbon to the other.

The known formation[19-31] of metal vinylidene complexes from reactions of 1-alkynes with metal complexes is proposed to proceed through a 1,2-hydrogen shift via an intermediate η^2-alkyne complex.[22,31] Similarly, the rear-

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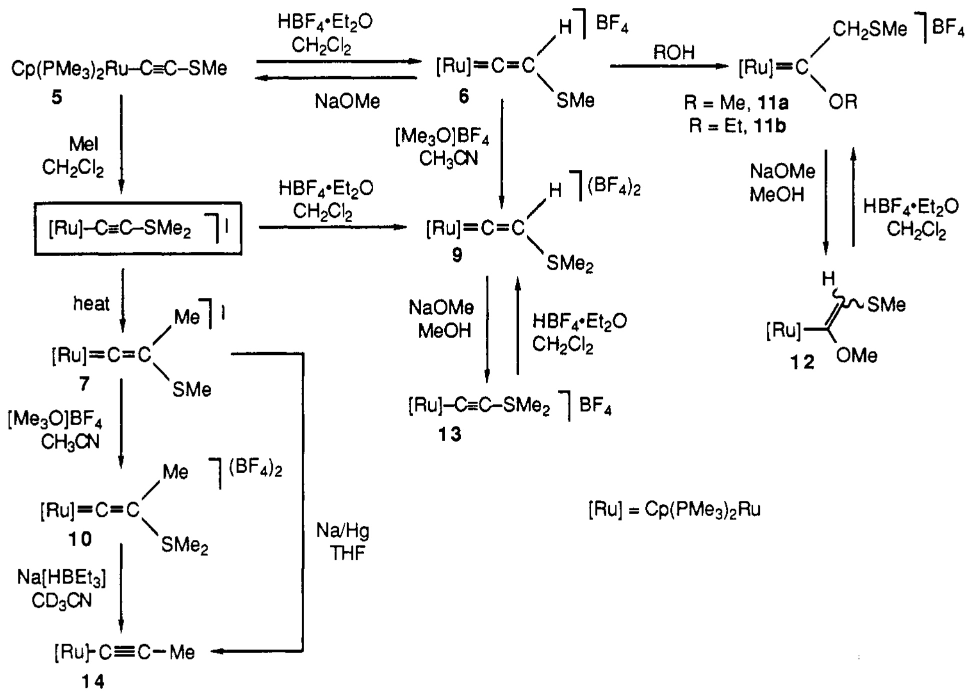
Scheme II



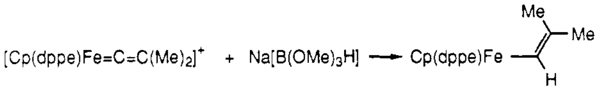
rangement of complex 1 to 2 is suggested to proceed via an undetected π-MeSC≡CSMe intermediate, which rearranges to the vinylidene product 2 by an intramolecular 1,2-SMe shift. There appears to be no precedent for such a SMe migration, although a somewhat related iodo migration has been reported for the iodoalkyne complex $Cp(CO)_2Mn(\eta^2\text{-}IC{\equiv}CCH(OR)_2)$.[58]

The fact that complex 3b does not undergo a 1,2-SMe rearrangement to form a vinylidene complex indicates that this rearrangement requires both SMe groups in the alkyne. While one of these groups migrates, the other must in some fashion stabilize an intermediate which promotes the SMe migration.

Reactions of $[Cp(PMe_3)_2Ru{=}C{=}C(SMe)_2]PF_6$ (2) with Reducing Agents. The Na/Hg amalgam reduction of complex 2 results in a yellow powder of 5 (Scheme I). This complex is characterized by an IR $\nu(C{\equiv}C)$ band at 2000 cm^{-1}, which is lower than those of other ruthenium acetylide complexes: $Cp(PPh_3)_2Ru{-}C{\equiv}CR$ (R = Me, 2100 cm^{-1}; Ph, 2068 cm^{-1}; CO_2Me, 2058 cm^{-1})[28] and $Cp(PMe_3)_2Ru{-}C{\equiv}CR$ (R = Ph, 2105 cm^{-1}; Me, 2098 cm^{-1}).[24] However, the free thioacetylene MeSC≡CSMe also has a Raman-active band (2082 cm^{-1})[48b] that is lower than those of free alkyl- and arylacetylenes, which occur in the region 2260–2100 cm^{-1}.[59] The lower $\nu(C{\equiv}C)$ band in MeSC≡CSMe and in 5 may be due to a combination of the effect of the heavy sulfur atom adjacent to the acetylenic carbon and/or the effect of carbon–sulfur vibrational coupling.[60] For 5, there may be an additional weakening of the C≡C bond caused by some contribution of a vinylidene resonance form of the type discussed later in eq 4, which would be stabilized by the sulfur atom on the β-carbon.

