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The reactivity of the thioalkyne, MeSC[triple bond]CSMe, with ruthenium and tungsten complexes

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Iowa State University, 1990

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The reactivity of the thioalkyne, $MeSC\equiv CSMe$, with ruthenium and tungsten complexes

by

David Charles Miller

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Department: Chemistry
Major: Inorganic Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

For the Major Department

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For the Graduate College

Iowa State University
Ames, Iowa
1990

DEDICATION

To my mom

EXPLANATION OF DISSERTATION FORMAT

This thesis consists of four separate sections: One consisting of an introduction and literature review; the other three sections describe the thesis research which has been submitted for journal publication. Each of these sections are self-contained: Literature citations, tables, and figures pertain only to the sections which they are in. Following the final section is a general summary of the thesis work.

GENERAL INTRODUCTION

Alkynes occupy a unique place in organometallic chemistry because of their ability, in the presence of transition metals, to undergo an unusually diverse range of reactions.[1] On one hand, ligand substitution can occur to give simple alkyne π-complexes. On the other, complex cyclooligomerization reactions are observed which lead to cyclic acetylene dimers, trimers, and tetramers some of which contain other ligands, such as carbon monoxide and olefins incorporated during the cyclization process. In many reactions it may be reasonable to assume that simple alkyne π-complexes function as precursors to the more complex products such as vinylidene, vinyl, cycloarene and metallacyclic complexes. Only in relatively few cases have the intermediates been detected or isolated.

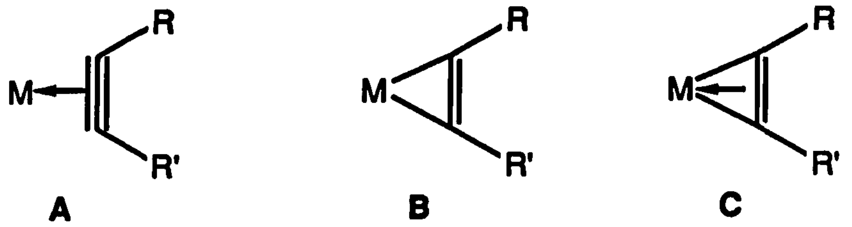
Many of the observed products are promoted by coordination of an alkyne to the metal, the products are a result from modifications to the electronic structure of the triple bond. This activation of the triple bond can be accomplished by electron donating, electon withdrawing, or potentially coordinating heteratom substituents. The ability of a ligand containing sulfur to undergo attack by nucleophilic and electrophilic reagents suggests that a thioalkyne ligand would display new types of reactivity on organometallic centers. It was attempted to explore this reactivity which is the basis for the studies described in this thesis on the reactivity of the heteratom alkyne, $MeSC\equiv CSMe$, in ruthenium and tungsten complexes.

Recently a number of useful reviews dealing with several aspects of reactivity between metal complexes and alkynes have appeared in the literature.[1,2] However, very little information is presented in them on the types of reactions that an alkyne might undergo at ruthenium metal centers. This review deals with the products resulting from the reactions of alkynes with mononuclear ruthenium metal complexes.

SECTION I. PRODUCTS RESULTING FROM THE REACTIONS OF ALKYNES WITH MONONUCLEAR RUTHENIUM METAL COMPLEXES

η^2-ALKYNE FORMATION

The bonding modes of alkynes to monometallic centers are characterized by the valence bond structures shown in eq 1.[1]

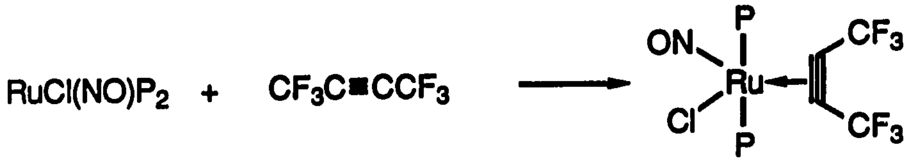


1

Structures A and B are, respectively, π- and σ-formulations of M-alkyne coordination when the alkyne acts as a formal two-electron donor. The metal alkyne is sometimes described in the literature as B because of the observed M-C and C=C distances and the R-C=C angles of coordinated alkynes best correlate with a metallacyclopropene structure. The metal may also interact strongly with both π molecular orbitals of the alkyne (C); in such π,σ-complexes the alkyne acts as a four-electron donor.[2]

Addition to a Coordinatively Unsaturated Center

Green and Stone[3] demonstrated the addition of $CF_3C{\equiv}CCF_3$ (hfb) to a benzene solution of the 4-coordinate $RuCl(NO)P_2$ ($P = PPh_3$, PPh_2Me, $PPhMe_2$) at room temperature (eq 2).

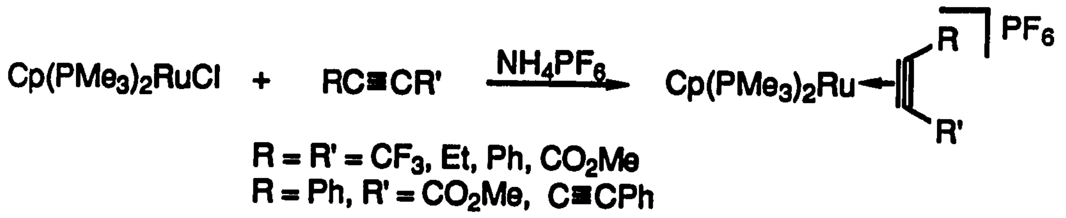


2

Similarly, the reaction in a toluene solution of $RuHCl(CO)(PCy_3)_2$ with acetylene gas affords $RuHCl(CO)(PCy_3)_2(\eta^2\text{-}HC\equiv CH)$.[4] These neutral η^2-alkynes show an IR $\nu(C\equiv C)$ band ranging from 2024 to 1742 cm^{-1}; this absorption is approximately 200 to 400 cm^{-1} lower than found for the free alkynes. The large decrease in the alkyne stretch is primarily due to the basicity of the metal and the metals ability to donate electron density into the π^*-orbitals of the alkyne, this therefore increases the $C\equiv C$ length.[3] Moers[4] reported that a similar reaction with $PhC\equiv CH$ formed $RuHCl(CO)(PCy_3)_2(\eta^2\text{-}PhC\equiv CH)$. Characterization was based on IR data; however, this is probably incorrect because the reported $\nu(C\equiv C)$ band at 1595 and 1575 cm^{-1} are more characteristic of $\nu(C=C)$ vibrational modes in ruthenium-vinylidene complexes; these will be discussed later.

Addition with Ligand Displacement

The displacement of a chloride ligand by polar solvents has been shown to occur on electron rich ruthenium metal centers. A number of η^2-alkyne complexes are isolated in refluxing methanol solutions of $Cp(PMe_3)_2RuCl$, NH_4PF_6 (used for anion exchange with the chloride anion), and the respective alkyne (eq 3).[5,6]



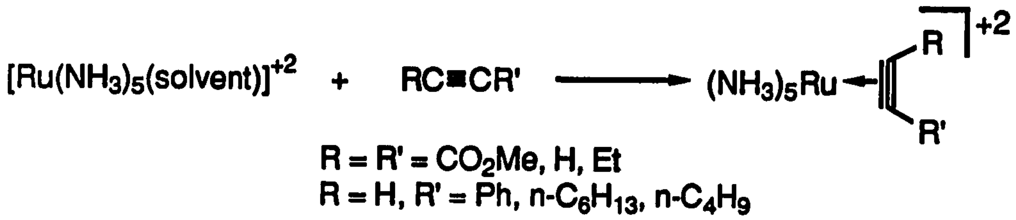
3

These air-stable pale yellow complexes are primarily characterized by the IR ν(C≡C) band observed between 1900 and 1852 cm^{-1}, and by ^{13}C NMR alkyne carbon resonances. These generally occur in the range of (δ) 74 to 53 ppm which are upfield compared to the free alkyne by approximately 25 ppm. Calvert and coworkers[7] reported the isolation of the dialkyne, [cis-Ru(bpy)$_2${η^2-(py)C≡C(py)}$_2$](PF$_6$)$_2$ (bpy = 2,2'-bipyridine), by refluxing an EtOH/H$_2$O solution of cis-Ru(bpy)$_2$Cl$_2$•2H$_2$O, bis(4-pyridyl)alkyne, and NH$_4$PF$_6$. Recently, Bullock[8] was able to isolate η^2-alkyne complexes of acetylene and propyne as air-stable pale yellow powders. The alkynes are bubbled through a methanol solution of Cp(PMe$_3$)$_2$RuCl containing excess NH$_4$PF$_6$ at room temperature for 15 min to give the isolated complexes [Cp(PMe$_3$)$_2$Ru(η^2-HC≡CR)]PF$_6$ (R = H, Me). These π-alkyne complexes rearrange to the vinylidene complexes [Cp(PMe$_3$)$_2$Ru=C=C(H)(R)]PF$_6$ in methanol or acetonitile at 40 to 60 °C via a 1,2-hydrogen shift; this rearrangement will be discussed later.

The displacement of a phosphine from Ru(CO)$_2$(PPh$_3$)$_3$ by

PhC≡CPh occurs rapidly to give $Ru(CO)_2(PPh_3)_2(\eta^2\text{-}PhC{\equiv}CPh)$.[9] This complex is characterized by an IR $\nu(C{\equiv}C)$ band at 1776 cm^{-1}; however, no additional information is reported.

A number of groups have shown interest in the ability of $[Ru(NH_3)_5(solvent)]^{2+}$ to bind alkynes by displacement of a coordinated solvent (H_2O or acetone) to form $[Ru(NH_3)_5(\eta^2\text{-}RC{\equiv}CR')]^{2+}$ (eq 4).[10-13]



R = R' = CO_2Me, H, Et
R = H, R' = Ph, n-C_6H_{13}, n-C_4H_9

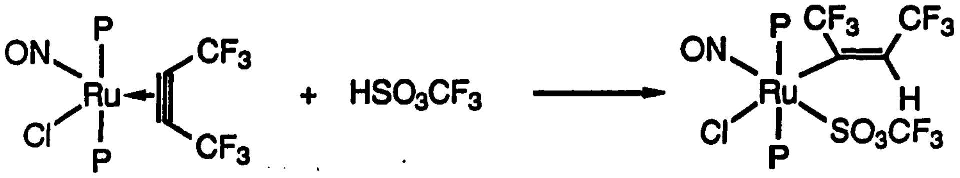
4

The IR $\nu(C{\equiv}C)$ bands are observed between 1995 and 1775 cm^{-1}, which is lower by over 200 cm^{-1} than that in the free alkynes.

The only X-ray determination of an η^2-alkyne was reported for $[Ru(NH_3)_5(\eta^2\text{-}MeO_2CC{\equiv}CCO_2Me)](PF_6)_2$.[10] This complex is discribed as a distorted octahedron in which the C_2 unit is twisted by 24.7° with respect to a plane created by three nitrogens. The carbon-carbon bond is lengthened to 1.238 (7) Å with respect to the 1.20 Å for free $MeO_2CC{\equiv}CCO_2Me$ (dma); however, it is still considerably shorter than the 1.34 Å of a normal carbon-carbon double bond. The Ru-C bond lengths, 2.144 (5) and 2.117 (6) Å, are slightly different since they are not required by symmetry to be identical.

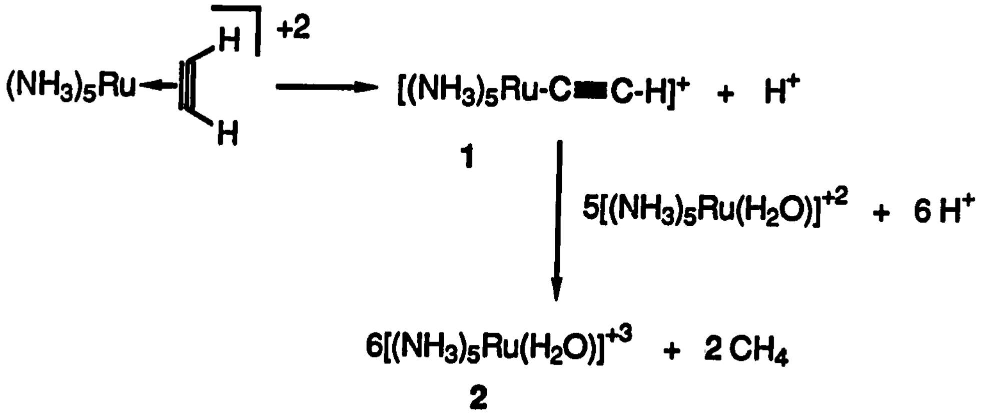
Reactions of η^2-alkynes

Direct attack of nucleophiles on coordinated η^2-alkynes are well known for complexes such as $[Cp(P(OPh)_3)(CO)Fe(\eta^2\text{-}RC{\equiv}CR')]PF_6$[14] and $CpW(\eta^2\text{-}CF_3C{\equiv}CCF_3)_2Cl$;[1] however, there are no known cases of direct addition of nucleophiles or electrophiles to ruthenium η^2-alkyne complexes. It has been reported[3] that the addition of $RuCl(NO)P_2(\eta^2\text{-}CF_3C{\equiv}CCF_3)$ ($P = PPh_3$, PPh_2Me) to stirred HSO_3CF_3 for 5 min gave the cis-vinyl complex (β-proton cis to the metal center) shown in eq 5.

 5

The formation of this complex suggests that initial addition of the proton is at the metal center forming a ruthenium hydride intermediate, followed by proton transfer to the alkyne to give the observed vinyl product.

Degani and Willner[12] demonstrated that $[Ru(NH_3)_5(\eta^2\text{-}HC{\equiv}CR)]^{+2}$ ($R = H$, Me, Et) undergoes photochemical activation in which the carbon-carbon triple bond is reductively cleaved to give the ruthenium aqua species 2 and the respective alkane (eq 6 for R = H).

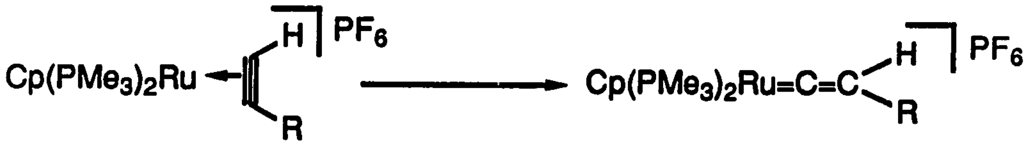


6

It is proposed that the initial reaction occurs by photochemical activation in which the η^2-alkyne is converted to 1 and H^+. An IR $\nu(C\equiv C)$ band is observed at 1930 cm^{-1} which is characteristic of other known acetylide metal complexes. The rest of the mechanism for the conversion to 2 is not known at present; it was suggested that the alkyl, vinylidene, and carbene intermediates might participate in the photochemical conversion to methane.

VINYLIDENE, =C=C(H)(R), FORMATION

Terminal alkynes (1-alkynes) in the presence of a variety of metal centers are observed to undergo a 1,2-hydrogen shift to form mono-substituted vinylidene complexes after initial η^2-alkyne complex formation.[15] Bullock[8] recently demonstrated this conversion by isolation of the first HC≡CR ruthenium complexes, $[Cp(PMe_3)_2Ru(\eta^2\text{-}HC{\equiv}CR)]PF_6$ (R = H, Me). These η^2-alkyne complexes in methanol or acetonitrile readily undergo first-order rearrangement to the vinylidene products $[Cp(PMe_3)_2Ru{=}C{=}C(H)(R)]PF_6$, at 40 °C with $t_{1/2}$ = 5.5 min (R = Me) and at 60 °C with $t_{1/2}$ = 5 h (R = H) (eq 7).



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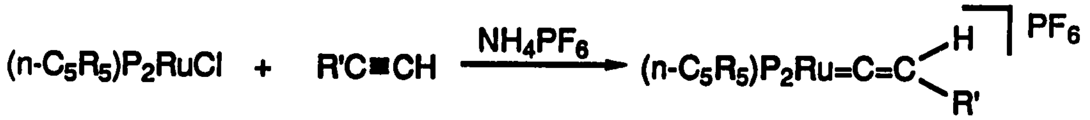
Similarly, a large number of ruthenium-vinylidene complexes are isolated from reactions of $Cp(P)_2RuCl$, HC≡CR, and NH_4PF_6 in refluxing MeOH for approximately 1 h; the products are obtained as air-stable, red crystalline complexes isolated in high yield (eq 8).[16]

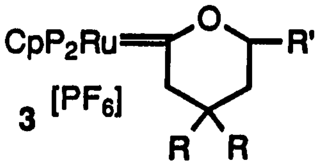


$$(n\text{-}C_5R_5)P_2RuCl + R'C{\equiv}CH \xrightarrow{NH_4PF_6} \left[(n\text{-}C_5R_5)P_2Ru{=}C{=}C\begin{smallmatrix}H\\R'\end{smallmatrix}\right]PF_6 \qquad 8$$

R = H, P = PPh_3, R' = Me, Ph, C_6F_5, CO_2Me, C_3H_7, p-C_6H_4F
R = H, P = PMe_3, R' = H, Me, Ph
R = H, P_2 = dppe, R' = Ph, n-C_4H_7
R = H, P_2 = dppm, R' = Ph
R = Me, P_2 = dppe, R' = Ph

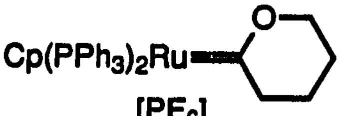
Consiglio and coworkers[17] used the pseudotetrahedral complex $Cp(Ph_2PCH(R)CH(R')PPh_2)RuCl$, to investigate the steriochemistry of the vinylidene formation when a number of 1-alkynes was reacted with the ruthenium-chloride to afford $[Cp(Ph_2PCH(R)CH(R')PPh_2)Ru{=}C{=}C(H)(R'')]PF_6$ (R = H; R' = H, Me; R'' = Ph, Me: R = Me; R' = H, Me; R'' = Me, Ph, t-Bu). The vinylidene complexes are readily characterized by an IR ν(C=C) band which occurs in the range of 1590 to 1660 cm^{-1}; the ^{13}C NMR α- and β-carbon resonances are located between δ 320 and 380 ppm, and between 118 and 142 ppm, respectively.[15]

Cyclic carbenes are formed when 1-alkynes with a terminal alcohol function are used. A MeOH solution of $Cp(P)_2RuCl$ (P = PPh_3, PMe_3)[18] with $HC{\equiv}CCR_2CH_2CHR'OH$ or $(\eta^6\text{-}C_6Me_6)RuCl_2(PMe_3)$[19] with $HC{\equiv}C(CH_2)_2OH$ when heated in the presence of NH_4PF_6, gives yellow crystalline complexes 3-5 in high yield (eq 9).



3 $[PF_6]$

R = H, R' = H, Me
R = Me, R' = H

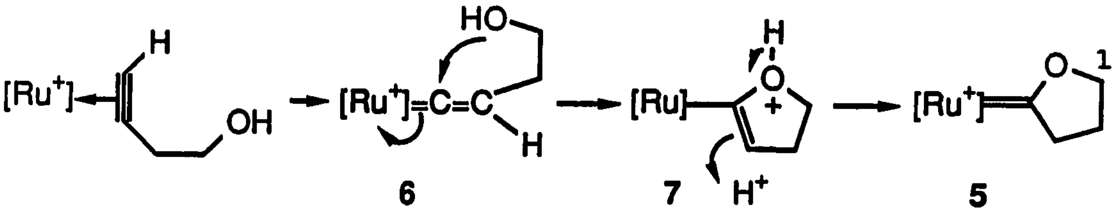


4 $[PF_6]$

5 $[PF_6]$

9

The formation of 3-5 is suggested[19] to proceed via an intermediate vinylidene complex; which, however, is not detected. The proposed mechanism shown for the formation of 5 is a facile intramolecular attack of the hydroxyl group on the vinylidene α-carbon (6); a proton shift in 7 results in the formation of the cyclic carbene ligand as shown in eq 10.



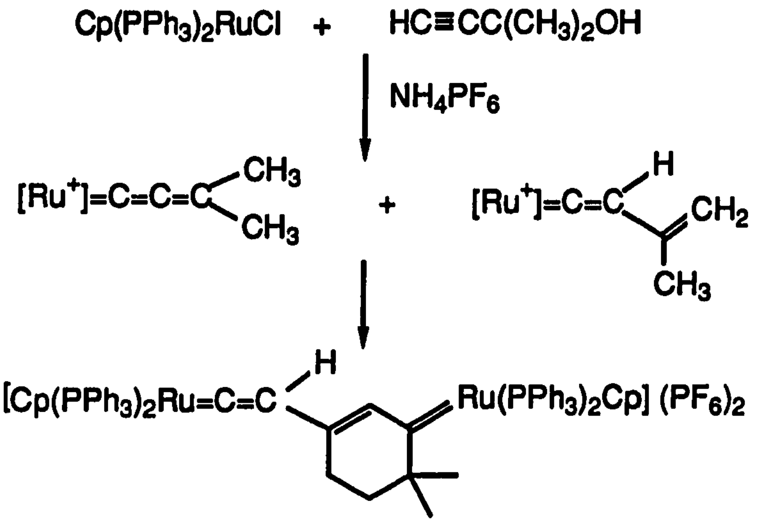
6 7 5

10

A similar reaction of $Cp(PMe_3)_2RuCl$ with $Ph_2C(OH)C\equiv CH$ and NH_4PF_6 in ethanol (25 °C, 27 h) gives in high yield the diphenylallenylidene complex $[Cp(PMe_3)_2Ru{=}C{=}C{=}C(Ph)_2]PF_6$.[20] The structural parameters obtained by an X-ray structure determination support substantial contributions from two different isomeric forms, the cationic charge being stabilized by both the metal and diphenylcarbenium centers (eq 11).