The ^{13}C NMR signal for the α-carbon in 5 occurs as a triplet (J_{PC} = 25.25 Hz) at 121.58 ppm, and the β-carbon occurs as a singlet at 82.02 ppm. In similar compounds, the α-carbon resonance is also characteristically a triplet at 87–103 ppm and the β-carbon is a singlet at 98–123 ppm: $Cp(PPh_3)_2Ru{-}C{\equiv}CR$ (R = n-Bu, 89.4 and 111.3 ppm; R = t-Bu, 87.8 and 120.9 ppm) and $Cp^*(dppe)Ru{-}C{\equiv}C\text{-}t\text{-}Bu$ (102.2 and 116.4 ppm).[20]

While other vinylidene complexes are known[61] to undergo attack at the α-carbon by anions such as H^-, MeO^-, and NH_2^- to give vinyl derivatives (eq 2), complex 2 reacts with $Na[HBEt_3]$ in CD_3CN in an NMR tube to give 5 and MeSSMe. Thus, the $Na[HBEt_3]$ is acting as a reducing agent. The formation of MeSSMe suggests an electron-transfer process, which is discussed in detail later. Similarly, the reactions of 2 with NaH, NaSEt, NaSPh, and NaOMe also give 5.



$$[Cp(dppe)Fe{=}C{=}C(Me)_2]^+ + Na[B(OMe)_3H] \longrightarrow Cp(dppe)Fe{-}C(H){=}C(Me)_2 \qquad (2)$$

Reactions of $Cp(PMe_3)_2Ru{-}C{\equiv}CSMe$ (5). Complex 5 readily reacts with $HBF_4{\cdot}Et_2O$ at room temperature to give $[Cp(PMe_3)_2Ru{=}C{=}C(H)(SMe)]BF_4$ (6) and with MeI in refluxing CH_2Cl_2 to give $[Cp(PMe_3)_2Ru{=}C{=}C(Me)(SMe)]I$ (7) in 85% and 75% yields, respectively (Scheme II). These additions of an electrophile to the β-carbon of a metal–acetylide complex to form a metal–vinylidene complex are presumably promoted by an accumulation of electron density that is localized on the β-carbon of the acetylide, as suggested by MO calculations.[61] Many acetylide complexes undergo β-carbon protonation or alkylation to give a variety of vinylidene derivatives.[23,24,28,62-67]

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The ^1H NMR spectrum of **6** shows a singlet at 5.08 ppm for the vinylidene proton; in **7** the corresponding methyl protons appear as a singlet at 2.08 ppm. In the similar complexes $[Cp(PMe_3)_2Ru{=}C{=}C(R)(Ph)]PF_6$ (R = H, Me),[24] the proton and methyl signals at 1.37 ppm (t, no J_{PH} value given) and 5.40 ppm (t, J_{PH} = 2.2 Hz), respectively, show coupling to phosphorus. The vinylidene resonances in the ^1H and ^{13}C NMR spectra of complexes **6** and **7** (Tables I and II) are comparable to those in **2**.

While the reaction of complex **5** with MeI in refluxing CH_2Cl_2 gives **7**, the same reaction at 0 °C in CH_2Cl_2 or $CDCl_3$ in an NMR tube first appears to give $[Cp(PMe_3)_2Ru{-}C{\equiv}CSMe_2]I$ (Scheme II); when the solution is warmed to room temperature for 10 min, this complex rearranges to the vinylidene complex **7**. The formulation of the intermediate as $[Cp(PMe_3)_2Ru{-}C{\equiv}CSMe_2]I$ is supported by a comparison of its IR and ^1H NMR spectra with those of complex **13** (see synthesis later); an IR $\nu(C{\equiv}C)$ band is present at 1960 cm^{-1}, and ^1H NMR resonances at 4.76, 3.22, and 1.49 (d) ppm are assigned to Cp, SMe_2, and PMe_3 groups, respectively. The ^1H NMR resonance (3.22 ppm) of the SMe_2 group in $[Cp(PMe_3)_2Ru{-}C{\equiv}CSMe_2]I$ is somewhat downfield of the SMe_2 group (3.00 ppm) in complex **13** (discussed in a later section); this may be due to an association of the sulfonium group with the iodide anion. The identity of the intermediate was further supported by a ^1H NMR tube study of the reaction of complex **5** and MeI at 0 °C until the formation of $[Cp(PMe_3)_2Ru{-}C{\equiv}CSMe_2]I$ was observed; then, addition of $HBF_4{\cdot}Et_2O$ to the reaction solution gave a ^1H NMR spectrum which was identical with that of $[Cp(PMe_3)_2Ru{=}C{=}C(H)(SMe_2)]^{2+}$ (**9**).

A 5-min reaction of complex **5** with 1 equiv of $[MeSSMe_2]SO_3CF_3$ at room temperature in CD_3CN in an NMR tube gives the vinylidene complex **2** in quantitative yield (Scheme I), as established by its ^1H NMR spectrum.

Reaction of **5** with a suspension of CuCl in CH_2Cl_2 affords the complex $Cp(PMe_3)_2Ru(C{\equiv}CSMe)(CuCl)$ (**8**) in 69% yield (Scheme I). The resulting yellow powder was characterized by its ^1H and ^{13}C NMR spectra (Tables I and II), IR and EIMS spectra, and elemental analyses. The IR $\nu(C{\equiv}C)$ frequency appears 118 cm^{-1} lower (1882 cm^{-1}) than for **5** (2000 cm^{-1}), indicating the side-on π-coordination of the $C{\equiv}C$ group to the copper.[1a] This decrease is similar to that observed upon coordination of CuCl to alkynes (81–173 cm^{-1})[68] and to acetylide complexes: $(dppe)(CO)_3Mn(C{\equiv}CR)(CuCl)$[69] (R = CH_2OMe, 1980 cm^{-1}; *t*-Bu, 1983 cm^{-1}; Ph, 1989 cm^{-1}) and $Cp(PPh_3)_2Ru(C{\equiv}CR)(CuCl)$[70] (R = Ph, 1979 cm^{-1}; *p*-MeC_6H_4, 1945 cm^{-1}; Me, 1982 cm^{-1}). The ^1H NMR spectrum of **8** shows a SMe resonance at 2.36 ppm that is slightly downfield of the 2.29 ppm shift observed for **5** (Table I). This further suggests that the copper is bound to the $C{\equiv}C$ group and not to the sulfur. If the copper were bound to the sulfur, a larger downfield methyl resonance shift would be expected, as is observed for $[Cp(PMe_3)_2Ru{-}C{\equiv}CSMe_2]BF_4$ (**13**; discussed later). An X-ray diffraction study carried out on $(dppe)(CO)_3Mn(C{\equiv}CPh)(CuCl)$[71] revealed that the complex is monomeric in the solid state and the copper is π-bound to the carbon–carbon triple bond of the σ-acetylide ligand.

Reactions of $[Cp(PMe_3)_2Ru{=}C{=}C(R)(SMe)]BF_4$ (R = H (6), Me (7)). The monocationic vinylidene complexes **6** and **7** react readily with $[Me_3O]BF_4$ in CH_3CN to form the dicationic sulfonio complexes $[Cp(PMe_3)_2Ru{=}C{=}C(R)(SMe_2)](BF_4)_2$ (R = H (**9**), Me (**10**)) in 72% and 55% yields, respectively (Scheme II). The products are isolated as air-stable yellow solids that are soluble in CH_3CN, sparingly soluble in acetone, and insoluble in less polar solvents such as CH_2Cl_2. In the ^1H NMR spectra of **9** and **10**, the sulfonio methyl resonances are at 2.87 and 2.83 ppm, respectively, which are downfield by approximately 0.6 ppm in comparison to the methyl resonances in complexes **6** and **7**. The ^1H NMR methyl resonance of the sulfonium group in $[Cp(PPh_3)(NO)ReCH_2SMe_2]PF_6$[72,73] (2.60 ppm) is also approximately 0.6 ppm downfield of that in the analogous thioether $Cp(PPh_3)(NO)ReCH_2SMe$ (2.01 ppm). The ^1H NMR chemical shift of the Cp group in complexes **9** and **10** is also downfield as compared to those of complexes **2**, **6**, and **7** (Table I); this suggests that the positive charge is not localized on the sulfonium group but is delocalized throughout much of the complex. In the ^1H NMR spectrum of **9** the vinylidene proton resonance appears as a broad triplet at 5.22 ppm. This signal collapses to a sharp triplet (J_{PH} = 1 Hz) when the sulfonium methyl resonance is irradiated in a selective decoupling experiment. The ^{13}C NMR signals of the α-carbons in complexes **9** and **10** are triplets at 322.64 and 323.22 ppm; the β-carbons in complexes **9** and **10** occur as singlets at 102.58 and 109.57 ppm (Table II).