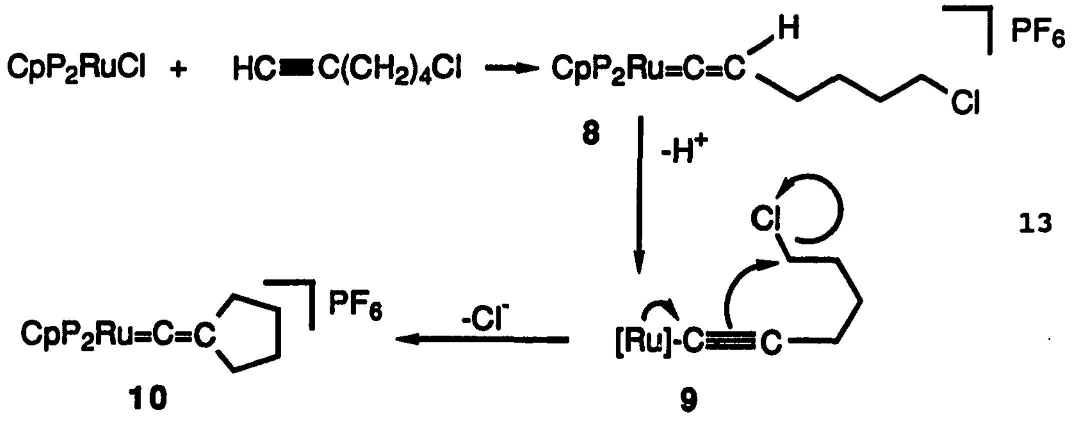
$$Cp(PMe_3)_2\overset{+}{Ru}{=}C{=}C{=}C(Ph)_2 \longleftrightarrow Cp(PMe_3)_2Ru{-}C{\equiv}C{-}\overset{+}{C}(Ph)_2 \qquad 11$$

However, when $Cp(PPh_3)_2RuCl$ is treated with $Me_2C(OH)C\equiv CH$ in methanol in the presence of NH_4PF_6, the reaction took a different course.[15] An X-ray determination revealed that the red-purple crystalline product formed is a result of the dimerization of an allenylidene and a vinylidene complex (eq 12).



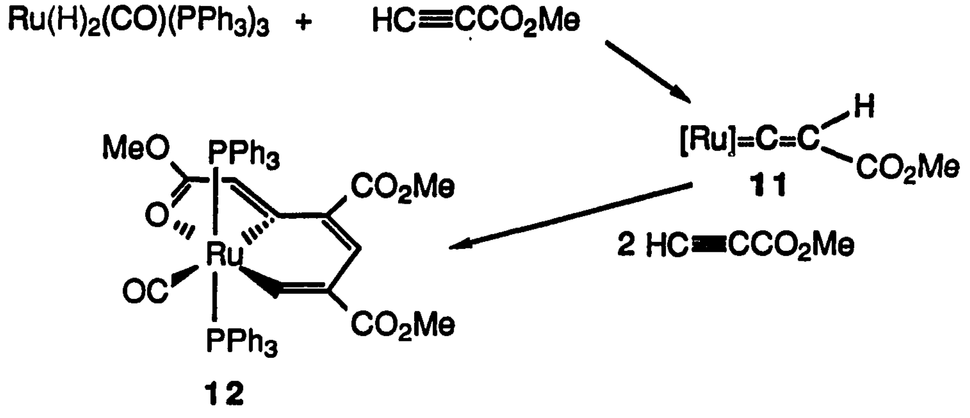
12

The reaction of $Cp(P)_2RuCl$ ($P = PPh_3$; $(P)_2$ = dppe) with $HC\equiv C(CH_2)_4Cl$ in MeOH affords the isolated vinylidene complex 8 (eq 13). Complex 8 is readily deprotonated by Al_2O_3 to give the acetylide complex 9, which slowly cyclizes to give, in this case, a cyclic vinylidene complex 10.[21]



13

In contrast to the above discussion of the formation of vinylidenes from 1-alkynes, multiple addition of 1-alkynes can also occur. The reaction between $Ru(H)_2(CO)(PPh_3)_3$ and $HC\equiv CCO_2Me$ in refluxing benzene, gave the structurally characterized complex 12 in 25% yield (eq 14).[22] The formation was suggested to proceed via a vinylidene intermediate 11 followed by successive addition of two molecules of $HC\equiv CCO_2Me$.



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Sullivan and coworkers[23] reported the reaction of $PhC\equiv CH$ with cis-$Ru(bpy)_2Cl_2$ at 100 °C, which reacts as cis-$[Ru(bpy)_2(H_2O)Cl]^+$ in aqueous solution. The only products isolated in this reaction is the carbonyl complex and toluene shown in eq 15.

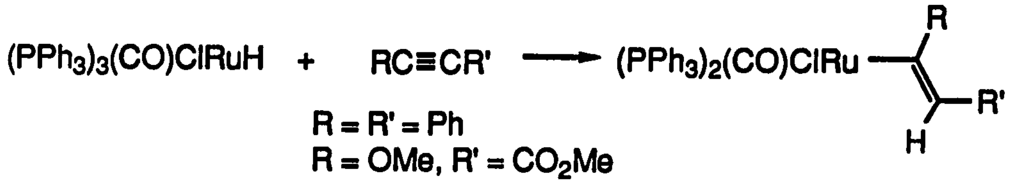
$$\text{cis-[Ru(bpy)}_2\text{(H}_2\text{O)Cl]}^+ + \text{PhC}\equiv\text{CH} \longrightarrow \text{cis-[Ru(bpy)}_2\text{(CO)Cl]}^+ + \text{PhCH}_3 \tag{15}$$

Although there are no studies of the mechanism for the conversion of phenylacetylene to CO and toluene, the authors speculate that the formation occurs via a vinylidene intermediate.

INSERTION REACTIONS

Insertion with Disubstituted Alkynes

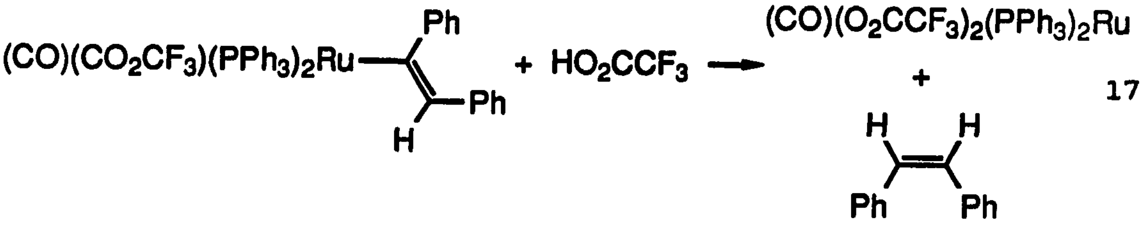
The insertion of disubstituted alkynes into ruthenium-hydride, -alkane, or -chloride bonds are shown to give predominantly cis-vinyl complexes (β-vinyl-substituent cis to the metal center). The disubstituted alkyne $RC\equiv CR'$ readily inserts into a Ru-H bond of $Ru(CO)HCl(PPh_3)_3$ in CH_2Cl_2 to give cis-vinyl ruthenium complexes via the dissociation of PPh_3 (eq 16).[24,25]



16

Similarly, $RuH(NO_3)(CO)(PPh_3)_2$ reacts with $PhC\equiv CPh$ in EtOH to give $Ru[cis\text{-}C(Ph)=C(H)Ph](NO_3)(CO)(PPh_3)_2$;[26] $PhC\equiv CPh$ and $MeC\equiv CPh$ insert into the Ru-H bond of $RuH(O_2CCF_3)(CO)(PPh_3)_2$ to afford the cis-addition vinyl derivatives $Ru[cis\text{-}C(R)=C(H)R'](O_2CCF_3)(CO)(PPh_3)_2$ (R = R' = Ph: R = Me; R' = Ph: R = Ph; R' = Me)[27,28] as yellow crystalline solids in excellent yields. This $MeC\equiv CPh$ insertion gives a 1:1 ratio of cis-vinyl isomers indicating that steric factors of the alkyne substituents are not predominant in this reaction. Dobson and coworkers[28] were able to isolate the identical cis-vinyl products as obtained in the previous reaction with

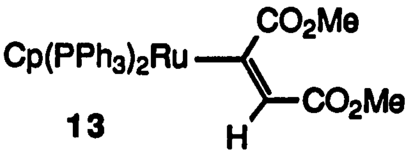
PhC=CR (R = Me, Ph); however, they started with the bistrifluoroacetate complex $Ru(CO)(O_2CCF_3)_2(PPh_3)_2$ in EtOH. The reactive species of this complex is acquired by a facile alcoholysis to afford the corresponding hydride $RuH(CO)(O_2CCF_3)(PPh_3)_2$. The hydride product in turn reacts with PhC=CR in refluxing ethanol in about 30 min to 1 h affording cis-vinylic species. The identification of the cis-vinyl conformation of $Ru(CO)(O_2CCF3)(PPh_3)_2$[cis-C(Ph)=C(H)Ph] (eq 17) was accomplished by the stereospecific cleavage of the metal vinyl linkage with trifluoroacetic acid; this gave the corresponding bistrifluoroacetate complex and cis-stilbene.



17

Holland and coworkers[29] have also shown that trans-$Ru(CO)_2Cl_2(PPhMe_2)_2$ reacts with dma in acetone to give trans-$Ru(CO)_2Cl(PPhMe_2)_2$[cis-$C(CO_2Me)=C(Cl)CO_2Me$].

A number of insertion products are known for $Cp(PPh_3)_2RuR$ (R = H, Me, CH_2Ph) when reacted with dma. The reaction of $Cp(PPh_3)_2RuH$ with dma in Et_2O at room temperature gives only the cis-vinyl complex $Cp(PPh_3)_2Ru$[cis-$C(CO_2Me)=C(H)CO_2Me$] (13) in 90% yield.[30,31] The X-ray determination of 13[30] positively identifies the vinyl proton as being cis to the metal; an earlier report[31] suggested 13 as the trans-vinylic species. A similar reaction of $Cp(PPh_3)_2RuR$ and dma in refluxing benzene (R = H) affords 13-15, or in dimethoxyethane (DME) (R = Me, CH_2Ph) affords 14, 16, and 17; in both reactions a phosphorane adduct 18 was isolated (eq 18).[30,32]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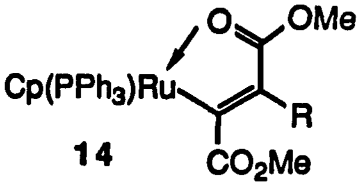
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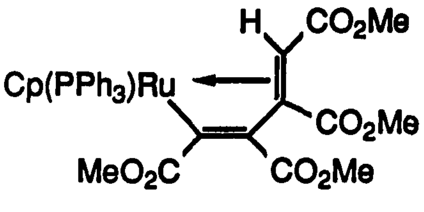
R = H, Me, CH_2Ph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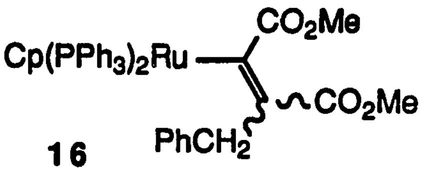
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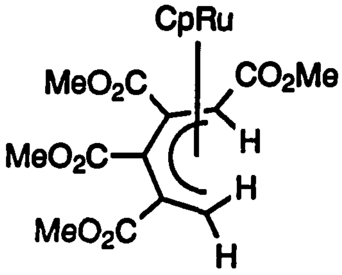
18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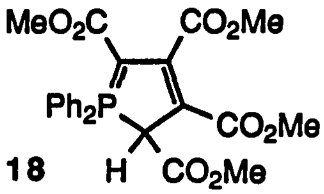
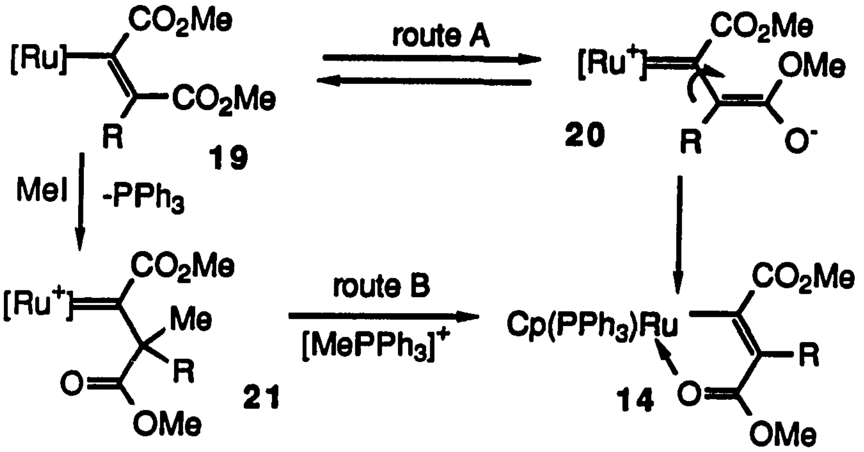
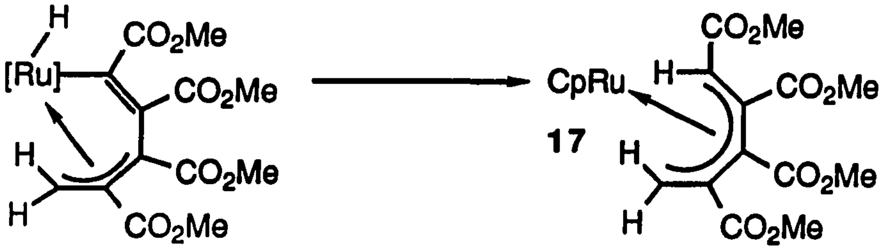

18

The formation of complexes 14, 15, and 17 occur via the loss of a PPh_3 ligand. When diphos complexes Cp(P^P)RuH (P^P = dppm, dppe), are reacted under identical conditions as above only the cis-vinyl adducts, Cp(P^P)Ru[cis-$C(CO_2Me)=C(H)CO_2Me$],[30] are identified. The formation of 14 occurs because the cis adduct **19** is able to convert to the trans isomer **20** due to the partial withdrawal of electron density from the C=C double bond on to the β-ester carbonyl group as shown by route A in eq 19.



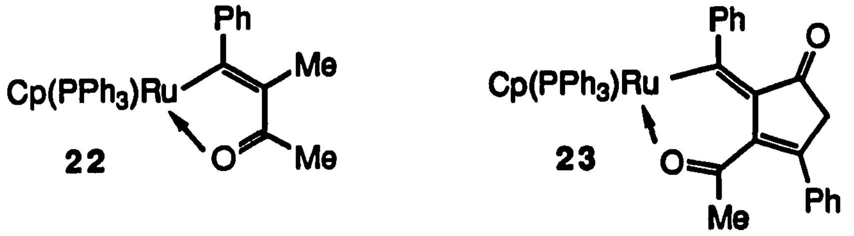
19

The formation of **14** was found to be accelerated by addition of iodomethane to **19** (eq 19). The primary role of the iodomethane is to alkylate the β-carbon, generating a carbene intermediate **21** (route B) which allows rotation and displacement of the PPh_3 to give the observed 5-coordinate metallacycle **14**. The formation of **17** is proposed to be derived from a (η^3-allyl)hydridoruthenium(IV) species as shown in eq 20.[30]



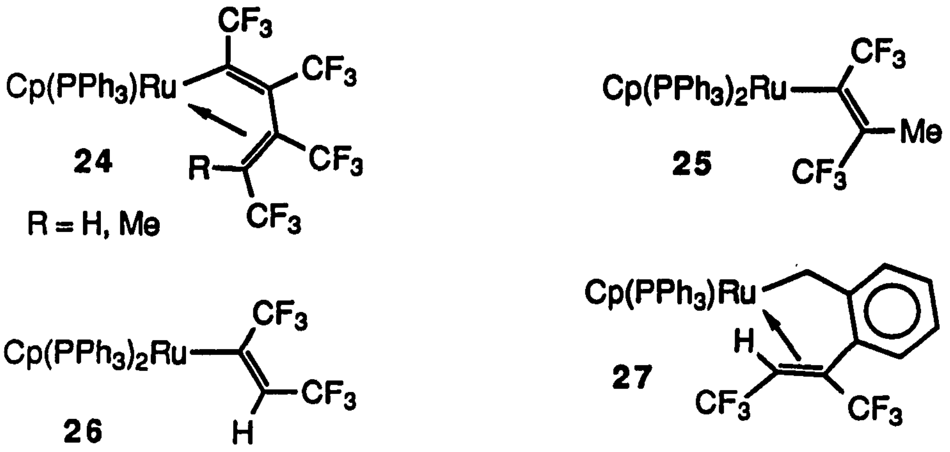
20

A similar reaction in which $Cp(PPh_3)_2RuMe$ and $PhC\equiv CCOMe$ were refluxed in DME for 16 h gave the mono-inserted 5-coordinate metallacycle (22) and a bis addition product (23) (eq 21).[32]



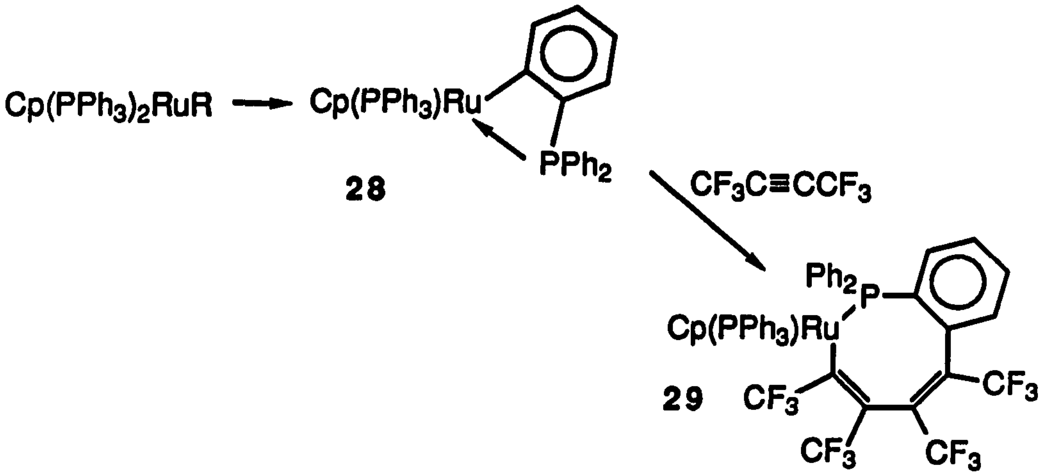
22 23 21

The reaction of hfb ($CF_3C\equiv CCF_3$) with $Cp(PPh_3)_2RuR$ (R = H, Me, CH_2Ph) in Et_2O at room temperature (R = H), or benzene between 50 and 100 °C in a sealed tube (R = Me, CH_2Ph), affords both di- (24) mono-dialkyne (25 - 27) insertion products as air-stable yellow crystalline complexes, and a cyclic phosphorane $Ph_3PC_8F_{12}$ similar to 18 (eq 22).[31,32]



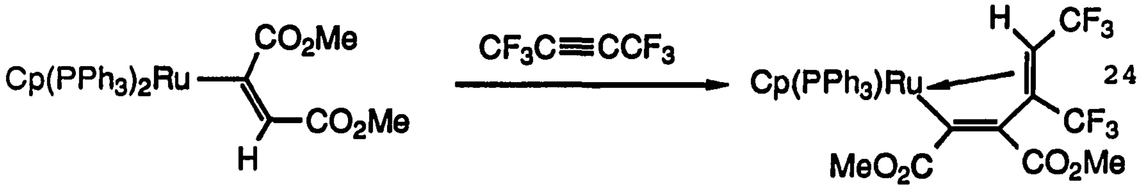
24 R = H, Me 25 22 26 27

The trans-configuration of 25 was based on the lack of any appreciable F-F coupling.[32] The formation of the trans-vinyl adduct 25, rather than the cis-vinyl adduct 26 suggest that the formation of 25 and 26 follow different reaction pathways.[32] Heating $Cp(PPh_3)_2RuR$ (R = Me, CH_2Ph) in decalin first affords the ortho-metallated complex 28 shown in eq 23; this complex in the presence of hfb in DME at 50 °C for 2 d affords a bis-alkyne insertion complex 29 in 12% yield.[33]



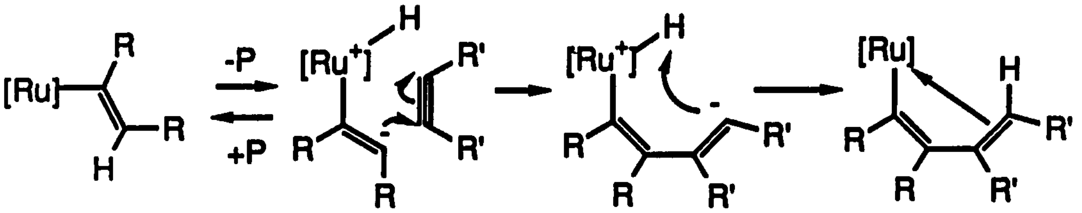
23

A novel reaction was reported by Blackmore and coworkers[34] between the vinylic complex $Cp(PPh_3)_2Ru[cis\text{-}C(CO_2Me){=}C(H)CO_2Me]$ and hfb in Et_2O at room temperature to give the structurally characterized bis-alkyne complex shown in eq 24.[35]