Complex **6** readily undergoes deprotonation with NaOMe in MeOH to give complex **5** in 90% yield (Scheme II). The reducing agent Na/Hg and bases such as $Na[HBEt_3]$, NaSEt (pK_a = 10–11), and $NaHCO_3$ (pK_a = 6.35) also readily deprotonate complex **6**; thus, **6** appears to be more acidic than similar vinylidene compounds of known pK_a: $[Cp(dppe)Fe{=}C{=}C(H)(Me)]^+$ (7.74 ± 0.05 in $THF{-}H_2O$)[74] and $[Cp(PMe_3)_2Ru{=}C{=}C(H)(CMe_3)]^+$ (20.8 ± 0.2 in CH_3CN).[75]

Alcohols are known to add across the vinylidene carbon–carbon double bonds to form alkoxycarbene complexes such as $[Cp(PPh_3)_2Ru{=}C(OMe)(CH_2Ph)]PF_6$ and $[Cp(PPh_3)(CO)Ru{=}C(OR)(CH_2Ph)]PF_6$ (R = Et, *i*-Pr);[26] on the other hand, di-β-substituted complexes such as $[Cp(PPh_3)_2Ru{=}C{=}C(Me)(Ph)]I$ do not react with alcohols. At room temperature MeOH and EtOH add to complex **6** to give $[Cp(PMe_3)_2Ru{=}C(OR)(CH_2SMe)]BF_4$ (R = Me (**11a**), Et (**11b**); Scheme II). The air-stable yellow powder of **11a** was characterized by its elemental analyses, FAB mass spectrum, and ^1H NMR (Table I) and ^{13}C NMR spectra (Table II). The reaction to form **11b** did not go to completion in a 10-h period, while the formation of **11a** was complete by that time. The ^{13}C NMR resonance of the methoxycarbene carbon in **11a** occurs at 295.92 ppm, which is similar to that in $[Cp(PPh_3)_2Ru{=}C(OMe)(CH_2Ph)]PF_6$[26] (308.7 ppm). Higher alcohols such as *i*-PrOH and *t*-BuOH did not react with **6** to give alkoxycarbene complexes under similar conditions.

The abstraction of a proton from **11a** with NaOMe gave two isomers of the vinyl complex $Cp(PMe_3)_2Ru[C(OMe){=}C(H)SMe]$ (**12**) in an 8:1 ratio (Scheme II), as determined by ^1H NMR spectra of the compound. The

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Table VI. Selected Bond Lengths (Å) and Angles (deg) in Ruthenium Vinylidene Complexes

compd	Ru=C	C=C	Ru–C(1)–C(2)
[Cp(PMe$_3$)$_2$Ru=C=C(H)(SMe$_2$)](BF$_4$)$_2$ (**9**)	1.792 (8)	1.36 (1)	178.7 (5)
[Cp(PPh$_3$)$_2$Ru=C=C(I)(Ph)]I$_3$[67]	1.839 (7)	1.31 (1)	171.0 (7)
[Cp(PPh$_3$)$_2$Ru=C=C(Br)(C$_6$H$_4$Br-4)]Br$_3$[67]	1.85 (1)	1.31 (2)	169.4 (14)
[Cp(PPh$_3$)$_2$Ru=C=C(Me)(Ph)]I[66]	1.863 (10)	1.293 (15)	172.8 (11)
[Cp(PPh$_3$)$_2$Ru=C=C(Ph)(N=NC$_6$H$_3$Me$_2$-3,4)]BF$_4$[65]	1.823 (9)	1.34 (1)	169.9 (7)
[Cp(dppe)Ru=C=C(Ph)(C$_7$H$_7$)]PF$_6$[65]	1.848 (9)	1.32 (1)	174.9 (6)
[Cp(PMe$_3$)$_2$Ru=C=C(H)(Me)]PF$_6$[24]	1.845 (7)	1.313 (10)	180 (2)

pale yellow powder of **12** was collected in 84% yield and was characterized by its EIMS, ^{1}H NMR (Table I), and ^{13}C NMR spectra (Table II). It showed appreciable decomposition in the solid form in approximately 6 h when exposed to air. The ^{1}H NMR spectrum of isomer A shows a broad vinyl proton signal at 5.33 ppm. This signal collapsed to a triplet with J_{PH} = 1.38 Hz when the methyl of the OMe group was irradiated in a ^{1}H NMR selective-decoupling experiment. The vinyl proton resonance of the less abundant isomer B was not located. The stereochemistry of isomer A cannot be assigned definitively; however, comparison with related complexes suggests an *E* conformation (proton cis to the metal). The complexes Cp(PPh$_3$)(CO)Ru[C(O-*i*-Pr)=C(H)Ph][21] and Cp(P(OMe)$_3$)$_3$Mo[C(H)=C(H)-*t*-Bu][76] have been assigned as *E* isomers and show β-vinyl proton resonances at 4.82 and 5.40 ppm with J_{PH} = 1.2 (d) and 2.0 (t) Hz, respectively. In the ^{13}C NMR spectrum of isomer A of **12**, the α-carbon appears at 190.62 ppm and the β-carbon at 102.82 ppm. The vinyl complex Cp(P(OPh)$_3$)(CO)Fe[C(Me)=C(Me)SPh][77] and Cp(PPh$_3$)(CO)Ru[C(O-*i*-Pr)=C(H)Ph][21] show similar resonances for the α-carbon at 157.8 and 206.08 ppm, respectively, and for the β-carbon at 127.7 and 88.76 ppm, respectively. Complex **12** readily adds 1 equiv of HBF$_4$·Et$_2$O in CDCl$_3$ to give back the carbene complex **11a** quantitatively (Scheme II), as indicated by the ^{1}H NMR spectrum.

X-ray Crystal Structure of [Cp(PMe$_3$)$_2$Ru=C=C(H)(SMe$_2$)](BF$_4$)$_2$ (9). Complex **9** is the first example of a mononuclear vinylidene complex with an overall +2 charge. The geometry about the ruthenium(II) center is nearly octahedral, as shown in Figure 1; one face of the octahedron is occupied by the Cp group and the opposite face by the two PMe$_3$ and vinylidene ligands. The most notable features of this structure are in the vinylidene moiety. The Ru–C(1)–C(2) system is essentially linear (178.7 (5)°). The Ru–C(1) distance (1.792 (8) Å) is the shortest reported ruthenium–vinylidene carbon bond distance; these distances range from 1.823 (9) to 1.863 (10) Å (Table VI). In fact, the Ru–C(1) distance is within the range for metal–carbyne complexes: (Cl)(CO)(PPh$_3$)$_2$Os(≡C-tolyl),[78] 1.77 (2) Å; (PPh$_3$)$_2$(Cl)$_2$(SCN)Os[≡C(4-C$_6$H$_4$NMe$_2$)],[79] 1.75 (1) Å; {(PPh$_3$)$_2$(Cl)$_2$[(tolyl)NC]Os[≡C(4-C$_6$H$_4$NMe$_2$)]}ClO$_4$,[79] 1.78 (1) Å.

The C(1)–C(2) distance at 1.36 (1) Å is slightly longer than the distances (1.293 (15)–1.34 (1) Å) in related ruthenium vinylidene complexes (Table VI); it is not as long as the C(sp)–C(sp^2) single-bond distance in (Cl)(CO)(PPh$_3$)$_2$Os(≡C-tolyl)[78] (1.45 (3) Å) but is similar to that in [Cp(CO)$_2$Mn≡CC(H)=CPh$_2$]BF$_4$[80] (1.389 (7) Å). The short Ru–C(1) and long C(1)–C(2) bonds as compared to those in other vinylidene complexes (Table VI) suggest that both vinylidene and carbyne resonance forms contribute to the bonding in **9** (eq 3).

(3)

The C(1)–C(2)–S angle (119.6 (5)°) is typical of C(sp^2) centers; the C(2)–S distance at 1.719 (9) Å is shorter than C(sp^2)–S single-bond distances found in Cp(PPh$_3$)(CO)W≡CSPh[81] (1.768 (12) Å) and [(PPh$_3$)$_2$(CO)$_3$Mn=C=C(NMe$_2$)SMe]BF$_4$[82] (1.784 (16) Å). The mean value of S(sulfonium)–C(sp^2) ylide bond lengths is 1.715 Å with a range from 1.707 (7) to 1.721 (4) Å.[83] The C(2)–S distance is short enough to suggest considerable double-bond character, as was also proposed for the thioester complexes (CO)$_2$(PPh$_3$)$_2$(H)Os[C(S)SMe][84] (1.724 (5) Å) and [Cp(dppe)Fe=C=C(Me)(C(S)SMe)]I·MeOH[85] (1.73 (2) Å). However, it is not as short as a full double bond, since C(sp^2)=S distances are much shorter, as in [Cp(CO)Fe]$_2$(μ-CO)(μ-C=S)[86] (1.596 (9) Å) and (CO)$_2$(PPh$_3$)$_2$(H)Os[C(=S)SMe][84] (1.648 (4) Å). The shortening of the Ru–C(1) and C(2)–S distances and the lengthening of the C(1)–C(2) distance support a resonance form with partial carbyne and ylide character as contributing to the bonding in **9** (eq 3).