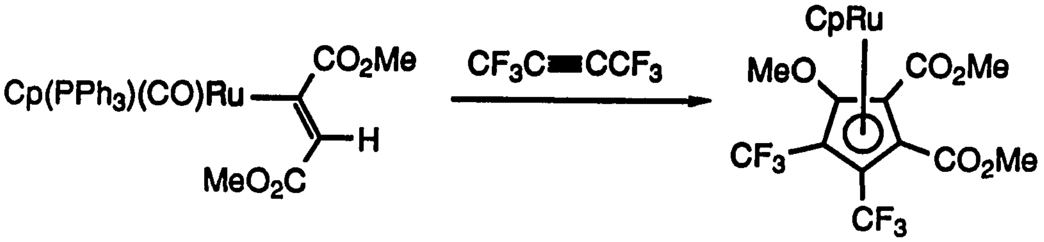
24

The mechanism proposed for the insertion of a second alkyne involves a dipolar intermediate that can attack a second alkyne in a nucleophilic reaction to give a butadienyl complex as shown in eq 25.[31]



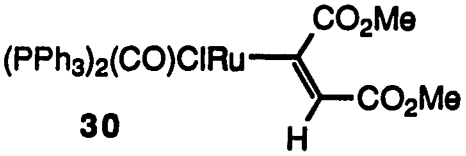
25

If the second alkyne differs from the first, as in the reaction shown in eq 24, the resulting product retains the initial metal-carbon σ-bond; dimerization occurs by the formation of a new carbon-carbon bond. In contrast, the reaction of $Cp(CO)(PPh_3)Ru[C(CO_2Me)=C(H)CO_2Me]$ with hfb in DME at 50 °C for 60 h gave a ruthenocene derivative shown in eq 26.[32]

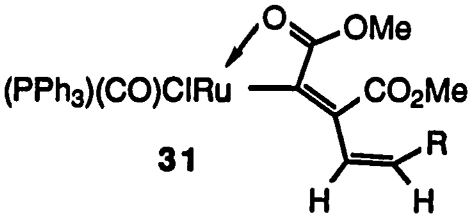


26

Recently it was reported that the alkenyl complexes $Ru(CO)Cl(PPh_3)_2[cis\text{-}C(H)=C(H)R]$ derived from terminal non-activated alkynes react with dma in CH_2Cl_2 to give the mono- (30) and bis-alkyne (31) complexes shown in eq 27.[36]



30



31

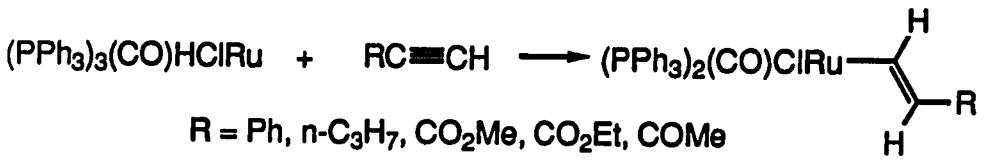
27

R = H, CMe₃, Ph, SiMe₃, n-C₃H₇

Complex 31 can be regarded as being formed by insertion of a dma molecule into the Ru-C bond of the alkenyl complex. The insertion of dma to give 31 seems to be competitive with the simple displacement reaction of the coordinated (non-activated) alkyne (30) by the free activated alkyne (electron withdrawing groups adjacent to the alkyne carbons); products of both reactions are always present. It was also reported that the reaction of dma with $Ru(CO)HCl(Me_2Hpz)(P)_2$ ($P = PPh_3$, $P(p\text{-tolyl})_3$)[37] in refluxing CH_2Cl_2 leads to the elimination of the pyrazole ligand and formation of the 5-coordinate complex similar to 31 where $R = CO_2Me$.

Insertion of Monosubstituted Alkynes

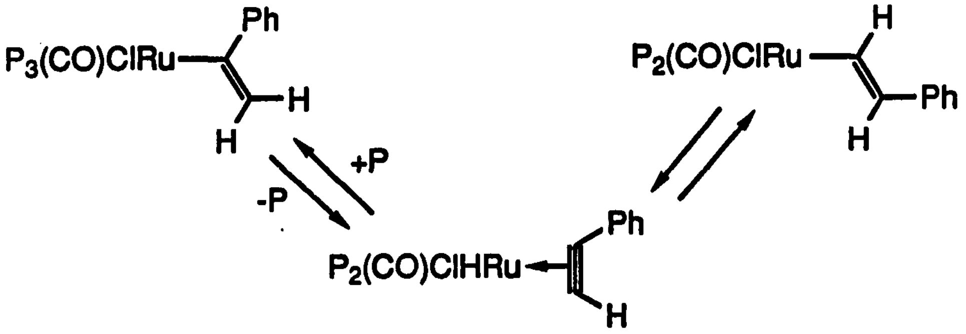
The reactions of 1-alkynes with ruthenium complexes are similar to those of disubstituted alkynes previously discussed; however, in a number of cases the reactivity differs. Like disubstituted alkynes, RC≡CH reacts with $Ru(CO)HCl(PPh_3)_3$ in CH_2Cl_2 to give the red crystalline 5-coordinate cis-vinyl complexes (via loss of PPh_3) shown in eq 28.[24,25]



$R = Ph$, $n\text{-}C_3H_7$, CO_2Me, CO_2Et, $COMe$

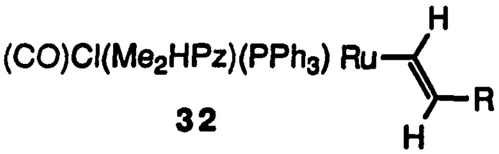
28

However, the reaction between $PhC\equiv CH$ and $Ru(CO)ClH(PPh_3)_3$ in $MeOH/CH_2Cl_2$ (1:1 ratio) affords the yellow crystalline 6-coordinate complex $Ru(CO)Cl(PPh_3)_3[C(Ph)=CH_2]$. In attempts to isolate this yellow 6-coordinate complex, red crystals of a 5-coordinate species are frequently obtained. The conversion from the 5- to 6-coordinate complex is proposed to involve an η^2-alkyne hydrido species as an intermediate (eq 29).[25]



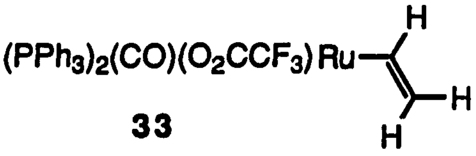
29

Similarly, the complexes $Ru(CO)HCl(Me_2Hpz)(PPh_3)_2$ (Me_2HPz = 3,5-dimethylpyrazole) in CH_2Cl_2,[37] $Ru(CO)HCl(Me_2Hpz)(P(p\text{-}MePh)_3)_2$ in CH_2Cl_2,[38] $Ru(CO)HCl(P\text{-}i\text{-}Pr_3)_2$ in hexanes,[39] and $Ru(O_2CCF_3)_2(CO)(PPh_3)_2$ in EtOH,[28] in the presence of $RC\equiv CH$ afford in all cases simple cis-insertion derivatives (eq 30).



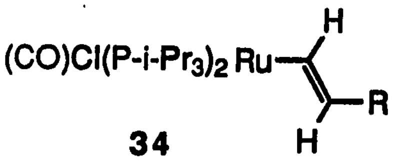
32

R = Ph, CMe_3, n-C_3H_7, CO_2Me



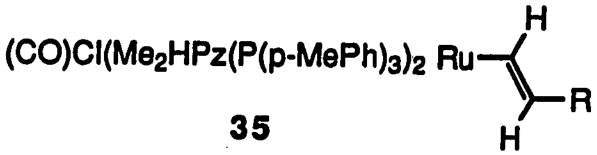
33

30



34

R = H, Ph



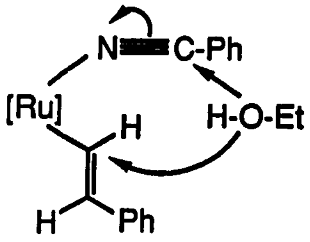
35

R = Ph, n-C_3H_7, CO_2Me

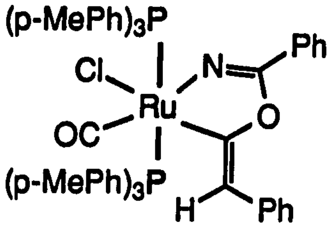
30

The vinyl-ruthenium complexes are primarily identified by a ν(C=C) band in the range of 1507 to 1560 cm^{-1}; the ^1H NMR spectra of the Ru[cis-C(H)=C(H)R] derivatives show two alkenyl proton signals as doublets ranging from J_{HH} = 16 to 22 Hz, which are characteristic of a trans-proton configuration of the alkyenyl group.[24]

A change in the solvent used in several of the reactions to form the products in eq 30 can drastically change the observed products. An EtOH or EtOH/CH_2Cl_2 solution of Ru(CO)HCl(Me_2Hpz)[P(p-MePh)$_3$]$_2$ with PhC≡CH affords the structurally-characterized 5-membered ruthenacycle 37 (eq 31).[38]



36



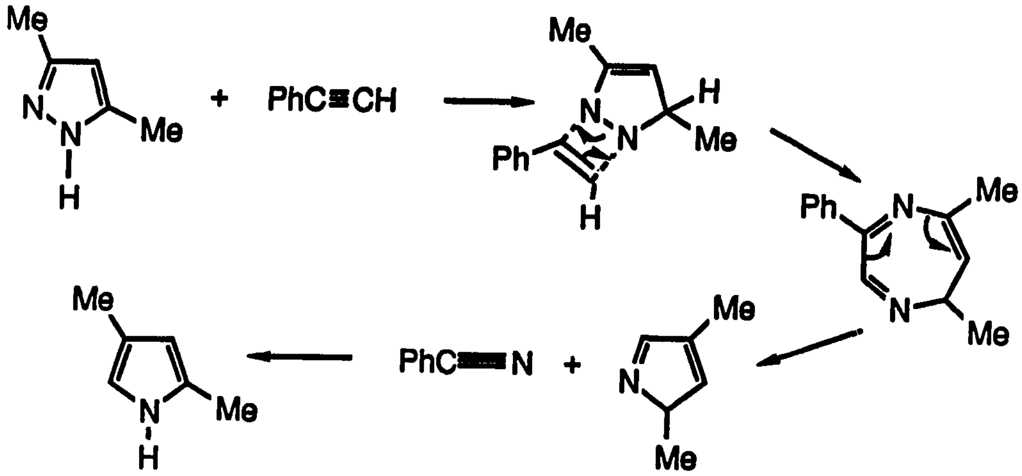
+ EtH

31

37

The mechanism proposed[38] for the formation of the metallacycle 37 shown in eq 32 could involve, in a first step of the reaction, a [2 + 2] attack of phenylacetylene on the N-N bond of the coordinated 3,5-dimethylpyrazole forming

$N\equiv CPh$. The so-formed benzonitrile molecule, a second molecule of phenyl acetylene (inserted previously into the Ru-H bond), and one ethanol molecule (36) could generate the metallacycle as shown in eq 31.

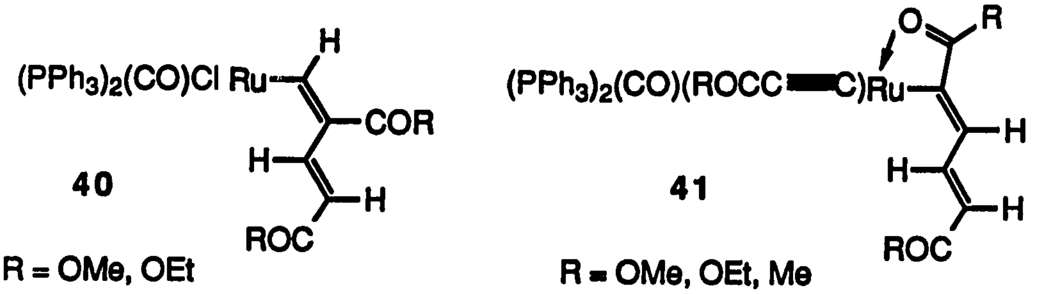


32

The reaction of $Ru(CO)HCl(P\text{-}i\text{-}Pr_3)_2$ with $PhC\equiv CH$ in the presence of stoichiometric amounts of KOH and MeOH affords the complexes $Ru(C\equiv CPh)_2(CO)[P(i\text{-}Pr_3)]_2$ (38) and $Ru(C\equiv CPh)[cis\text{-}C(H)=C(H)Ph](CO)[P(i\text{-}Pr_3)]_2$ (39) in a 1:1 ratio.[39] The mechanism for the formation of 39 is proposed to involve initial insertion of the alkyne into the Ru-H bond followed by displacement of the chloride ligand by the alkynyl anion.

The addition of a second 1-alkyne to ruthenium cis-vinyl complexes results in a number of products. The addition of $HC\equiv CCOR$ to a CH_2Cl_2/MeOH solution of

$Ru(CO)Cl(PPh_3)_2[cis\text{-}C(H)=(H)R]$ afford products 40 and 41 shown in eq 33.[24]



40

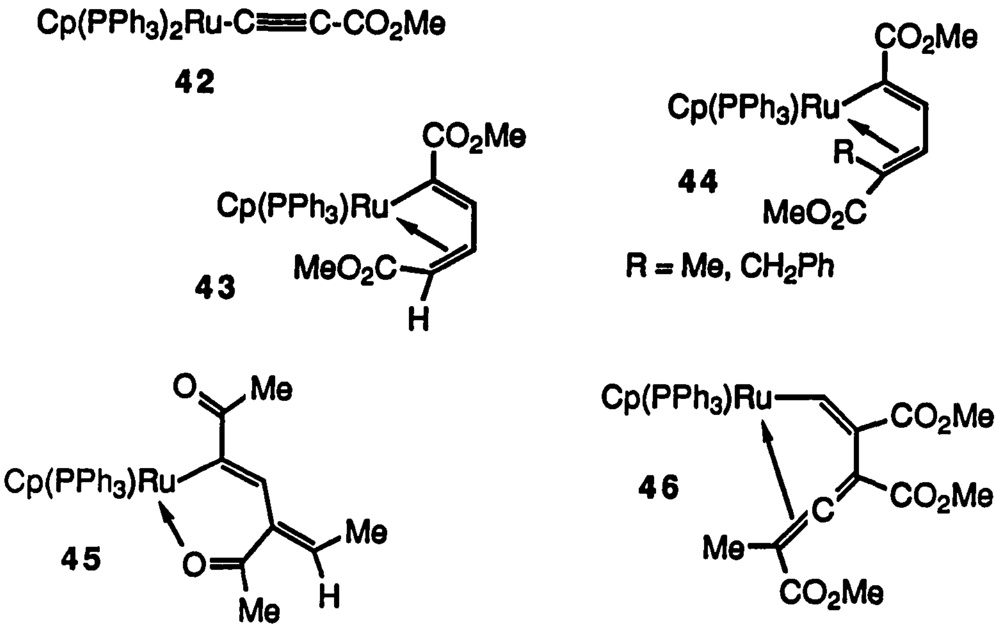
R = OMe, OEt

41

R = OMe, OEt, Me

33

Bruce and coworkers[40] have demonstrated that $Cp(PPh_3)_2RuR$ (R = H, Me, CH_2Ph) reacts with $HC\equiv CR'$ ($R' = CF_3$, CO_2Me) in refluxing DME to give the products shown in eq 34.



42

43

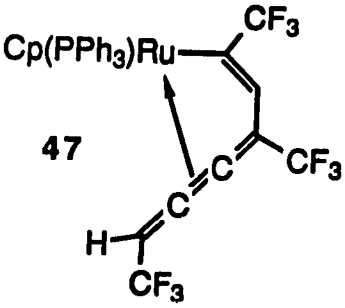
44

R = Me, CH_2Ph

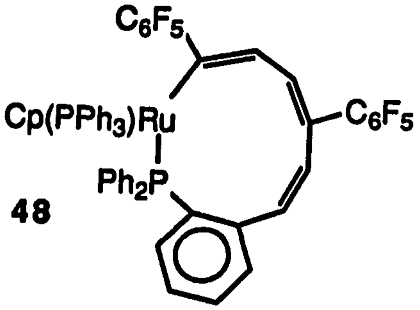
45

46

34



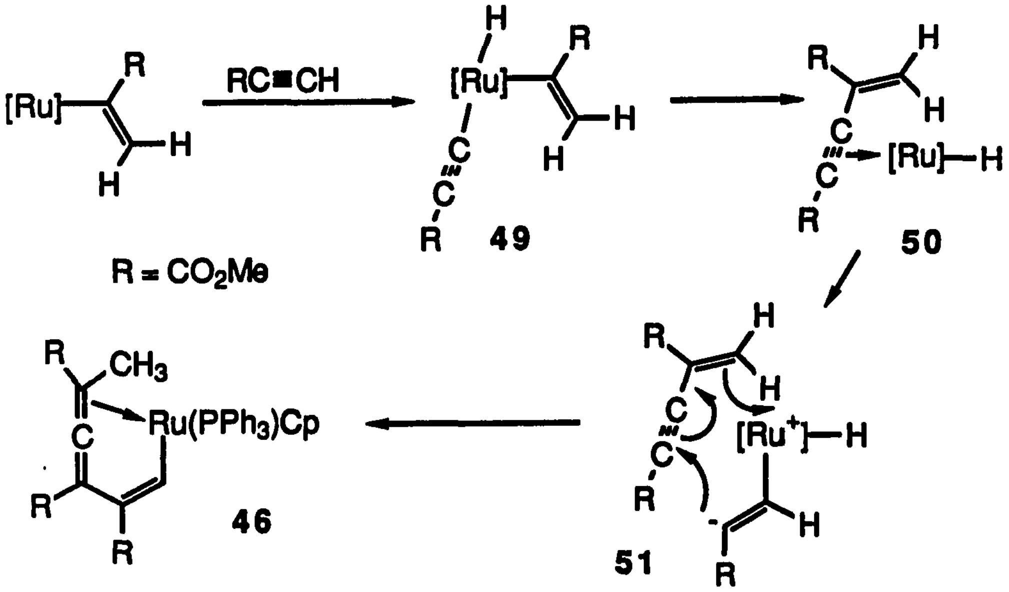
47



48

34

The general mechanism for the formation of 43-46 is considered to involve initial formation of an η^2-alkyne-metal complex. This is followed by insertion of the coordinated alkyne into the metal-hydrogen or metal-carbon bond, or by a combination of the coordinated alkyne in a head to tail (h-t) manner with a second molecule of alkyne, which may or may not be first coordinated. For example, the formation of the tris-adduct 46 containing the η^2-allenyl system, is essentially a t-h, h-t, t-h trimer. The mechanism is proposed to involve oxidative-addition of a second molecule of alkyne to the vinyl derivative (49) as shown in eq 35. This is followed by coupling of the vinyl and acetylide residues to give intermediate 50. The third molecule of alkyne reacts with the vinylalkyne as in 51 to give the observed product 46.

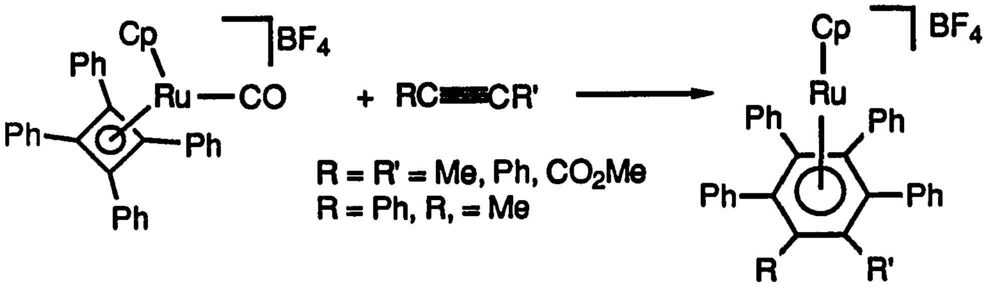

[Ru]
R
H
H
RC≡CH
49
50
51
46
[Ru]—H
[Ru+]—H
Ru(PPh3)Cp
CH3
R = CO2Me

CYCLOOLIGOMER FORMATION

Formation of Aromatic Complexes

Early on in the development of organometallic chemistry the idea was proposed[41] that η^4-cyclobutadiene complexes act as relay points on the path from alkynes to arenes; however, this was not supported by a study[42] of the cyclotrimerization of $CD_3C{\equiv}CCH_3$ by a variety of transition metal catalysts which suggested that η^6-arene complexes are formed through metallacyclic intermediates. However, the observations summarized in eq 36 refocused attention on reactive cyclobutadiene complexes as possible precursors to arenes.