Preparation of [Cp(PMe$_3$)$_2$Ru–C≡CSMe$_2$]BF$_4$ (13). Just as the monocationic vinylidene complex **6** can be deprotonated with a base to give **5**, complex **9** is deprotonated by a slight excess of NaOMe to give a red powder of **13** in 94% yield (Scheme II). The complex readily decomposes in the solid state over approximately 12 h; however, it can be handled in air for short periods of time without any appreciable decomposition. The ^{1}H NMR Cp resonance (4.76 ppm) of complex **13** is nearly identical with that of **5**; the ^{13}C NMR α-carbon resonance of **13** at 183.39 ppm is downfield by 60 ppm from that of **5** and the β-carbon at 88.03 ppm is nearly identical with that of **5**. The IR ν(C≡C) band in **13** is 40 cm^{-1} lower than that in **5** (2000 cm^{-1}); in the only known alkynylsulfonium salt, [PhC≡CS(Me)Et](picrate),[87] the IR ν(C≡C) band is found at 2195 cm^{-1}, which is also shifted by 60 cm^{-1} as compared to that of MeC≡CSMe (2255 cm^{-1}). In the complexes (L)Rh–C≡CR (L = N(CH$_2$CH$_2$PPh$_2$)$_3$, P(CH$_2$CH$_2$PPh$_2$)$_3$)[88] the ν(C≡C) band decreases (~30 cm^{-1}) upon replacing R = Ph with R = CO$_2$Et; these results were interpreted to mean greater π-back-bonding from the Rh

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to the acetylide ligand. The lower $\nu(C\equiv C)$ value in **13** as compared with that of **5** suggests a weaker carbon–carbon triple bond. This together with the downfield shift of the α-carbon resonance toward those of vinylidene compounds suggests that a resonance form with partial double-bond character created by C(2p)–S(3d) overlap contributes to the bonding in **13** (eq 4).[89] A structural study of the

$$[\mathrm{Ru}]-C\equiv C-\mathrm{S}(\mathrm{Me})_2]^+ \longrightarrow [\mathrm{Ru}]=C=C=\mathrm{S}(\mathrm{Me})_2]^+ \quad (4)$$

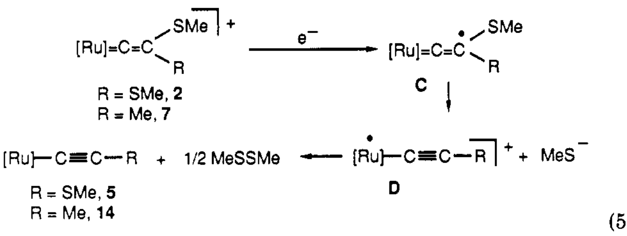
diphenylallenylidene complex $[Cp(PMe_3)_2Ru{=}C{=}C{=}CPh_2]PF_6$[90] also indicated a substantial contribution from two different forms, $[CpL_2Ru{=}C{=}C{=}CPh_2]^+ \leftrightarrow [CpL_2Ru{-}C{\equiv}C{-}CPh_2]^+$, with the cationic charge stabilized by both the metal center and the diphenylcarbenium moiety.

Like the protonation of complex **5** to form **6**, the sulfonioacetylide **13** can be protonated quantitatively, as indicated in the ^{1}H NMR spectrum, with 1 equiv of $HBF_4{\cdot}Et_2O$ in CD_3CN to form complex **9**, which was isolated in greater than 70% yield (0.020-mmol scale).

Reduction Reactions of $[Cp(PMe_3)_2Ru{=}C{=}C(Me)(SMe)]I$ (7) and $[Cp(PMe_3)_2Ru{=}C{=}C(Me)(SMe_2)](BF_4)_2$ (10). Similar to the reduction of complex **2** to **5** (Scheme I), complex **7** is reduced by equimolar $Na[HBEt_3]$ in $CDCl_3$ to give a stoichiometric conversion to the desulfurized acetylide $Cp(PMe_3)_2Ru{-}C{\equiv}CMe$ (**14**) and MeSSMe (Scheme II), as indicated by the ^{1}H NMR spectrum. Complex **14** is also obtained in over 80% yield from the reaction of **7** with a Na/Hg suspension in THF. Complex **14** was previously reported by Bruce and coworkers[24] and identified by its $\nu(C\equiv C)$ band at 2095 cm^{-1} and characteristic triplet in the ^{1}H NMR spectrum for the acetylide methyl group at 1.98 ppm (J_{PH} = 2.6 Hz).

The reduction of the dicationic complex **10** with 2 equiv of $Na[HBEt_3]$ in CD_3CN gives a stoichiometric conversion to the desulfurized acetylide **14** and Me_2S, as indicated by the ^{1}H NMR spectrum.