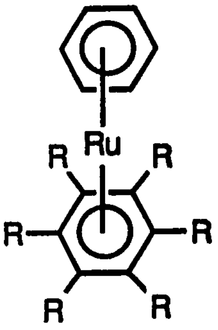
Irradiation (hν) of CH_2Cl_2 solutions of $[CpRu(CO)(\eta^4\text{-}C_4Ph_4)]BF_4$ and disubstituted alkynes lead to the formation of a number of air-stable ruthenium arene cations in high yield (eq 36).[43,44]



36

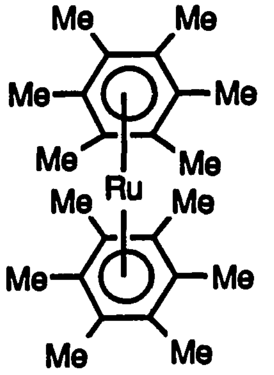
The reaction of $[Cp(CO)_2Ru(\eta^2\text{-}PhC{\equiv}CPh)]BF_4$ with $PhC{\equiv}CPh$ does not react thermally; however, irradiation for 52 h in CH_2Cl_2 solution leads to the hexaphenyl arene $[CpRu(\eta^6\text{-}C_6Ph_6)]BF_4$

in low yield (12%).[43] Similarly, treatment of $(\eta^6\text{-}C_6H_6)(\eta^4\text{-}C_6H_8)Ru$ with an excess of $RC\equiv CR$ in n-hexane at 40 °C for 1-2 days under $h\nu$ irradiation gives the bis-arene ruthenium(0) complexes 52 and 53 in 20-50% yield (eq 37).[45]



52

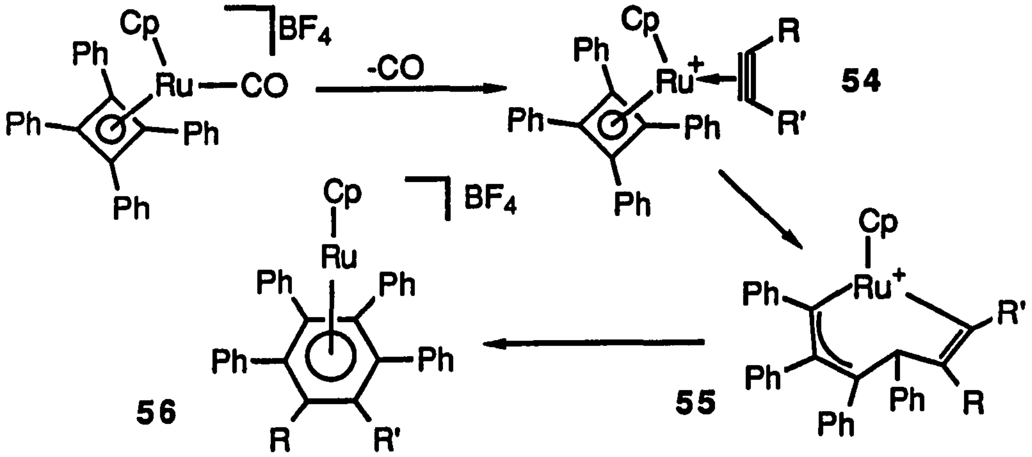
R = Ph, CO_2Me



53

37

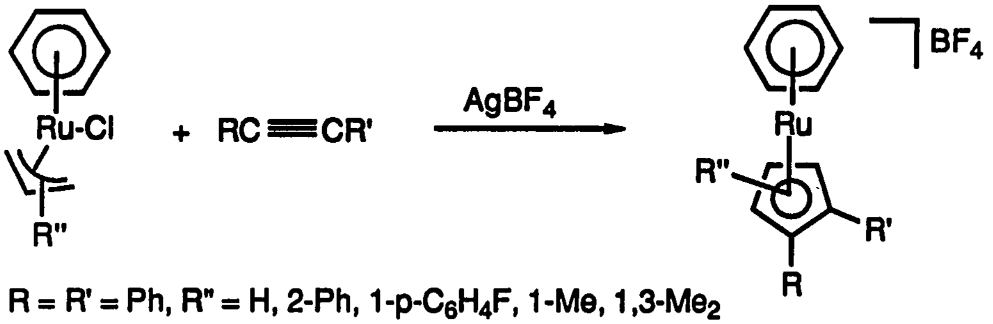
Crocker and coworkers[44] suggested that a plausible reaction pathway for the formation of the ruthenium arene cations initially involves coordination of an alkyne to the cyclobutadiene complex with the loss of a CO (54, eq 38). This is followed by C-C and Ru-C bond formation to give the intermediate 55, which undergoes reductive C-C coupling to form the arene complex 56 as shown in eq 38.



38

Insight into this $C_4 + C_2 \rightarrow C_6$ ring expansion reaction is obtained from the reaction of [CpClRu(η^4-C_4Ph_4)]BF_4 with $AgBF_4$ and PhC≡CPh in CH_2Cl_2 to give [CpRu(η^6-C_6Ph_6)]BF_4 in 76% yield.[43] This reaction futher supports the proposal that the coordinatively unsaturated cation [CpRu(η^4-C_4Ph_4)]BF_4 is first generated; this intermediate then captures a molecule of PhC≡CPh as in the sequence shown in eq 38. There are a number of possible pathways from the adduct 54 to the arene cation 56 which cannot be distinguished with the evidence presently available.

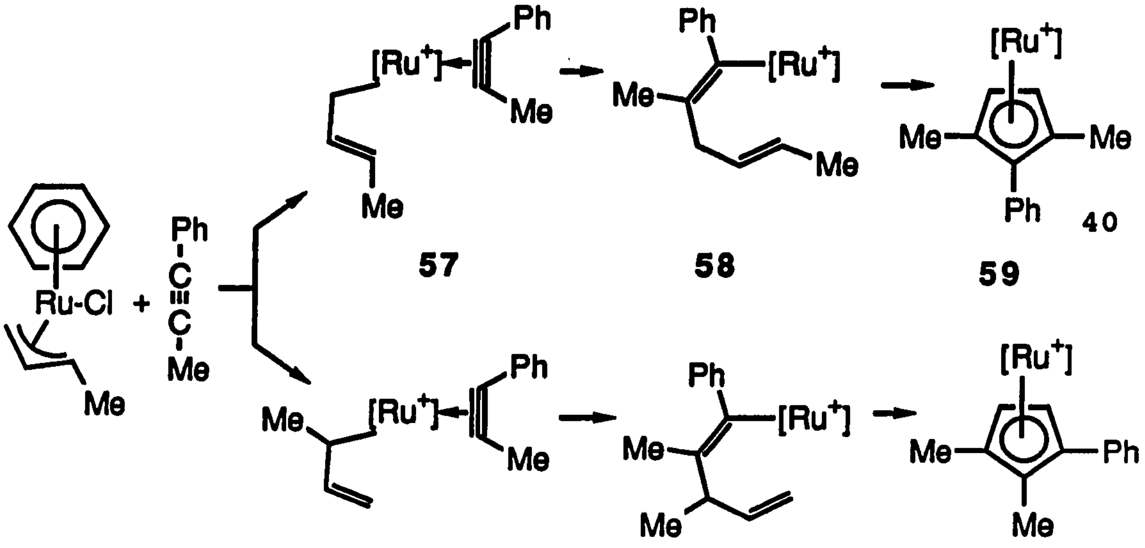
Treatment of an acetone solution of (η^3-C_3H_5R)Ru(η^6-C_6H_6)Cl with $AgBF_4$, followed by addition of disubstituted alkynes RC≡CR′ gave stable pale yellow, crystalline cyclopentadienyl products in high yields (eq 39).[46]



39

R = R' = Ph, R" = H, 2-Ph, 1-p-C_6H_4F, 1-Me, 1,3-Me_2
R" = H, R = Ph, R' = Me, Et
R" = H, R = Et, R' = n-C_3H_7

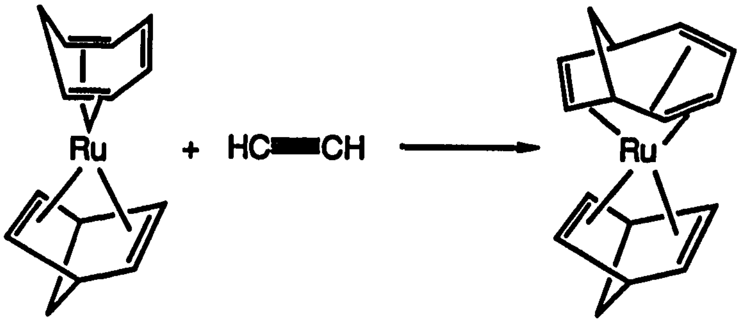
The proposed formation of the η^5-cyclopentadienyl ligand from the η^3-allyl ligand and an alkyne is shown in eq 40. The initial η^3-allyl cation is a 16-electron coordinately unsaturated species; the reaction is suggested to proceed by π-coordination of the alkyne with the transition metal atom (57).



57 58 59 40

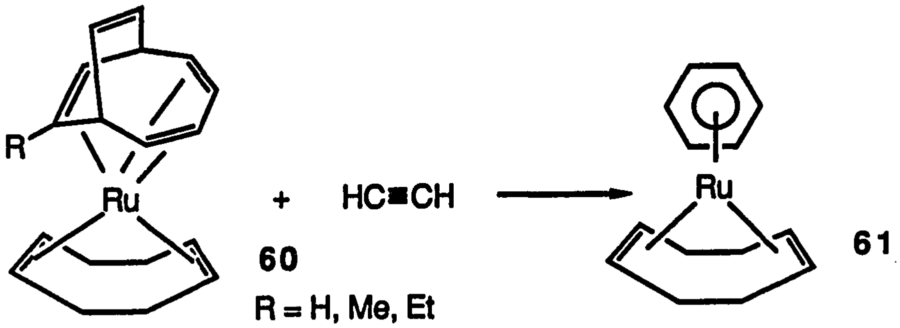
This is followed by insertion of the alkyne into the metal-allyl bond (58). It is conceivable that prior to the intramolecular alkyne insertion, rearrangement of the η^3-allyl ligand into a σ-allylic transient species occurs as a result of the increased electron density at the metal atom caused by coordination of the donor alkyne. The resulting η^5-cyclopentadienyl complexes 59 is then formed via the loss of two hydrogen atoms; the mechanism is presently unknown.[46]

The ruthenium(0) complex, (η^6-cycloheptatriene)(η^4-norbornadiene)ruthenium, reacts with $HC\equiv CH$ in a CH_2Cl_2 solution at 0 °C in 1-1.5 h, to afford orange crystals of a η^6-coordinated bicyclo[4.2.1]nona-2,4,7-triene complex (eq 41).[47]



41

A similar synthesis of the bicyclo[4.2.2]decatetraene ligand occurs via a formal [π6s + π2s] cycloaddition of $HC\equiv CR$ to $(1\text{-}6\text{-}\eta\text{-}C_8H_{10})(1,5\text{-}\eta\text{-}C_8H_{12})Ru$ in CH_2Cl_2; in the 1 h reaction at 0 °C, orange crystals of **60** were obtained in over 95% yield (eq 42).[48]



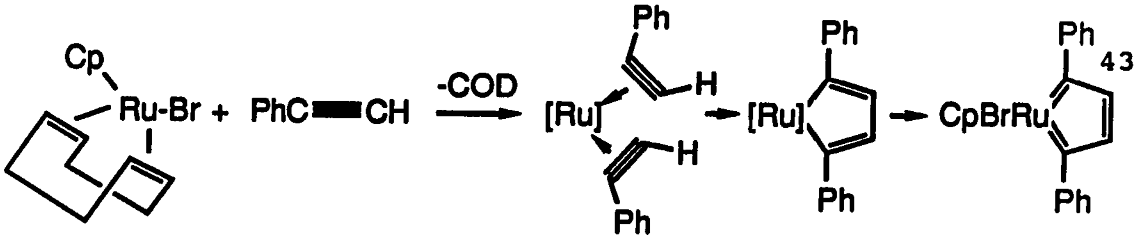
42

Liberation of the bicyclodecatetraene ligand of **60** is observed by further reaction of **60** with $HC\equiv CH$ in CH_2Cl_2 to give **61**; this displacement occurs at room temperature.[48] The η^6-arene derivative **61** was isolated in 42% yield.

Formation of Metallacyclic Complexes

Insertion of two alkynes into a mononuclear ruthenium complex can also give metallacyclopentadiene complexes, these complexes may further add more alkynes to give metallacyclic complexes. Factors determining the reaction paths are not clear presently.[49]

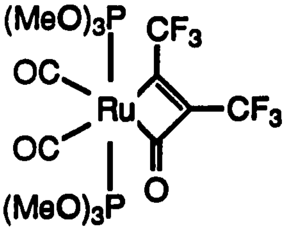
The complex $CpRu(\eta^4\text{-}COD)Br$ (COD = 1,5-cyclooctadiene) reacts with $PhC\equiv CH$ in CH_2Cl_2 at 0 °C to afford dark green crystals of the metallacyclopentadiene 63 in approximately 65% yield (eq 43).[50]



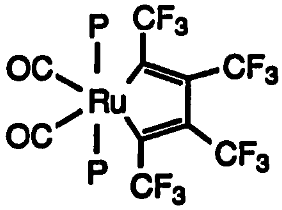
62 **63**

The cyclodimerization of two molecules of $PhC\equiv CH$ together with concomitant oxidative addition to the metal atom is suggested to form initially a coordinatively unsaturated 16-electron ruthenium(IV)-metallacyclopentadiene complex 62. Conversion of 62 into the formal 18-electron ruthenium(II) complex 63 is by a redistribution of a pair of ruthenium-based electrons which would give the metallacyclopentatriene 63 (eq 43).

The irradiation ($h\nu$) of a hexane solution of trans-$(CO)_3Ru(P)_2$ (P = $P(OMe)_3$, PMe_2Ph) and one mole equivalent of hfb gives yellow crystalline cyclobutadienone complex 64 (eq 44).[51] However, the above complex in the presence of excess hfb under identical reaction conditions, the cyclopentadiene complexes 65-67 are also isolated.

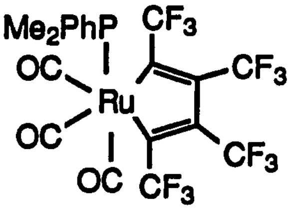


64



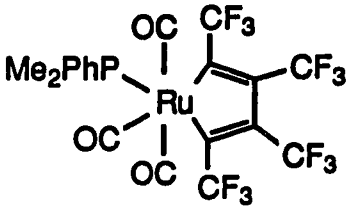
65

P = P(OMe)$_3$, PMe$_2$Ph

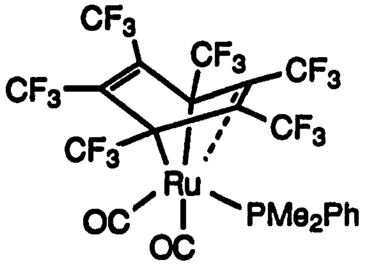


66

44



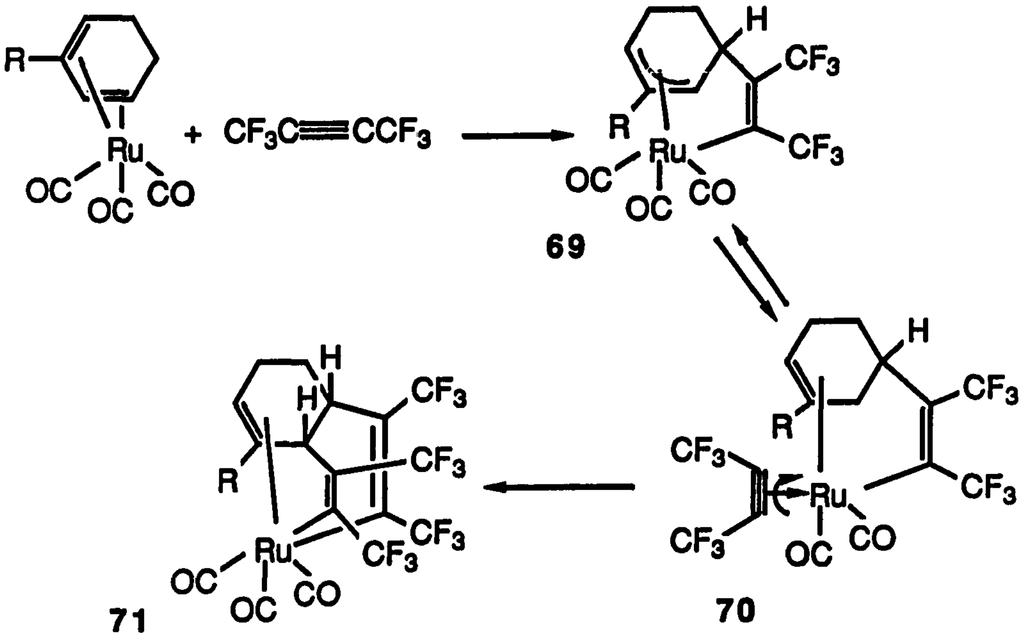
67



68

When the reaction mixture which produces 66 and 67 is irradiated for longer periods, or if 65 (P = PMe$_2$Ph) is irradiated in the presence of hfb, then a subsequent reaction occurred affording the white crystalline complex 68.[51]

Finally, Bottrill and coworkers[52] found that irradiation (hν) of (CO)$_3$Ru(η^4-2-RC$_6$H$_7$) (R = H, Me) with hfb gave colorless crystalline complex 71 shown in eq 45.



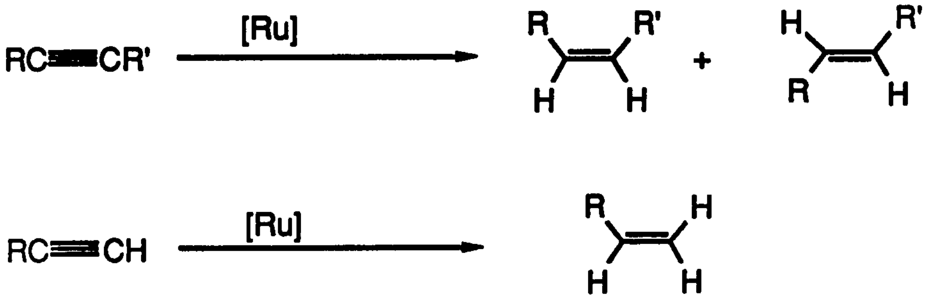
45

The formation of 71 is proposed to involve the formal addition of two hfb molecules to one olefinic double bond, which is incorporated into a ruthenacyclohepta-2,6-diene ring 69. The second hfb molecule, after initial addition to the metal center 70, inserts into a σ-allyl bond to form the observed product 71.

CATALYTIC REACTIONS

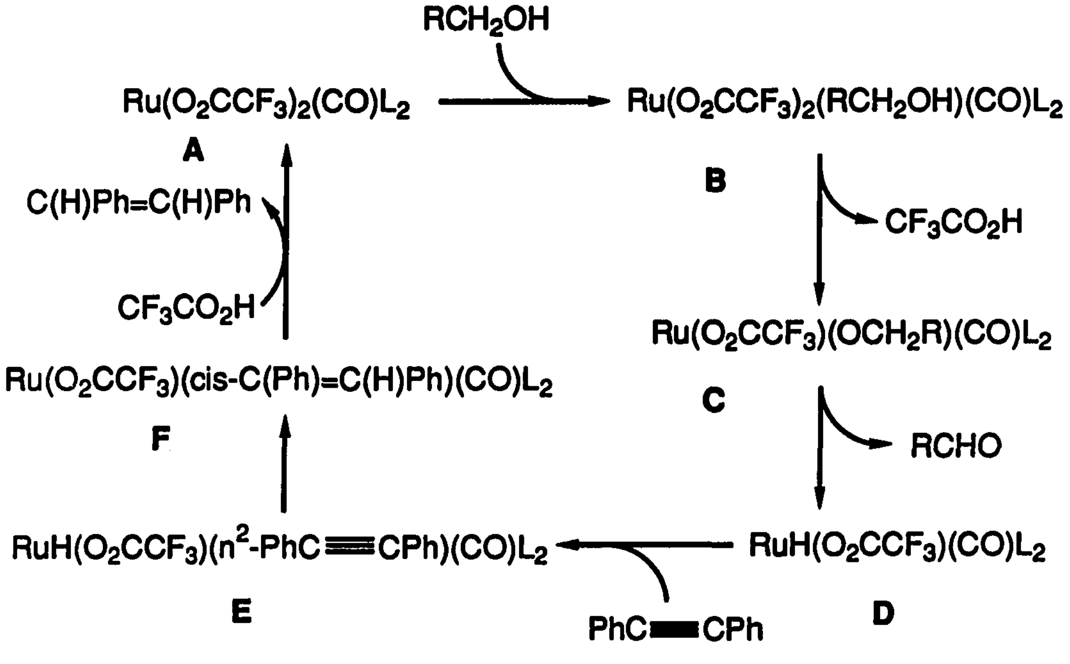
Hydrogenation Reactions

Catalytic hydrogenation of organic substrates by soluble transition-metal complexes is a widely studied class of organometallic reactions.[49] The hydrogenation of a variety of internal and terminal alkynes have been shown to give olefin compounds in the presence of a ruthenium catalysts such as $[Ru(dppb)_2]PF_6$,[53] $[RuH(COD)(PMe_2Ph)]PF_6$,[54] $RuCl_2[PhP(CH_2CH_2PPh_2)_2]$,[55] $[RuH(P)_5]PF_6$ (P = PMe_2Ph, $PPh(OMe)_2$, $PMe_2(2\text{-}C_6H_4OMe)$, $AsMe_3$),[56] and $RuHCl(PPh_3)_3$[57] (eq 46).



46

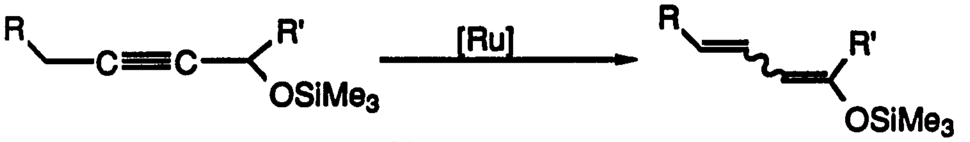
Dobson and coworkers[28] studied the mechanism of the catalytic hydrogenation of PhC≡CPh in a BuOH solution as catalyzed by $Ru(O_2CCF_3)_2(CO)(PPh_3)_2$ to afford C(Ph)H=C(Ph)H. The proposed mechanism as shown in Scheme I involves initial alcoholysis of the precatalyst $Ru(O_2CCF_3)_2(CO)(PPh_3)_2$ with BuOH to give the hydride catalyst $RuH(O_2CCF_3)(CO)(PPh_3)_2$. This step is proposed to occur via initial alcohol coordination to the metal center (B); then, the coordinated alcohol loses a proton to form an alkoxide ligand (C) which subsequently undergoes β-elimination to generate a molecule of aldehyde (or ketone) forming the catalyst $RuH(O_2CCF_3)(CO)(PPh_3)_2$ (D). The cycle is completed by coordination of $PhC\equiv CPh$ (E), migration of the hydride ligand onto the coordinated $PhC\equiv CPh$ (F), and finally acidolysis of the ruthenium-vinyl linkage to liberate trans-stilbene and regenerate $Ru(O_2CCF_3)_2(CO)(PPh_3)_2$.



Scheme I

Catalytic Additions to Alkynes

The catalyst $RuHCl(PPh_3)_3$ in benzene readily converts acetylenic silyl ethers to dienol silyl ethers as shown in eq 47.[58]



47

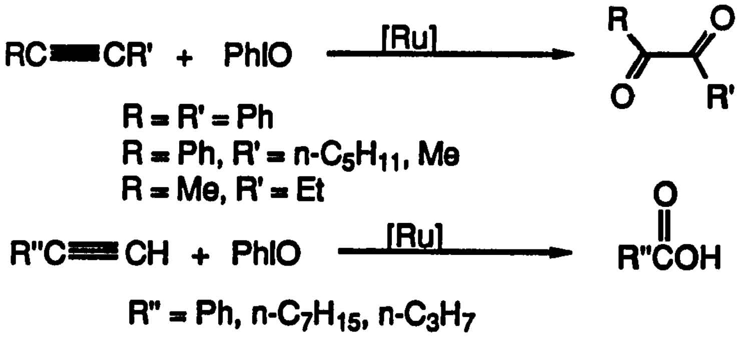
R = $OSiMe_3$, R' = H
R = OMe, R' = Me, Et
R = n-Pr, R' = H, Me
R = n-Pent, R' = Me

Similarly, $RuCl_2(PPh_3)_3$ catalyzes the reaction of acetylene with trisubstituted silanes to give vinylsilane compounds (eq 48).[59]

$$HSiRR'_2 + HC\equiv CH \xrightarrow{[Ru]} CH_2{=}CHSiRR'_2 + (R'_2RSiCH_2\text{-})_2 \qquad 48$$

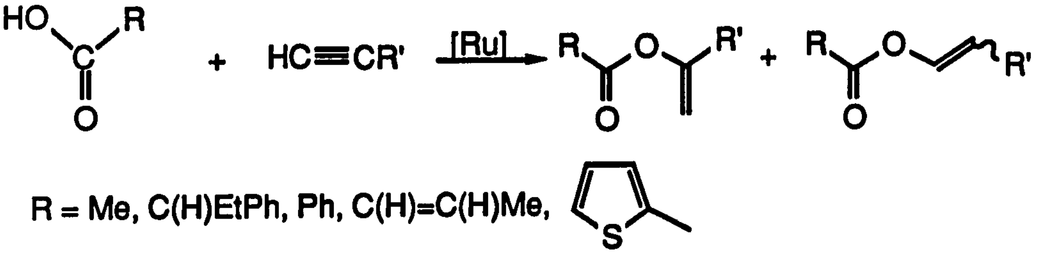
R = R' = Cl, OEt
R = Me, R' = OEt, Cl
R = Cy, R' = Cl

The compounds $RuCl_2(PPh_3)_3$, $RuCl_2(CO)_2(PPh_3)_2$, $RuCl_3$, and ruthenocene catalyze the reactions of disubstituted- or 1-alkynes and iodosobenzene to give diketone and carboxylic acid compounds, respectively (eq 49).[60]



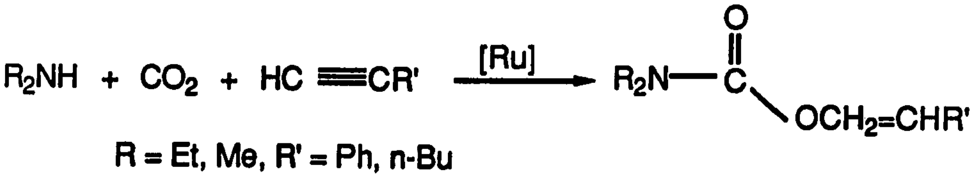
49

Enol carboxylates are formed by the catalytic coupling of carboxylic acids and terminal alkynes in the presence of $RuCl_3 \cdot 3H_2O$,[61] $RuCl_2(PMe_3)$(p-cymene),[61] and bis-(η^5-cyclooctadienyl)$RuPR_3''$ (R'' = n-Bu, Ph)[62] (eq 50).



50

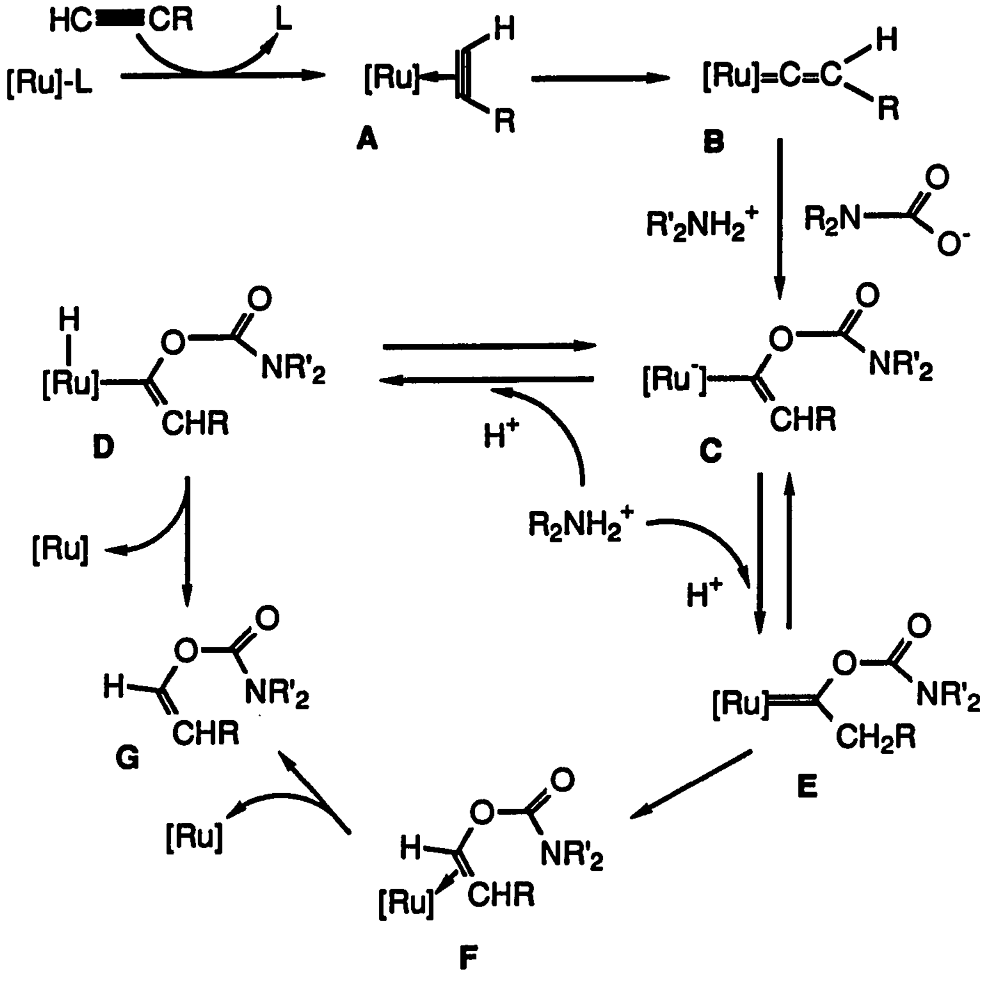
The synthesis of vinyl carbamate derivatives from terminal alkynes, secondary amines, and CO_2 in the presence of catalytic amounts of $RuCl_3 \cdot H_2O$, $RuCl_2$(NBD),[63] $RuCl_2(CH_3CN)$(p-cymene), $RuCl_2(py)_2$(NBD), $RuCl_2(PMe_3)(\eta^6$-$C_6Me_6)$,[64] bis(η^5-cyclooctadienyl)Ru, and (COD)(COT)Ru,[65] affords a variety of vinyl carbamates (eq 51).



$$R_2NH + CO_2 + HC{\equiv}CR' \xrightarrow{[Ru]} R_2N{-}\overset{O}{\overset{\|}{C}}{-}OCH_2{=}CHR' \qquad 51$$

R = Et, Me, R' = Ph, n-Bu

The formation of vinyl carbamates, shown in Scheme II, is proposed to be by initial complexation of the terminal alkyne to the ruthenium metal center in a η^2-alkyne fashion (A) followed by rearrangement to a ruthenium-vinylidene complex (B). The carbamate adds to the vinylidene intermediate to form C. Protonation of the metal by ammonium cation, followed by reductive elimination from D, is expected to lead to the observed enol carbamates.



Scheme II

An alternative route may involve the protonation of species C at the basic β-carbon atom followed by a 1,2-hydrogen shift in E, giving F, which on elimination affords the enol carbamate product.

CONCLUDING COMMENTS

It is apparent from the preceding discussion that alkynes can react with single ruthenium metal centers to give a variety of different complexes. What is surprising is the lack of information known about the reactivity of alkynes with metal centers when heteroatoms are adjacent to the unsaturated carbons. The research contained in this thesis develops the novel reactivity of the thioalkyne, $MeSC\equiv CSMe$, with ruthenium and tungsten complexes.

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SECTION II. VINYLIDENE, ACETYLIDE, AND CARBENE COMPLEXES FROM REACTIONS OF 2,5-DITHIAHEX-3-YNE ($MeSC{\equiv}CSMe$) WITH $Cp(PMe_3)_2Ru^+$

ABSTRACT

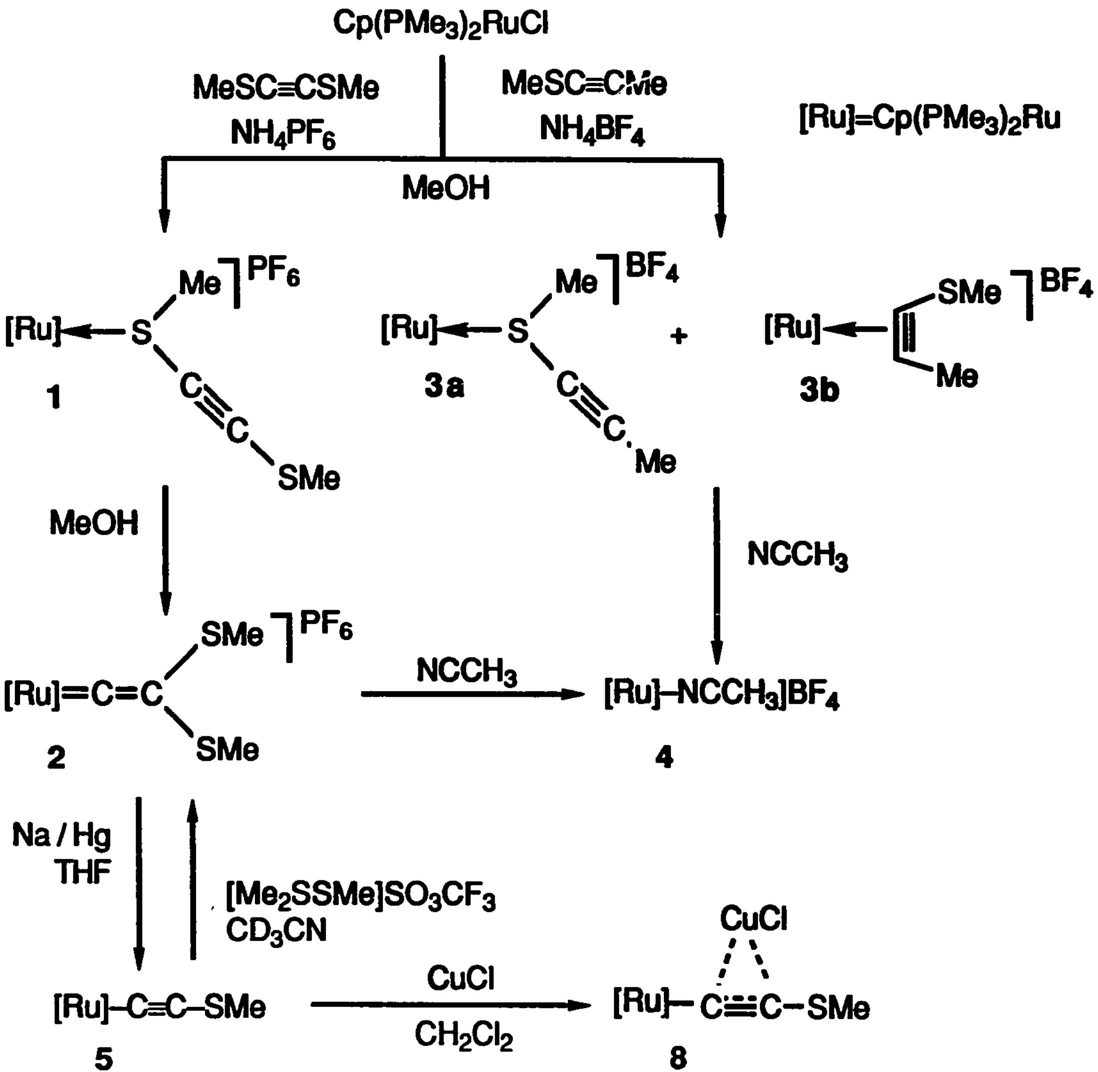
The alkyne, $MeSC\equiv CSMe$, initially displaces Cl^- in $Cp(PMe_3)_2RuCl$ at room temperature in MeOH to form a sulfur-bound alkyne complex $\{Cp(PMe_3)_2Ru[S(Me)C\equiv CSMe]\}PF_6$ (1). Upon warming, 1 rearranges to the vinylidene complex $[Cp(PMe_3)_2Ru=C=C(SMe)_2]PF_6$ (2). Complex 2 is reduced by $Na[HBEt_3]$ or Na/Hg to give the thioacetylide, $Cp(PMe_3)_2Ru-C\equiv C-SMe$ (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 $Cp(PMe_3)_2Ru(CuCl)(C\equiv C-SMe)$ (8) in which the copper is π-bound through the $C\equiv C$ group. Reaction of 6 with methanol and ethanol yields the methoxycarbene 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). Further addition of $[Me_3O]BF_4$ to complexes 6 and 7 yields the first examples of sulfonium vinylidene 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, β = 114.80 (1)°, and Z = 4. Complexes 7 and 10 undergo one and two-electron reductions, respectively, to

give the acetylide $Cp(PMe_3)_2Ru-C\equiv C-Me$ (14) and MeSSMe (for 7) or SMe_2 (for 10). Complexes 6 and 9 are readily deprotonated to give 5 and the sulfonium acetylide $[Cp(PMe_3)_2Ru-C\equiv C-SMe_2]BF_4$ (13), respectively. Mechanisms of the reactions and structural features of the vinylidenes are discussed.

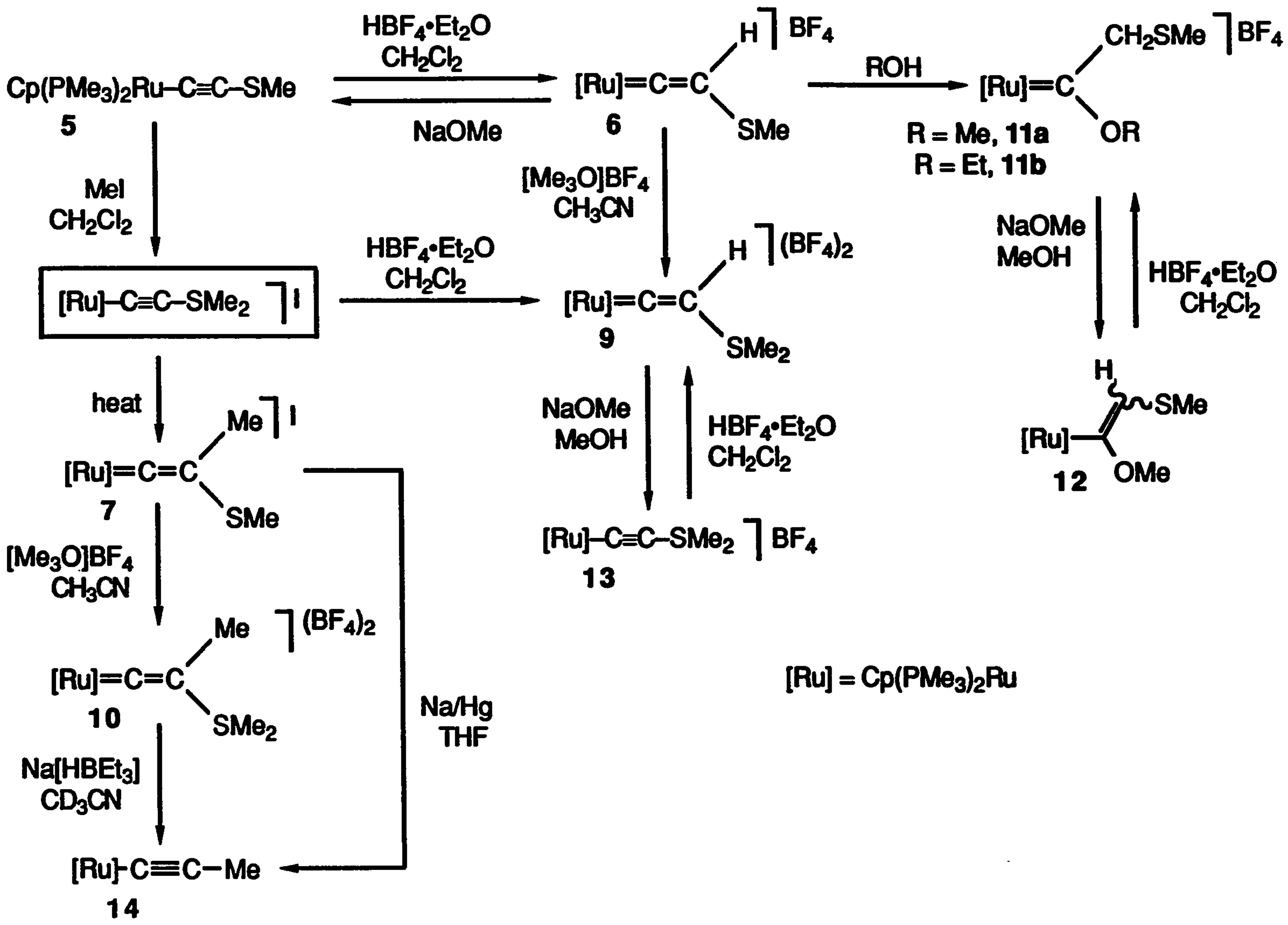
INTRODUCTION

There has been considerable experimental and theoretical interest in reactions between transition-metal centers and alkynes.[1] 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;[2-10] 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 complexes resulting from metallocyclization 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 the acetylene could alter this reactivity. I thus set out to explore the effect of mercapto groups on the chemistry of mononuclear complexes of $MeSC\equiv CSMe$. There are only two previous reports[44] on the chemistry of mononuclear complexes of $MeSC\equiv CSMe$: $CpM(MeSC\equiv CSMe)_2Cl$, $M(CO)(MeSC\equiv CSMe)_3$ (M = Mo, W), $CpMoCl(CO)(C_9H_{12}OS_4)$, $M(CO)_3(C_9H_{12}OS_4)$ (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, I examine the synthesis and reactions of a series of vinylidene, acetylide, and carbene complexes derived from reactions of $MeSC{\equiv}CSMe$ with the $Cp(PMe_3)_2Ru^+$ group.


Cp(PMe3)2RuCl
MeSC≡CSMe
NH4PF6
MeSC≡CMe
NH4BF4
MeOH
[Ru]=Cp(PMe3)2Ru
[Ru]
Me
PF6
S
C
SMe
1
3a
BF4
3b
+
MeOH
NCCH3
SMe
[Ru]=C=C
2
[Ru]-NCCH3]BF4
4
Na / Hg
THF
[Me2SSMe]SO3CF3
CD3CN
[Ru]-C≡C-SMe
5
CuCl
CH2Cl2
[Ru]-C≡C-SMe
8

Scheme I


HBF4•Et2O
CH2Cl2
NaOMe
Cp(PMe3)2Ru–C≡C–SMe
5
[Ru]=C=C
H
SMe
BF4
6
ROH
[Ru]=C
CH2SMe
OR
BF4
R = Me, 11a
R = Et, 11b
MeI
CH2Cl2
[Me3O]BF4
CH3CN
[Ru]–C≡C–SMe2
I
HBF4•Et2O
CH2Cl2
[Ru]=C=C
H
SMe2
(BF4)2
9
NaOMe
MeOH
HBF4•Et2O
CH2Cl2
[Ru]–C≡C–SMe2
BF4
13
NaOMe
MeOH
HBF4•Et2O
CH2Cl2
H
SMe
[Ru]
OMe
12
heat
[Ru]=C=C
Me
SMe
I
7
[Me3O]BF4
CH3CN
[Ru]=C=C
Me
SMe2
(BF4)2
10
Na[HBEt3]
CD3CN
Na/Hg
THF
[Ru]–C≡C–Me
14
[Ru] = Cp(PMe3)2Ru

Scheme II

EXPERIMENTAL SECTION

General Procedures

All reactions, filtrations, distillations, and recrystallizations were carried out under N_2 using standard inert atmosphere and Schlenk techniques.[45] Methylene chloride, hexanes, 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. ^1H NMR spectra (Table I) were obtained with a Nicolet NT-300 (300 MHz) spectrometer, using Me_4Si (TMS) as the internal reference. Proton-decoupled ^{13}C NMR spectra (Table II) were recorded on the 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 using 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 $(\eta^5\text{-}C_5H_5)(PMe_3)_2RuCl$[47] (Cp = $\eta^5\text{-}C_5H_5$), $MeSC{\equiv}CSMe$,[48] $MeSC{\equiv}CMe$,[49] and $(Me_2SSMe)SO_3CF_3$[50] were prepared by using previously described procedures. All other chemicals were used as received from commercial sources.