Mechanisms for the Reduction of $[Cp(PMe_3)_2Ru{=}C{=}C(SMe)_2]BF_4$ (2), $[Cp(PMe_3)_2Ru{=}C{=}C(Me)(SMe)]I$ (7), and $[Cp(PMe_3)_2Ru{=}C{=}C(Me)(SMe_2)](BF_4)_2$ (10). In earlier sections we have described reductions (Na/Hg or $Na[HBEt_3]$) that convert **2** to **5**, **7** to **14**, and **10** to **14** with loss of MeS$^{\bullet}$ or Me_2S. To our knowledge, reactions of this type have not previously been reported. Of the possible mechanisms for these reactions, initial electron transfer to the metal seems unlikely since the Ru already has 18 electrons and ruthenium vinylidene complexes have not been reported to undergo reduction. A more likely possibility is initial electron transfer to the sulfur of the vinylidene ligand in complexes **2**, **7**, and **10**. This suggestion is based on the considerable amount of information that is known about mechanisms of reduction of organic thioethers[91] and sulfonium compounds.[92] As applied to the reduction of **2** and **7**, the initial step would be a one-electron addition to form a radical intermediate (C, eq 5); carbon–sulfur bond cleavage with electron rearrangement in the vinylidene unit would form a metal-centered radical cation acetylide (D) and MeS$^-$. Related radical cation acetylides were generated by Bitcon and Whiteley[20] in the reversible one-electron oxidations of $Cp(PPh_3)_2Ru{-}C{\equiv}CR$ and $Cp(PPh_3)(CO)Fe{-}C{\equiv}CR$ (R = Ph, *n*-Bu, *t*-Bu). The final step (eq 5) is electron transfer from MeS$^-$ to the metal acetylide cation; the resulting MeS$^{\bullet}$ radicals would couple to form the observed MeSSMe.



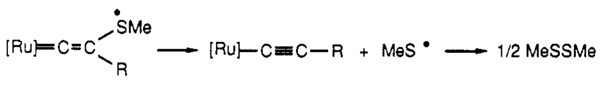
$$[\mathrm{Ru}]{=}C{=}C(\mathrm{SMe})(R)]^+ \xrightarrow{e^-} [\mathrm{Ru}]{=}C{=}\overset{\bullet}{C}(\mathrm{SMe})(R)\ \mathbf{C}$$

R = SMe, **2**; R = Me, **7**

$$[\mathrm{Ru}]{-}C{\equiv}C{-}R + 1/2\,\mathrm{MeSSMe} \longleftarrow [\mathrm{Ru}]{-}C{\equiv}C{-}R]^{\bullet +} + \mathrm{MeS}^-\ \mathbf{D} \quad (5)$$

R = SMe, **5**; R = Me, **14**

It seems possible that intermediate C in this mechanism (eq 5) could undergo carbon–sulfur bond cleavage to give a neutral metal acetylide and MeS$^{\bullet}$ radical (eq 6). Although carbon–sulfur bond cleavage to form MeS$^{\bullet}$ has not been observed previously in organic systems, it is possible that the ruthenium–acetylide complex is sufficiently stabilized that MeS$^{\bullet}$ would be produced.

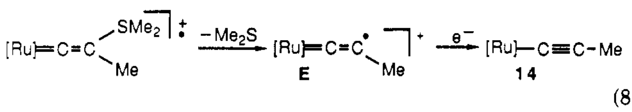


$$[\mathrm{Ru}]{=}C{=}\overset{\bullet}{C}(\mathrm{SMe})(R) \longrightarrow [\mathrm{Ru}]{-}C{\equiv}C{-}R + \mathrm{MeS}^{\bullet} \longrightarrow 1/2\,\mathrm{MeSSMe} \quad (6)$$

The two-electron reduction of sulfonium complex **10** with the formation of the Me_2S product presumably proceeds via a mechanism similar to that for the reduction of organic sulfonium ions (eq 7).[92] The rate-determining

$$\mathrm{Me_3S^+} \xrightarrow{e^-} [\mathrm{Me_3S}]^{\bullet} \longrightarrow \mathrm{Me_2S} + \mathrm{Me}^{\bullet} \xrightarrow[\mathrm{H^+}]{e^-} \mathrm{CH_4} \quad (7)$$

step would be initial electron transfer to the sulfonium group in **10** (eq 8). This is followed by carbon–sulfur bond cleavage to give Me_2S and the radical E, which rapidly adds another electron to give the acetylide product **14**.



$$[\mathrm{Ru}]{=}C{=}C(\mathrm{SMe_2})(\mathrm{Me})]^{\overset{+}{\bullet}} \xrightarrow{-\mathrm{Me_2S}} [\mathrm{Ru}]{=}C{=}\overset{\bullet}{C}(\mathrm{Me})]^+\ \mathbf{E} \xrightarrow{e^-} [\mathrm{Ru}]{-}C{\equiv}C{-}\mathrm{Me}\ \mathbf{14} \quad (8)$$