$\{Cp(PMe_3)_2Ru[S(Me)C{\equiv}CSMe]\}(PF_6)$ (1)

A solution of $Cp(PMe_3)_2RuCl$ (50 mg, 0.14 mmol), $MeSC{\equiv}CSMe$ (0.15 mL, 200 mg, 1.7 mmol), and NH_4PF_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_2Cl_2 (0 °C), and the solution was filtered. The resulting yellow solution was reduced to 1 mL under vacuum, and 10 mL of Et_2O was added producing a yellow precipitate which was collected and dried under vacuum. The yellow powder of 1 was collected in 27% yield (22 mg, 0.039 mmol). Anal. Calcd for $C_{15}H_{29}F_6P_3RuS_2$: C, 30.98; H, 5.03. Found: C, 31.35; H, 5.07. IR (CH_2Cl_2): $\nu(C{\equiv}C)$ 2103 cm^{-1}.

$[Cp(PMe_3)_2Ru{=}C{=}C(SMe)_2](PF_6)$ (2)

A solution of $Cp(PMe_3)_2RuCl$ (240 mg, 0.68 mmol) and $MeSC{\equiv}CSMe$ (0.41 mg, 3.5 mmol) in 15 mL of methanol was

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

Compound	Cp	PMe_3	J_{PH}, Hz	SMe_n (n=1 or 2)	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)
$[Cp(PMe_3)_2Ru[n^2\text{-}MeSC\equiv CSMe]BF_4$ (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]
$Cp(PMe_3)_2Ru\text{-}C\equiv C\text{-}SMe$ (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)
$Cp(PMe_3)_2Ru(CuCl)(C\equiv C\text{-}SMe)$ (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)	(CH_3)[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 tq (H)[j]

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[a] Abbreviations: d, doublet; t, triplet; q, quartet.

[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, $J_{HH} = 0.49$ Hz.

Table I (continued)

Compound	Cp	PMe_3	J_{PH}, Hz	SMe_n (n=1 or 2)	Other
isomer B	4.59	1.41 t	8.58	2.13 (1)	3.43 (Me) (H)[k]
$[Cp(PMe_3)_2Ru{-}C{\equiv}C{-}SMe_2]BF_4$ (13)[b]	4.76	1.49 t	9.17	3.00 (2)	
$Cp(PMe_3)_2Ru{-}C{\equiv}C{-}Me$ (14)[b]	4.62	1.45 t	9.03		1.98 t (Me)[l]

[k] Not observed.

[l] J_{PH} = 2.6 Hz.

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

Compound	Cp	PMe_3 t	J_{PC}, Hz	SMe_n (n=1 or 2)	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 (≡C-S) 70.66 (≡$\underline{\mathrm{C}}$-)
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	

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[a] Abbreviations: d, doublet; t, triplet.

[b] $CDCl_3$.

[c] CD_3CN.

[d] Not observed.

[e] PMe_3 and Ru-C not observed.

refluxed for 1 h under N_2. The heating mantle was removed from the reaction flask, and NH_4PF_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_2Cl_2, the resulting solution was filtered under vacuum using a Schlenk frit containing Celite, and the frit was washed with CH_2Cl_2 (2 x 10 mL). The filtrate solution was reduced to 5 mL, and 20 mL of Et_2O was added producing a red oily residue. The solvent was removed and the residue dried under reduced pressure. Crystallization at -20 °C from CH_2Cl_2/Et_2O yielded red platelets of 2 in 76% yield (310 mg, 0.53 mmol). Anal. Calcd for $C_{15}H_{29}F_6P_3RuS_2$: C, 30.98; H, 5.03. Found: C, 30.79; H, 5.05. MS(FAB): m/e 437 (M^+), 319 ($M^+-Me_2S_2C_2$); IR (CH_3CN): ν(C=C) 1603 cm^{-1}.

{Cp(PMe_3)$_2$Ru[S(Me)C≡CMe]}(BF_4) (3a) and
[Cp(PMe_3)$_2$Ru(η^2-MeSC≡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≡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_4BF_4 (1.16 g, 11.0 mmol). The reaction produced a yellow powder containing isomers 3a and 3b (2 to 1 ratio, respectively) in 79% yield (969 mg, 1.97 mmol).

Complex 3a was separated by TLC (Whatman, K6 silica gel, 20 x 20 cm, layer thickness 250 μ). The mixture of 3a and 3b (152 mg, 0.310 mmol) was dissolved in 1 mL of CH_2Cl_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_2Cl_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_2O were added to produce a yellow powder of 3a in 28% yield (42 mg, 0.085 mmol). Anal. Calcd for $C_{15}H_{29}BF_4P_2RuS$: C, 36.67; H, 5.95. Found: C, 36.76; H, 5.87. MS(FAB): m/e 405 (M^+), 319 (M^+ -MeSC≡CMe); IR (CH_2Cl_2): ν(C≡C) 2203 cm^{-1}. Isomer 3b decomposed on the silica gel plate; it was characterized spectroscopically (Tables I and II).

$Cp(PMe_3)_2Ru$-C≡C-SMe (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, complex 2 (310 mg, 0.53 mmol) in 15 mL of THF was added 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 x 5 mL). The solvent was removed from the resulting solution under reduced pressure. The residue was dissolved in CH_2Cl_2 (3 x 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_2O and passed through a column of alumina (activity grade 4, 1 x 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}.

$[Cp(PMe_3)_2Ru{=}C{=}C(H)(SMe)](BF_4)$ (6)

To a solution of 5 (28 mg, 0.072 mmol) in 10 mL of CH_2Cl_2, $HBF_4 \cdot Et_2O$ (0.010 mL, 11 mg, 0.068 mmol) was added under N_2. The resulting red solution was stirred for 10 min, filtered through a bed of Celite, and the frit was washed with CH_2Cl_2 (2 x 10 mL). The solution was reduced to 3 mL, and 20 mL of Et_2O was added producing a red precipitate which 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}.

[$Cp(PMe_3)_2Ru=C=C(Me)(SMe)$](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}.

$Cp(PMe_3)_2Ru(CuCl)(C=C-SMe)$ (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 cm x 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}.

$[Cp(PMe_3)_2Ru{=}C{=}C(H)(SMe_2)](BF_4)_2$ (9)

To a stirred solution of complex 6 (98 mg, 0.21 mmol) in 20 mL of CH_3CN, $[Me_3O]BF_4$ (100 mg, 0.68 mmol) was added. 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 x 10 mL), the suspension was filtered through Celite, and the solid remaining on the Celite was washed with Et_2O (2 x 10 mL). The solid was dissolved with acetone (3 x 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.

$[Cp(PMe_3)_2Ru{=}C{=}C(Me)(SMe_2)](BF_4)_2$ (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 x 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}.

$[Cp(PMe_3)_2Ru{=}C(OMe)(CH_2SMe)](BF_4)$ (11a) and $[Cp(PMe_3)_2Ru{=}C(OEt)(CH_2SMe)](BF_4)$ (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, was 60%. 11a. Anal. Calcd for $C_{15}H_{31}BF_4OP_2RuS$: C, 35.38; H, 6.14. Found: C, 35.12; H, 6.02. MS(FAB): m/e 423 (M^+), 319 ($Cp(PMe_3)_2Ru^+$).

$Cp(PMe_3)_2Ru[C(OMe){=}C(H)SMe]$ (12)

To a stirred solution of 11a (33 mg, 0.065 mmol) in 10 mL of MeOH, 1.3 mL of a 0.10 M solution of NaOMe (0.13 mmol) was added 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 x 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.

$[Cp(PMe_3)_2Ru{-}C{\equiv}C{-}SMe_2](BF_4)$ (13)

To a stirred solution of complex 9 (86 mg, 0.15 mmol) in 15 mL of methanol, 1 mL of a 0.16 M methanolic solution of NaOMe (0.16 mmol) was added. 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 x 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): $\nu(C{\equiv}C)$ 1960 cm^{-1}. Elemental analyses were not obtained due to noticeable thermal decomposition of the product in 12 h at room temperature.

$Cp(PMe_3)_2Ru-C\equiv C-Me$ (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), $\nu(C\equiv C)$ 2095 cm^{-1}. Complex 14 has been previously characterized by Bruce and coworkers.[24]

X-ray Structure Determination of
$[Cp(PMe_3)_2Ru=C=C(H)(SMe_2)](BF_4)_2$ (9)

Data collection and reduction

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, ±l quadrant. An empirical absorption correction was made, based on a series of psi-scans. The agreement factors for the averaging of 222 observed reflections were 1.3% based on intensity and 1.2% based on F_{obs}.

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 allowed to refine with anisotropic temperature factors in the final refinement cycles.

While the cationic complex 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 allowed to refine 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 and 22% occupied; those on B(2), B(2′), and B(2′′) were 40, 37, and 23% 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 using 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.

Table III. Crystal and Data Collection Parameters for $[Cp(PMe_3)_2Ru{=}C{=}C(H)(SMe_2)](BF_4)_2$ (9)

Formula	$RuSP_2F_8C_{15}B_2H_{30}$
Formula weight	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
Crystal size, mm	0.30 x 0.36 x 0.15
$\mu(MoK_\alpha)$, cm^{-1}	9.036
Data collection instrument	Enraf-Nonius CAD4
Radiation (monochromated in incident beam)	MoK_α (λ = 0.71073 Å)
Orientation reflections, number, range (2θ)	25, 18° < 2θ < 30°
Temperature, °C	22 ± 1
Scan method	θ-2θ
Data collection range, 2θ, deg	0-45
No. unique data, total:	4276
with $F_o^2 > 3\sigma(F_o^2)$:	3200

Table III (continued)

Number of parameters refined	207
Trans. factors, max., min. (psi-scans)	0.999, 0.940
R[a]	0.0514
R_w[b]	0.0743
Quality-of-fit indicator[c]	1.914
Largest shift/esd, final cycle	0.09
Largest peak, e/Å^3	0.819

[a] $R = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$.

[b] $R_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w|F_o|^2]^{1/2}$; $w = 1/[\sigma^2(|F_o|) + 0.001\ |F_o|^2]$.

[c] Quality-of-fit = $[\Sigma w(|F_o| - |F_c|)^2 / (N_{obs} - N_{parameters})]^{1/2}$.

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(60	0.474(1)	0.6039(6)	7.4(3)

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[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^2*B(1,1) + b^2*B(2,2) + c^2*(B(3,3) + ab(cos gamma)*B(1,2) + ac(cos beta)*(1,3) + bc(cos alpha)*B(2,3)].

Table IV (continued)

Atom	x	y	z	B(Å^2)^a
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(10	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′)	-0.13991)	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

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^{b}Atoms were refined isotropically.

Table IV (continued)

Atom	x	y	z	B(Å^2)[a]
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(20[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]

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 for 2; R = Me for 3a) are formed in room temperature reactions of $Cp(PMe_3)_2RuCl$ 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 $\nu(C{\equiv}C)$ 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 sulfonium 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 to 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 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; R = H, 5.43). 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 of 1.41 to 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=C-SMe (5), -C=C-Me (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; 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 to 23.65 ppm with coupling constants ranging from 13.30 to 18.93 ppm. The key observation which 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 beta-carbon (β-carbon) occurs as a singlet at 116.62 ppm. The α-carbon and β-carbon resonances are characteristic of related vinylidene complexes: $[Cp(PMe_3)_2Ru{=}C{=}C(H)(Me)]PF_6$[19] (347.9 and 103.4 ppm), $[Cp\{(MeO)_3P\}_2Mo{=}C{=}C(H)(Bu\text{-}t)]Li$[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 $MeSC{\equiv}CSMe$ to give 1 and 2, under similar conditions $Cp(PMe_3)_2RuCl$ reacts with $MeSC{\equiv}CMe$ to give a 2 to 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 d_4-MeOH at 40 °C for 4 h again gave a 2 to 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: $[Cp(PMe_3)_2Ru(\eta^2\text{-alkyne})]PF_6$ ($HC{\equiv}CMe$, 5.02; $HC{\equiv}CH$, 5.02 ppm)[19] and ($EtC{\equiv}CEt$, 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 CD_3CN at 95 °C to liberate $MeSC{\equiv}CSMe$ and form complex 4 (eq 1); an equlibrium mixture of complexes 2 and 4 (1.25:1 ratio) is established after 72 h.

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

The facile reaction of the vinylidene complex 2 with CD_3CN to generate free $MeSC{\equiv}CSMe$ must result from SMe migration from one carbon to the other.

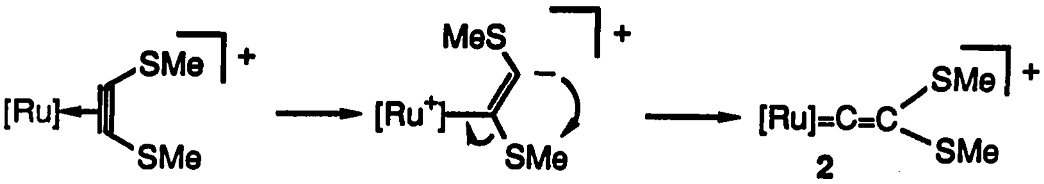
The known formation[19-31] of metal vinylidene complexes from reactions of 1-alkynes with metal complexes is proposed to proceed through a 1,2-hydrogen shift via an intermediate η^2-alkyne complex.[22] Similarly, the rearrangement of complex 1 to 2 is suggested to proceed via an undetected π-MeSC≡CSMe 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. One might consider this SMe rearrangement to proceed through either a cationic or anionic vinyl intermediate. Otsuka and Nakamura[16] have discussed the activation of π-alkynes by formation of such intermediates, as shown in eqs 2 and 3.

2

3

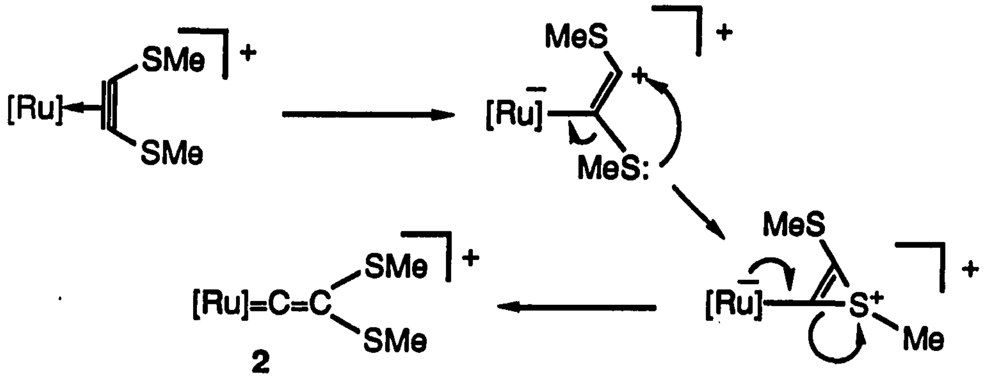
The amount of cationic (eq 2) or anionic (eq 3) character of the η^1-acetylene would vary from complex to complex, but more cationic character (eq 2) would be expected when R is an electron donating substituent, whereas electron withdrawing groups, e.g., R = CF_3 and CO_2Me, would stabilize the anionic structure in eq 3.

A sulfur group might also stabilize the carbanionic intermediate. Such stablilization of carbanions by sulfur is proposed to arise from overlap of the unshared electron pair on the carbon with an empty d-orbital on the sulfur (pπ - dπ bonding), although other reasons have also been suggested.[58] A mechanism for the SMe migration involving such an intermediate is shown in eq 4.



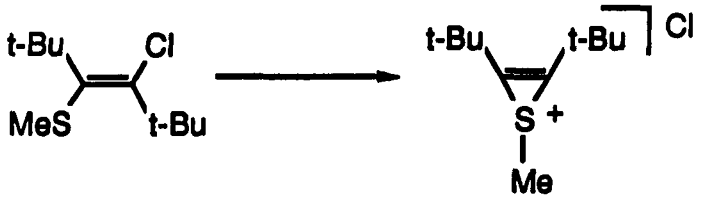
4

An alternative mechanism may involve a 1,2-SMe migration via a cationic vinyl intermediate (eq 2). In this intermediate, a lone pair of electrons on the sulfur of the α-SMe group would form a bond with the electron deficient β-carbon to form a thiirenium-type intermediate (eq 5).



5

A similar thiirenium salt was actually isolated from the ionization of a mercapto vinyl chloride at room temperature (eq 6).[59]



6

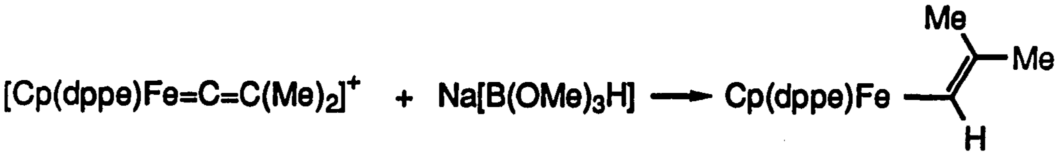
Based on the evidence which is now available, it is not possible to decide whether the mechanism in eq 4 or in eq 5 is involved, or perhaps a concerted process not proceeding through a vinyl intermediate occurs.

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$_3$)$_2$Ru=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 ν(C≡C) band at 2000 cm^{-1} which is lower than those of other ruthenium acetylide complexes: Cp(PPh$_3$)$_2$Ru-C≡C-R (R = Me, 2100; Ph, 2068; and CO$_2$Me, 2058 cm^{-1})[28] and Cp(PMe$_3$)$_2$Ru-C≡C-R (R = Ph, 2105; and 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 these of free alkyl and aryl acetylenes which occur in the region of 2260 to 2100 cm^{-1}. The lower $\nu(C\equiv C)$ band in $MeSC\equiv CSMe$ 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] 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 to 103 ppm and the β-carbon is a singlet at 98 to 123 ppm: $Cp(PPh_3)_2Ru{-}C\equiv C{-}R$ (R = n-Bu, 89.4 and 111.3 ppm; R = t-Bu, 87.8 and 120.9 ppm); $Cp^*(dppe)Ru{-}C\equiv C{-}t{-}Bu$ (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 7), complex 2 reacts with $Na[HBEt_3]$ in CD_3CN in an NMR tube to give 5 and MeSSMe.



7

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.

Reactions of $Cp(PMe_3)_2Ru-C\equiv C-SMe$ (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 which is localized on the β-carbon of the acetylide as suggested by MO calculations.[62] Many acetylide complexes undergo β-carbon protonation or alkylation to give a variety of vinylidene derivatives.[23,24,28,63-67]

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 similar complexes, $[Cp(PMe_3)_2Ru=C=C(R)(Ph)]PF_6$ (R = H or 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 $[Cp(PMe_3)_2Ru-C\equiv C-SMe_2]I$

(Scheme II); upon warming the solution to room temperature for 10 min, this complex rearranges to the vinylidene complex 7. The formulation of the intermediate as $[Cp(PMe_3)_2Ru-C\equiv C-SMe_2]I$ 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, repectively. The ^1H NMR resonance (3.22 ppm) of the SMe_2 group in $[Cp(PMe_3)_2Ru-C\equiv C-SMe_2]I$ 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 study of a ^1H NMR tube reaction of complex 5 and MeI at 0 °C until the formation of $[Cp(PMe_3)_2Ru-C\equiv C-SMe_2]I$ was observed; then, addition of $HBF_4 \cdot Et_2O$ to the reaction solution gave a ^1H NMR spectrum which was identical to that of $[Cp(PMe_3)_2Ru{=}C{=}C(H)(SMe_2)]^{2+}$ (9).

A 5-min reaction of complex 5 with one equivalent 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 etablished by its ^1H NMR spectrum.

Reaction of 5 with a suspension of CuCl in CH_2Cl_2 affords the complex $Cp(PMe_3)_2Ru(CuCl)(C\equiv C-SMe)$ (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, EIMS, and elemental analyses. The IR ν(C≡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≡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)$_3$Mn(CuCl)(C≡CR)[69] (R = CH$_2$OMe, 1980; t-Bu, 1983; Ph, 1989 cm^{-1}) and Cp(PPh$_3$)$_2$Ru(CuCl)(C≡CR)[70] (R = Ph, 1979; p-MeC$_6$H$_4$, 1945; Me, 1982 cm^{-1}). The ^1H NMR spectrum of 8 show a SMe resonance at 2.36 ppm which 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≡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$_3$)$_2$Ru-C≡C-SMe$_2$]BF$_4$ (13) (discussed later). An X-ray diffraction study carried out on (dppe)(CO)$_3$Mn(CuCl)(C≡CPh)[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$_3$)$_2$Ru=C=C(R)(SMe)]BF$_4$ {R = H (6) and Me (7)}

The monocationic vinylidene complexes 6 and 7, react readily with [Me$_3$O]BF$_4$ in CH$_3$CN to form the dicationic sulfonium complexes $[Cp(PMe_3)_2Ru{=}C{=}C(R)(SMe_2)](BF_4)_2$ (R = H (9) and Me (10)) in 72% and 55% yields, respectively (Scheme II). The products are isolated as air-stable yellow solids which 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 sulfonium 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 $[Cp(PPh_3)(NO)Re\text{-}CH_2SMe_2]PF_6$[72,73] (2.60 ppm) is also approximately 0.6 ppm downfield of that in the analogous thioether $Cp(PPh_3)(NO)Re\text{-}CH_2SMe$ (2.01 ppm). The ^1H NMR chemical shift of the Cp group in complexes 9 and 10 is also downfield as compared to 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 bond 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 or i-Pr);[26] on the other hand, dialkylated complexes such as $[Cp(PPh_3)_2Ru=C=C(Me)(Ph)]I$ do not react with alcohols. Similarly, MeOH and EtOH add at room temperature to complex 6 to give $[Cp(PMe_3)_2Ru=C(OR)(CH_2SMe)]BF_4$ (R = Me for 11a, and Et for 11b) (Scheme II). The air-stable yellow powder of 11a was characterized by its elemental analyses, FAB mass spectrum, ^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 pale yellow powder of 12 was collected in 84% yield and was characterized by its EIMS, ^1H 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 ^1H NMR spectrum of isomer A shows a broad vinyl proton signal at 5.33 ppm. This signal collapsed to a quartet with J_{H-OMe} = 0.5 Hz and a triplet with J_{PH} = 1.4 Hz, respectively, when the methyls of the PMe_3 and OMe groups were irradiated in ^1H NMR selective decoupling experiments. 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 $Cp(PPh_3)(CO)Ru[C(O\text{-}i\text{-}Pr)=C(H)Ph]$[21] and $Cp(P(OMe)_3)_3Mo[C(H)=C(H)t\text{-}Bu]$[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 complexes $Cp(P(OPh)_3)(CO)Fe[C(Me)=C(Me)SPh]$[77] and

$Cp(PPh_3)(CO)Ru[C(O\text{-}i\text{-}Pr){=}C(H)Ph]$[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 one equivalent of $HBF_4{\cdot}Et_2O$ in $CDCl_3$ to give back the carbene complex 11a quantitatively (Scheme II), as indicated by the ^1H NMR spectrum.

X-ray Crystal Structure of
$[Cp(PMe_3)_2Ru{=}C{=}C(H)(SMe_2)](BF_4)_2$ (8)

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 distances from the metal to the five carbon atoms of the C_5-ring range from 2.256 (7) to 2.27 (1) Å and to the phosphorus atoms are 2.334 (2) and 2.298 (2) Å. The values fall within the range found for several related ruthenium complexes.[24,65-67] 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; they range from 1.823 (9) to 1.863 (10) Å (Table VI). In fact, the Ru-C(1) distance is close to those in metal-

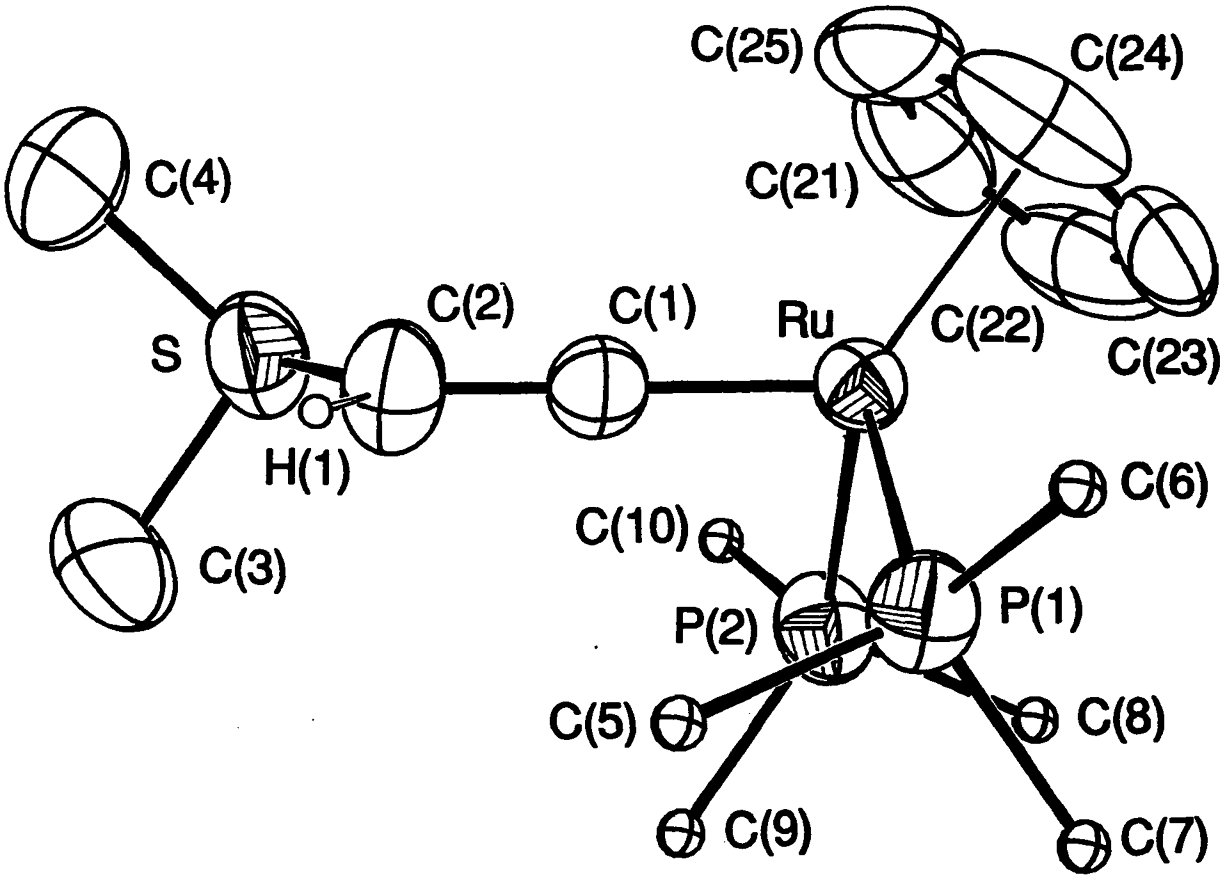


Figure 1. An ORTEP drawing of $[Cp(PMe_3)_2Ru{=}C{=}C(H)(SMe_2)](BF_4)_2$ (9). The phosphine methyls are shown as arbitrary spheres

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)

---

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

[b] Fixed.

Table V (continued)

Bond Angles (deg)							
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)

carbyne complexes: $(Cl)(CO)(PPh_3)_2Os(\equiv C\text{-tolyl})$,[78] 1.77 (2) Å; $(PPh_3)_2(Cl)_2(SCN)Os[\equiv C\text{-}(4\text{-}C_6H_4NMe_2)]$,[79] 1.75 (1) Å; and $\{(PPh_3)_2(Cl)_2[(\text{tolyl})NC]Os[\equiv C\text{-}(4\text{-}C_6H_4NMe_2)]\}ClO_4$,[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) to 1.34 (1) Å) in related ruthenium vinylidene complexes (Table VI), but it is not quite as long as the $C(sp)\text{-}C(sp^2)$ single bond distances found in $(Cl)(CO)(PPh_3)_2Os(\equiv C\text{-Tolyl})$[78] (1.45 (3) Å) and $[Cp(CO)_2Mn\equiv C\text{-}C(H){=}CPh_2]BF_4$[80] (1.389 (7) Å). The short Ru-C(1) and long C(1)-C(2) bonds as compared to other vinylidene complexes (Table VI) suggest that both vinylidene and carbyne resonance forms contribute to the bonding in 9 (eq 8).

8

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 $C(sp^2)\text{-}S$ single bond distances found in $Cp(PPh_3)(CO)W\equiv C\text{-}SPh$[81] (1.768 (12) Å) and $[(PPh_3)_2(CO)_3Mn{=}C{=}C(NMe_2)SMe]BF_4$[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 $(CO)_2(PPh_3)_2(H)Os[C(S)\text{-}SMe]$[84]

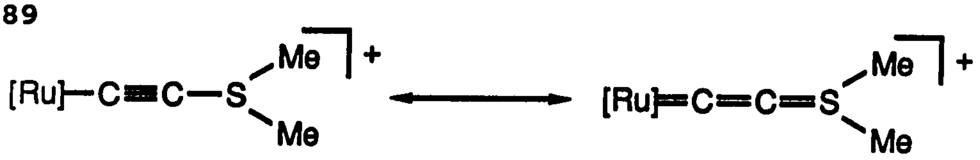
Table VI. Selected Bond Lengths (Å) and Angles (deg) in Ruthenium Vinylidene Complexes

Compound	Ru=C	C=C	Ru-C(1)-C(2)
$\mathrm{[Cp(PMe_3)_2Ru{=}C{=}C(H)(SMe_2)](BF_4)_2}$ (9)	1.792(8)	1.36(1)	178.7(5)
$\mathrm{[Cp(PPh_3)_2Ru{=}C{=}C(I)(Ph)](I_3)}$[67]	1.839(7)	1.31(1)	171.0(7)
$\mathrm{[Cp(PPh_3)_2Ru{=}C{=}C(Br)(C_2H_4Br\text{-}4)](Br_3)}$[67]	1.85(1)	1.31(2)	169.4(14)
$\mathrm{[Cp(PPh_3)_2Ru{=}C{=}C(Me)(Ph)](I)}$[66]	1.863(10)	1.293(15)	172.8(11)
$\mathrm{[Cp(PPh_3)_2Ru{=}C{=}C(Ph)(N{=}NC_6H_3Me_2\text{-}3,4)](BF_4)}$[65]	1.823(9)	1.34(1)	169.9(7)
$\mathrm{[Cp(dppe)Ru{=}C{=}C(Ph)(C_7H_7)](PF_6)}$[65]	1.848(9)	1.32(1)	174.9(6)
$\mathrm{[Cp(PMe_3)_2Ru{=}C{=}C(H)(Me)](PF_6)}$[24]	1.845(7)	1.313(10)	180(2)

(1.724 (5) Å) and $[Cp(dppe)Fe{=}C{=}C(Me)(C(S)\text{-}SMe)]I{\cdot}MeOH$[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 $[Cp(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}C{=}S)$[86] (1.596 (9) Å) and $(CO)_2(PPh_3)_2(H)Os[C({=}S)SMe]$[84] (1.648 (4) Å). The C(3)-S (1.78 (1) Å) and C(4)-S (1.83 (1) Å) distances are similar to sulfonium $C(sp^3)$-S distances found in the complexes $\{[Cp(PPh_3)(NO)ReCH_2\text{-}]_2SMe\}I{\cdot}(CH_3CN)_2$[72] (1.807 (7) and 1.813 (15) Å) and $[Cp(CO)_2Fe(CH_2SMe_2)]FSO_3$[87] (1.786 (3) and 1.788 (3) 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 8).

Preparation of $[Cp(PMe_3)_2Ru\text{-}C{=}C\text{-}SMe_2]BF_4$ (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 ^1H NMR Cp resonance (4.76 ppm) of complex 13 is nearly identical to 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 to that of 5. The IR $\nu(C{\equiv}C)$ band in 13 is 40 cm^{-1} lower than that in 5 (2000 cm^{-1}); in the only known alkynylsulfonium salt, $[PhC{\equiv}CS(Me)Et]$(picrate),[88] the IR $\nu(C{\equiv}C)$ band is found at 2195 cm^{-1}, which is also shifted by 60 cm^{-1} as compared to $MeC{\equiv}CSMe$ (2255 cm^{-1}). The lower $\nu(C{\equiv}C)$ band in 13 as compared with 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 9).[89]



9

A structural study of the 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 sulfonium acetylide (13) can be protonated quantitatively, as indicated in the ^1H NMR spectrum, with one equivalent of $HBF_4{\cdot}Et_2O$ in CD_3CN to form complex 9 and 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)

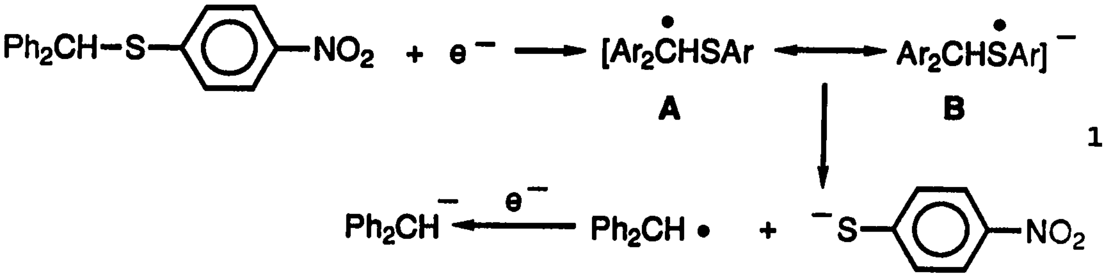
Similar to the reduction of complex 2 to 5 (Scheme I), complex 7 is reduced by equimolar $Na[HBEt_3]$ in $CDCl_3$ to give a stoichiometric conversion to the desulfurized acetylide $Cp(PMe_3)_2Ru-C=C-Me$ (14) and MeSSMe (Scheme II), as indicated by the ^1H NMR spectrum. Complex 14 is also obtained in 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 $\nu(C=C)$ band at 2095 cm^{-1} and characteristic triplet in the ^1H NMR spectrum for the acetylide methyl group at 1.98 ppm (J_{PH} = 2.6 Hz).

The reduction of the dicationic complex 10 with two equivalents of $Na[HBEt_3]$ in CD_3CN gives a stoichiometric conversion to the desulfurized acetylide 14 and Me_2S, as indicated by the ^1H 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 reduction reactions (Na/Hg or $Na[HBEt_3]$) which convert 2 to 5, 7 to 14, and 10 to 14 with loss of MeS· 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]

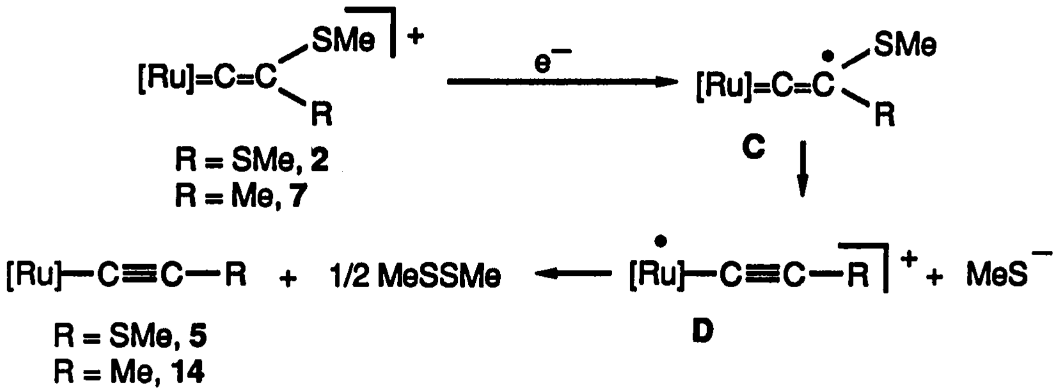
In a mechanistic study of the electro-reduction of substituted thioethers, Farnia and coworkers[93] suggested that the first intermediate formed at the cathode (rate-determining step) is an anion radical (eq 10). The intermediate anion radical formed from diphenylmethyl-p-nitrophenyl sulfide has been detected by ESR spectrometry. Resonance forms with the unpaired electron density at the carbon (A) and sulfur (B) center were proposed to account for the ESR results.



10

Form B was proposed to contribute more than A. In the second step, carbon-sulfur bond cleavage to give the sulfide and diphenylmethyl radical occurs; this is followed by a second electron transfer to form the diphenylmethyl anion (eq 10).

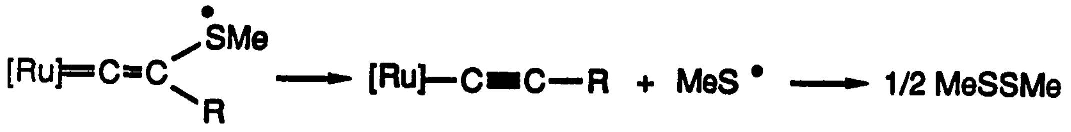
A similar mechanism may be proposed for the reduction of complexes 2 and 7. The initial step would be a one electron addition, as depicted in eq 10 (A), to complexes 2 and 7 to form a radical intermediate (C, eq 11); carbon-sulfur bond cleavage with electron rearrangement in the vinylidene unit would form a metal centered radical cation acetylide (D) and MeS^-.



11

Related radical cation acetylides were generated by Bitcon and Whiteley[20] in the reversible one-electron oxidations of $Cp(PPh_3)_2Ru-C\equiv C-R$ and $Cp(PPh_3)(CO)Fe-C\equiv C-R$ (R = Ph, n-Bu, and t-Bu). The final step (eq 11) is electron transfer from MeS^- to the metal acetylide cation; the resulting MeS• radicals would couple to form the observed MeSSMe.

It seems possible that intermediate C in this mechanism (eq 11) could undergo carbon-sulfur bond cleavage to give a neutral metal acetylide and MeS• radical (eq 12).



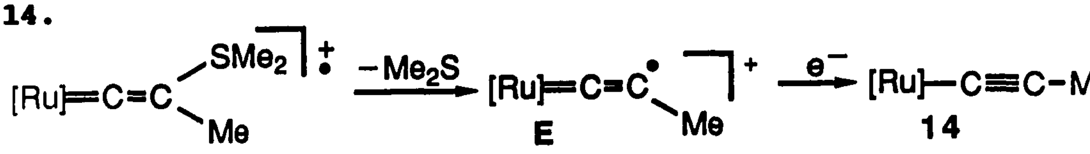
$$[Ru]{=}C{=}C(\dot{S}Me)R \longrightarrow [Ru]{-}C{\equiv}C{-}R + MeS^{\bullet} \longrightarrow 1/2\ MeSSMe \qquad 12$$

Although carbon-sulfur bond cleavage to form MeS• has not been observed previously in organic systems, it is possible that the ruthenium-vinylidene complex is sufficiently stabilized and that MeS• would be produced.

The two-electron reduction of sulfonium complex 10 with the formation of the Me_2S product presumably proceeds via a similar mechanism as in the reduction of organic sulfonium ions (eq 13).[92]

$$Me_3S^+ \xrightarrow{e^-} [Me_3S]^{\bullet} \longrightarrow Me_2S + Me^{\bullet} \xrightarrow[H^+]{e^-} CH_4 \qquad 13$$

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



$$\left[[Ru]{=}C{=}C(SMe_2)Me\right]^{+\bullet} \xrightarrow{-Me_2S} \underset{\mathbf{E}}{\left[[Ru]{=}C{=}\dot{C}Me\right]^{+}} \xrightarrow{e^-} \underset{\mathbf{14}}{[Ru]{-}C{\equiv}C{-}Me} \qquad 14$$

CONCLUSIONS

In contrast to the alkyl and aryl acetylenes which react with $Cp(PMe_3)_2RuCl$ to give the π-acetylene complexes $[Cp(PMe_3)_2Ru(\eta^2\text{-}RC{\equiv}CR)]^+$, the mercapto acetylene $MeSC{\equiv}CSMe$ 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• and produce the acetylide $Cp(PMe_3)_2Ru\text{-}C{\equiv}C\text{-}SMe$ (5). This acetylide is similar to other acetylides in that the β-carbon reacts with electrophiles ($R = H^+$ or 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 sulfonium acetylide $[Cp(PMe_3)_2Ru\text{-}C{\equiv}C\text{-}SMe_2]^+$. The sulfur atoms in the vinylidene complexes $[Cp(PMe_3)_2Ru{=}C{=}C(R)(SMe)]^+$ (R = H for 6, and Me for 7) are also alkylated to give the dicationic vinylidene complexes $[Cp(PMe_3)_2Ru{=}C{=}C(R)(SMe_2)](BF_4)_2$ (R = H for 9, and Me for 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, I have attempted to evaluate their effects on the electron density at the 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:

$-C\equiv C-SMe \approx -C(OMe)=C(H)SMe > -C\equiv C-SMe_2 > S(Me)C\equiv CSMe >$

$MeSC\equiv CMe > =C(OR)CH_2SMe > =C=C(R)SMe > =C=C(R)SMe_2^+$.

The trend indictes that sigma bound ligands such as acetylides and vinyl groups, and sulfur bound ligands are the better donors, while the π-alkyne, carbene, and vinylidene ligands are good π-acceptors. The sulfonium vinylidene complex $[Cp(PMe_3)_2Ru=C=C(H)(SMe_2)](BF_4)_2$, is the best π-acceptor partly due to bonding which involves some $Ru\equiv C$ carbyne character.

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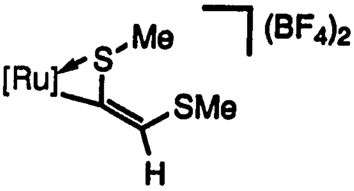
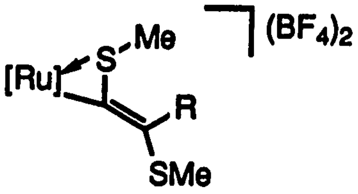
SECTION III. ELECTROPHILIC AND NUCLEOPHILIC REACTIONS OF THE VINYLIDENE COMPLEX $[Cp(PMe_3)_2Ru{=}C{=}C(SMe)_2]BF_4$ AND ITS DERIVATIVES

ABSTRACT

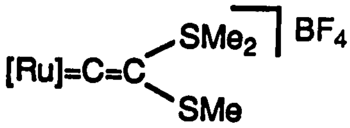
The cationic vinylidene complex $[Cp(PMe_3)_2Ru{=}C{=}C(SMe)_2]BF_4$ (1) undergoes addition of electrophiles such as $HBF_4 \cdot Et_2O$, $[MeSSMe_2]SO_3CF_3$, and $[Me_3O]BF_4$ to give the following complexes {[Ru] = $Cp(PMe_3)_2Ru$}:



2a



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



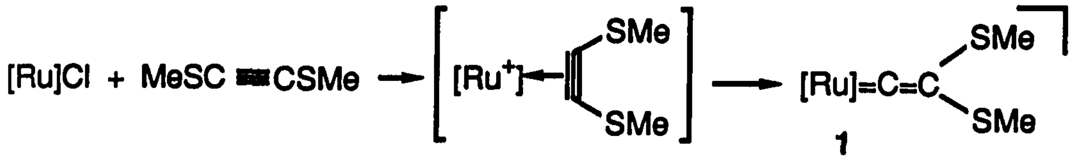
4

An X-ray diffraction investigation shows that 2a crystallizes in space group $C_{2/c}$ 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 sulfonium acetylide $[Cp(PMe_3)_2Ru{-}C{\equiv}C{-}SMe_2]BF_4$ (5) and $[MeS{-}PPh_2R]^+$ (R = Me and Ph). Anionic nucleophiles such as NaSR (R = Et and Me) displace Me_2S from 4 to yield the vinylidene complexes $[Cp(PMe_3)_2Ru{=}C{=}C(SR)(SMe)]BF_4$ (R = Et (7), R = Me (1)). Complex 4 also reacts with pyridines, $4\text{-}NC_5H_4R$ (R = H, Et, and NMe_2 (DMAP)), and SEt_2 to displace Me_2S to yield dicationic vinylidene complexes $[Cp(PMe_3)_2Ru{=}C{=}C(4\text{-}NC_5H_4R)(SMe)](BF_4)_2$ {R = H (8), Et (9), and 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.