Conclusions

In contrast to the alkyl- and arylacetylenes that react with $Cp(PMe_3)_2RuCl$ to give the π-acetylene complexes $[Cp(PMe_3)_2Ru(\eta^2\text{-}RC{\equiv}CR)]^+$, the mercaptoacetylene $MeSC{\equiv}CSMe$ reacts with $Cp(PMe_3)_2RuCl$ to give the S-coordinated $\{Cp(PMe_3)_2Ru[S(Me)C{\equiv}CSMe]\}PF_6$ (**1**), which readily rearranges to the vinylidene $[Cp(PMe_3)_2Ru{=}C{=}C(SMe)_2]PF_6$ (**2**). Although the π-complex $[Cp(PMe_3)_2Ru(\eta^2\text{-}MeSC{\equiv}CSMe)]^+$ is not detected, it is a likely intermediate in the rearrangement of **1** to **2**. Unlike related vinylidene complexes $[Cp(PMe_3)_2Ru{=}C{=}CR_2]^+$, **2** reacts with one-electron-reducing agents to lose MeS$^{\bullet}$ and produce the acetylide $Cp(PMe_3)_2Ru{-}C{\equiv}CSMe$ (**5**). This acetylide is similar to other acetylides in that the β-carbon reacts with electrophiles (R = H$^+$, Me$^+$) to give vinylidene complexes $[Cp(PMe_3)_2Ru{=}C{=}C(R)(SMe)]^+$, but in addition it alkylates at the sulfur to give the unusual sulfonioacetylide $[Cp(PMe_3)_2Ru{-}C{\equiv}CSMe_2]^+$. The sulfur atoms in the vinylidene complexes $[Cp(PMe_3)_2Ru{=}C{=}C(R)(SMe)]^+$ (R = H (**6**), Me (**7**)) are also alkylated to give the dicationic vinylidene complexes $[Cp(PMe_3)_2Ru{=}C{=}C(R)(SMe_2)](BF_4)_2$ (R = H (**9**), Me (**10**)). It is clear from these studies that both the acetylene functionality and MeS groups are sites of reactivity in the vinylidene, acetylide, and carbene chemistry of the $MeSC{\equiv}CSMe$ ligand.

Since a variety of ligands have been attached to the $Cp(PMe_3)_2Ru^+$ center in these investigations, we have

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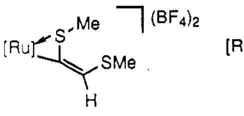
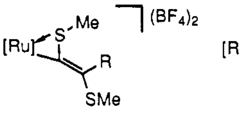
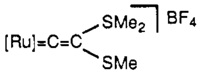
The cationic vinylidene complex $[Cp(PMe_3)_2Ru{=}C{=}C(SMe)_2]BF_4$ (**1**) undergoes addition of electrophiles such as $HBF_4{\cdot}Et_2O$, $[MeSSMe_2]SO_3CF_3$, and $[Me_3O]BF_4$ to give the complexes ($[Ru] = Cp(PMe_3)_2Ru$)



2a



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

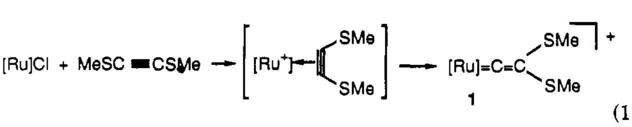


4

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, $4\text{-}NC_5H_4R$ (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 = $k_1[\mathbf{4}] + k_2[\mathbf{4}][\text{Nuc}]$. 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.

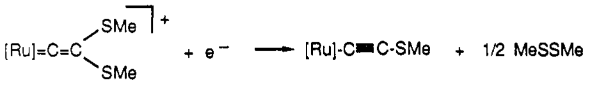
Introduction

In the previous paper,[2] we examined the influence of mercapto groups (SR) on the reactions of the alkynes $MeSC{\equiv}CSMe$ and $MeSC{\equiv}CMe$ with $Cp(PMe_3)_2RuCl$ (Cp = $\eta^5\text{-}C_5H_5$). We noted that the reaction with $MeSC{\equiv}CSMe$ 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(PMe$_3$)$_2$Ru).



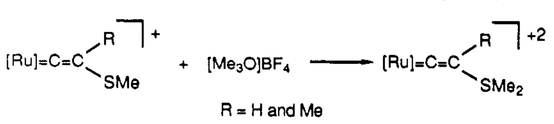
(1)

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



$$[Ru]{=}C{=}C(SMe)_2^{\,+} + e^- \longrightarrow [Ru]{-}C{\equiv}C{-}SMe + 1/2\ MeSSMe \quad (2)$$

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



$$[Ru]{=}C{=}C(R)(SMe)^{\,+} + [Me_3O]BF_4 \longrightarrow [Ru]{=}C{=}C(R)(SMe_2)^{\,+2} \quad (3)$$

R = H and Me

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