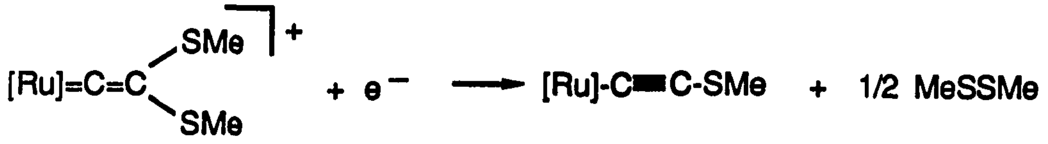
INTRODUCTION

In Section II,[1] I 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). I noted that the reaction with MeSC≡CSMe gave the thiomethyl vinylidene complex $[Cp(PMe_3)_2Ru{=}C{=}C(SMe)_2]BF_4$ (1); this presumably occurred via an η^2-alkyne intermediate which rearranged to the product by a 1,2-SMe migration (eq 1, [Ru] = $Cp(PMe_3)_2Ru$).



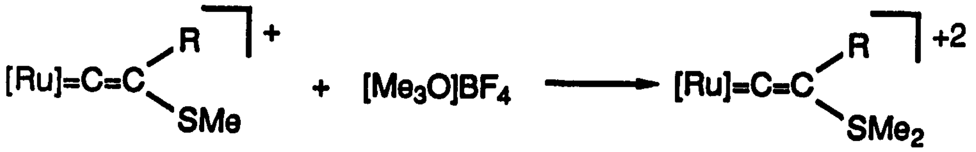
1

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



2

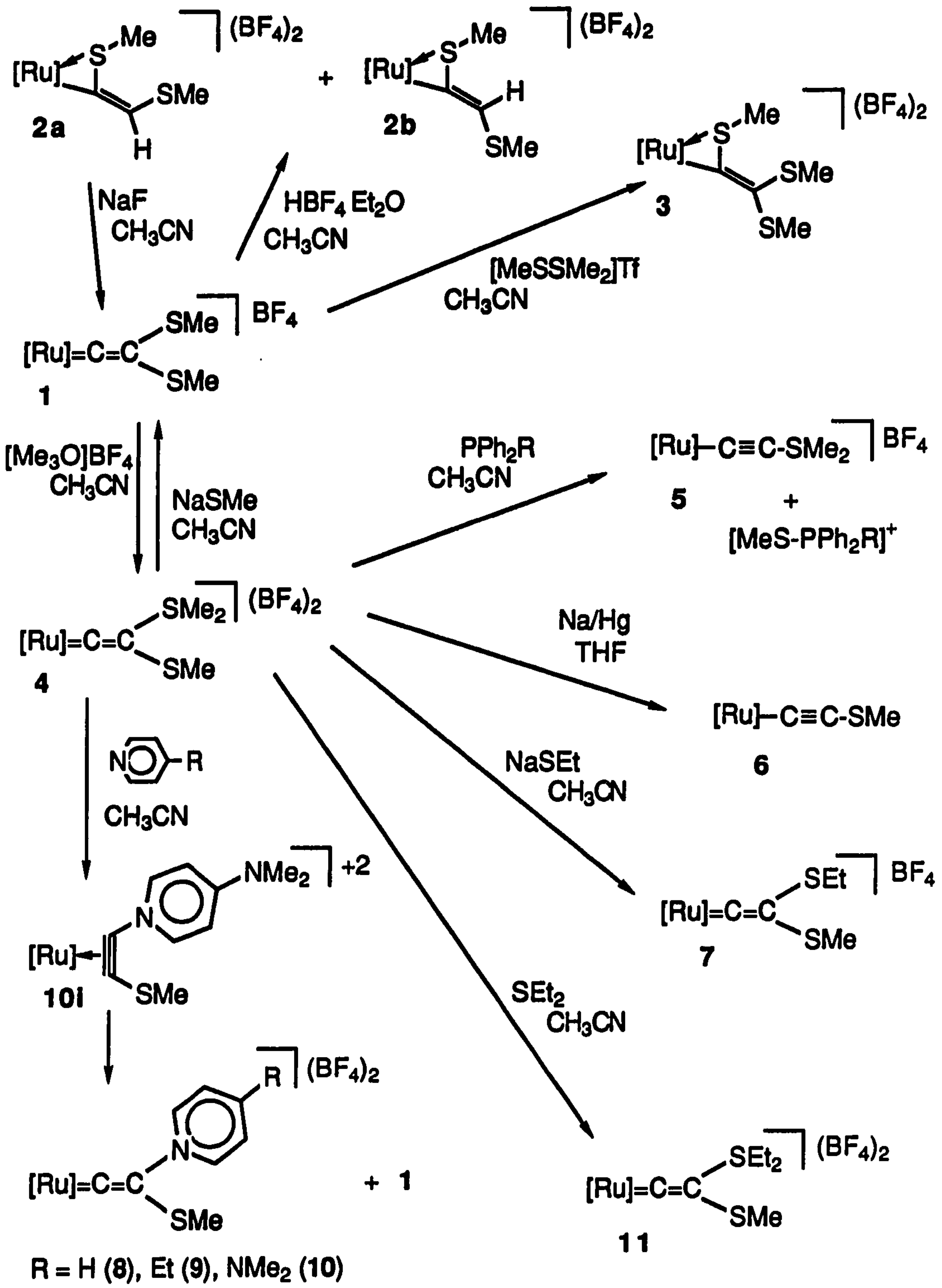
I further reported that the thiomethyl moiety of the vinylidene complexes $[Cp(PMe_3)_2Ru{=}C{=}C(R)(SMe)]BF_4$, are alkylated to give the dicationic sulfonium vinylidene complexes (eq 3).



3

R = H and Me

In order to explore the effects of SR groups on the reactivity of the vinylidene ligand in 1, I 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.


$[Ru]$
Me
SMe
H
$(BF_4)_2$
2a
+
2b
3
NaF CH_3CN
$HBF_4 \cdot Et_2O$ CH_3CN
$[MeSSMe_2]Tf$ CH_3CN
$[Ru]=C=C(SMe)(SMe)$ BF_4
1
$[Me_3O]BF_4$ CH_3CN
$NaSMe$ CH_3CN
PPh_2R CH_3CN
$[Ru]-C\equiv C-SMe_2$ BF_4
5
+
$[MeS-PPh_2R]^+$
$[Ru]=C=C(SMe_2)(SMe)$ $(BF_4)_2$
4
Na/Hg THF
$[Ru]-C\equiv C-SMe$
6
$NaSEt$ CH_3CN
$[Ru]=C=C(SEt)(SMe)$ BF_4
7
SEt_2 CH_3CN
CH_3CN
NMe_2 $+2$
N
R
10i
$[Ru]=C=C$
SMe
$(BF_4)_2$
+ 1
$R = H$ (8), Et (9), NMe_2 (10)
$[Ru]=C=C(SEt_2)(SMe)$ $(BF_4)_2$
11

Scheme I

EXPERIMENTAL SECTION

General Procedures

All reactions, filtrations, distillations, and recrystallizations were carried out under N_2 using standard inert atmosphere and Schlenk techniques.[2] Methylene chloride 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.[3] Acetone and chloroform were dried and stored over molecular sieves (4 Å). 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. ^1H NMR spectra (Table I) were obtained with a Nicolet NT-300 (300 MHz) spectrometer using Me_4Si (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. The ^{31}P NMR spectra were recorded on the Bruker WM-300 MHz instrument; the ^{31}P signals which are upfield of the H_3PO_4 external reference are given as negative values. Fast atom bombardment (FAB, 3-nitrobenzyl alcohol matrix) spectra were obtained using a Kratos MS-50 spectrometer. GCMS were obtained on a Hewlett Packard Gas Chromatograph 5890A (30 m x 0.25 mm DB5 column, TRW) interfaced to a 5970 Series Mass Selective Detector. Elemental microanalyses were performed by Galbraith Laboratories Inc., Knoxville, TN.

The compounds $(\eta^5\text{-}C_5H_5)(PMe_3)_2RuCl^{4,5}$ $(\eta^5\text{-}C_5H_5 = Cp)$, $[Cp(PMe_3)_2Ru{=}C{=}C(SMe)_2]BF_4$ (1),[1] $[Me_2SSMe]SO_3CF_3$ (SO_3CF_3 = Tf),[6] and NaSR[7] were prepared by using previously described procedures. All other chemicals were used as received from commercial sources.

$\{Cp(PMe_3)_2Ru[S(Me)C{=}C(H)(SMe)]\}(BF_4)_2$ (2a) and $\{Cp(PMe_3)_2Ru[S(Me)C(H){=}C(SMe)]\}(BF_4)_2$ (2b)

To a solution of complex 1 (537 mg, 1.02 mmol) in 40 mL of CH_3CN, $HBF_4{\cdot}Et_2O$ (0.30 mL, 2.0 mmol) was added 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

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

Compound	Cp	PMe_3	J_{PH}, Hz	SMe_n (n=1 or 2)	Other
$[Cp(PMe_3)_2Ru{=}C{=}C(SMe_2)]BF_4$ (1)[b]					
	5.48	1.47 d	10.56	2.22 (1)	
$\{Cp(PMe_3)_2Ru[S(Me)C{=}C(H)SMe]\}(BF_4)_2$ (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)	
$\{Cp(PMe_3)_2Ru[S(Me)C(H){=}C(SMe)]\}(BF_4)_2$ (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)	
$\{Cp(PMe_3)_2Ru[S(Me)C(SMe){=}C(SMe)]\}(BF_4)_2$ (3)[c]					
	6.03	1.99 d	10.52	2.60 (1)	
		1.56 d	10.24	2.57 (1)	
				2.49 (1)	

$[Cp(PMe_3)_2Ru{=}C{=}C(SMe_2)(SMe)](BF_4)_2$ (4)[c]					
	5.77	1.73 d	10.80	2.83 (2) 2.43 (1)	
$[Cp(PMe_3)_2Ru{-}C{\equiv}C{-}SMe_2]BF_4$ (5)[c]					
	4.83	1.48 t	9.17	2.83 (2)	
$Cp(PMe_3)_2Ru{-}C{\equiv}C{-}SMe$ (6)[b]					
	4.62	1.45 t	9.03		1.98 t (Me)[g]
$[Cp(PMe_3)_2Ru{=}C{=}C(SEt)(SMe)]BF_4$ (7)[c]					
	5.52	1.64 d	10.80	2.22 (1)	2.65 q (CH_2)[h]

---

[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.

Table I (continued)

Compound	Cp	PMe_3	J_{PH}, Hz	SMe_n (n=1 or 2)	Other
$[Cp(PMe_3)_2Ru=C=C(NC_5H_5)(SMe)](BF_4)_2$ (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]
$[Cp(PMe_3)_2Ru=C=C(4\text{-}NC_5H_4Et)(SMe)](BF_4)_2$ (9)[c]					
	5.84	1.61 d	10.54	2.29 (1)	2.98, 2.95 2q (CH_2)[i]
					1.33, 1.30 2t (CH_3)[i]
					8.74 d (H)[l]
					7.92 d (H)[l]
$[Cp(PMe_3)_2Ru=C=C(4\text{-}NC_5H_4NMe_2)(SMe)](BF_4)_2$ (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]

$[Cp(PMe_3)_2Ru(n^2\text{-}MeSC{\equiv}C\text{-}4\text{-}NC_5H_4NMe_2)](BF_4)_2$ (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]
$[Cp(PMe_3)_2Ru{=}C{=}C(SEt_2)(SMe)](BF_4)_2$ (11)[c]					
	5.77	1.74 d	10.93	2.44 (1)	3.26 2q2q (CH_2)[p]
					1.36 t (CH_3)[k]

[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]

Compound	Cp	PMe_3	J_{PC}, Hz	SMe_n (n=1 or 2)	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.

(-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.

$\{Cp(PMe_3)_2Ru[S(Me)C(SMe)=C(SMe)]\}(BF_4)_2$ (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 x 10 mL) and the solvent discarded. The washed residue was dissolved in acetone (3 x 10 mL), and the solution was filtered through a column of Celite (40 x 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.

$[Cp(PMe_3)_2Ru{=}C{=}C(SMe_2)(SMe)](BF_4)_2$ (4)

To a stirred solution of complex 1 (327 mg, 0.60 mmol) in 15 mL of CH_3CN, $[Me_3O]BF_4$ (200 mg, 1.2 mmol) was added. After being 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 $[Cp(PMe_3)_2Ru{=}C{=}C(SMe_2)(SMe)](PF_6)_2$. 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_2R (R = Me and 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_2R (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 $[Cp(PMe_3)_2Ru{-}C{\equiv}C{-}SMe_2](BF_4)$ (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 [MeS-SMe$_2$]Tf (R = Me, 89 mg, 0.34 mmol; R = Ph, 51 mg, 0.20 mmol) was stirred in 10 mL of CH$_2$Cl$_2$ for 10 min. The solution was reduced to 3 mL, and 15 mL of Et$_2$O 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 and Ph) was dried under vacuum. R = Me. ^{1}H 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. ^{1}H 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$_2$Me.

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, complex 4 (81 mg, 0.13 mmol) in 5 mL of THF was added 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 x 5 mL). The solvent was removed from the filtrate under reduced pressure, and the residue was dissolved in CH_2Cl_2 (2 x 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 x 20 mL) and the solution was passed through a column of Celite (40 x 5 mm). The solvent was removed from the resulting yellow solution under reduced pressure to give a yellow powder of $Cp(PMe_3)_2Ru-C{\equiv}C-SMe$ (6) in 69% yield (35 mg, 0.089 mmol). Complex 6 has previously been characterized.[1] IR (CH_2Cl_2): $\nu(C{\equiv}C)$ 2000 cm^{-1}.

Reactions of 4 with NaSR (R = Et and 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, NaSR (R = Et, 9.0 mg, 0.11 mmol; R = Me, 10 mg, 0.14 mmol) was added. 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 x 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 $[Cp(PMe_3)_2Ru{=}C{=}C(SEt)(SMe)]BF_4$ (7) and 1 were obtained in 54% (28 mg, 0.051 mmol) and 50% yield (21 mg, 0.040 mmol), respectively. 7. Anal. Calcd for $C_{16}H_{31}BF_4P_2RuS_2$: C, 35.76; H, 5.81. Found: C, 35.46; H, 5.78. MS(FAB): 451

(M^+), 404 (M^+-SMe), 390 (M^+-SEt), 319 ($Cp(PMe_3)_2Ru^+$); IR (CH_2Cl_2): ν(C=C) 1600 cm^{-1}.

Reaction of 4 with NC_5H_5

A solution of complex 4 (88 mg, 0.14 mmol) and NC_5H_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 x 7 mL), and the solution was filtered through a column of Celite (40 x 5 mm), leaving undissolved $[Cp(PMe_3)_2Ru{=}C{=}C(NC_5H_5)(SMe)](BF_4)_2$ (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 x 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-$NC_5H_4NMe_2$ (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 x 5 mL) to remove the excess DMAP and the $CHCl_3$ solution was filtered through a column of Celite (40 x 5 mm), leaving undissolved $[Cp(PMe_3)_2Ru=C=C(4-NC_5H_4NMe_2)(SMe)](BF_4)_2$ (10) on the Celite. The insoluble residue that did not dissolve in $CHCl_3$ was dissolved in CH_2Cl_2 (3 x 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 $[Cp(PMe_3)_2Ru=C=C(SEt_2)(SMe)](BF_4)_2$ (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.

Kinetics 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 0 °C. The NMR tube was loaded with a solution of 4 (0.010 mg, 0.016 mmol) and 0.4 mL of CD_3CN; the NMR tube was cooled inside the NMR probe for 15 min. The NMR tube was ejected, the DMAP added, 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 2 dummy scans, 8 acquisitions, and a delay time between points which 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 similar manner to that of 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

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 According to Eq 10 and 11[a]

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

[a] Estimated standard deviations are given in parentheses.

0.4 mL of CD_3CN; then SEt_2 was added in 10-, 15-, 20-, 30-, or 40-fold excesses (Table III). The collection of data points for the reaction of 4 with 10-, 15-, and 20-fold excesses of SEt_2 was the same as described for DMAP; data points for the reactions of 30- and 40-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 using a NMR1 program.[8] Pseudo-first-order rate constants, k_{obs}, were obtained from the slope of the plots of the absolute integrals of the Cp (for DMAP) or SMe_2 (for SEt_2) ^1H NMR resonances 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).

Data collection and reduction

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.

A total of 4806 reflections were collected in the ±h,

+k, ±l quadrants. An empirical absorption correction was made, based on a series of psi-scans. The agreement factors for the averaging of 125 observed reflections were 1.9% based on intensity and 1.5% based on F_{obs}.

Structure solution and refinement

The position of the metal atom was taken from a Patterson map. The postions 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 two-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 refining 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 the final refinement, the two BF_4 orientations were 51 and 49%

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 using 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.

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	$RuS_2P_2F_8C_{15}B_2H_{30} \cdot 0.5CH_3CN$
Formula weight	631.67
Space group	$C_{2/c}$ (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
Crystal size, mm	0.40 x 0.25 x 0.20
$\mu(MoK_\alpha)$, cm^{-1}	9.01
Data collection instrument	Enraf-Nonius CAD4
Radiation (monochromated in incident beam)	MoK_α (λ = 0.71073 Å)
Orientation reflections, number, range (2θ)	25, $18° < 2\theta < 33°$
Temperature, °C	22 ± 1
Scan method	θ-2θ
Data collection range, 2θ, deg	0-50

Table IV (continued)

No. unique data, total:	4714
with $F_o^2 > 3\sigma(F_o^2)$:	2823
Number of parameters refined	202
Trans. factors, max., min. (psi scans)	1.00, 0.938
R^a	0.0733
$R_w{}^b$	0.1064
Quality-of-fit indicator^c	2.08
Largest shift/esd, final cycle	<0.01
Largest peak, e/Å^3	1.06

$^aR = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$.

$^bR_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|) + 0.001|F_o|^2]$.

^{c}Quality-of-fit $= [\Sigma w(|F_o| - |F_c|)^2 / (N_{obs} - N_{parameters})]^{1/2}$.

Table V. Positional and Thermal Parameters for $\{Cp(PMe_3)_2Ru[S(Me)C{=}C(H)(SMe)]\}(BF_4)_2 \cdot 1/2CH_3CN$ (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)

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[a] Estimated standard deviations are given in parentheses. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3) * [a^2*B(1,1) + b^2*B(2,2) + c^2*B(3,3) + ab(\cos \gamma)*B(1,2) + ac(\cos \beta)*B(1,3) + bc(\cos \alpha)*B(2,3)]$.

Table V (continued)

Atom	x	y	z	$B(\AA^2)^a$
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]

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[b] Atoms were refined isotropically.

Table V (continued)

Atom	x	y	z	$B(\text{Å}^2)^a$
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

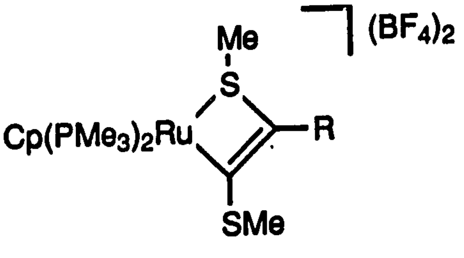
RESULTS AND DISCUSSION

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, 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 and 2b each show two SMe resonances which are nearly identical 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 $\{Cp(PMe_3)_2Ru[S(Me)C{=}CSMe]\}BF_4$[1] 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 ^{1}H 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. Based on a structural determination of Cp(CO)(PPh$_3$)Ru[(Z)-C(CO$_2$Me)=C(H)CO$_2$Me]^{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$_2$Me)=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 for 2, the β-vinyl resonance of the cis isomer (2a) is downfield of that for the trans isomer (2b). Another possible structure for 2b is a four-member metallacyclic complex as shown in eq 4; however, this seems less likely because of steric conjestion about the ruthenium center.



4

Complex 3 is prepared by the reaction of [MeSSMe$_2$]Tf and [Cp(PMe$_3$)$_2$Ru=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** and **2b** (Table I).

The ^{13}C NMR spectra of **2a**, **2b**, 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, 2b, and 3 are similar to those of the E and Z isomers of the vinyl complex $Cp(CO)[P(OPh)_3]Fe[C(Me)=C(Me)Ph]$;[14] 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 which 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, 2b, 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, 2b, 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 ($J_{PC} \approx 32$ Hz). The appearance of inequivalent PMe_3 resonances in the ^1H and ^{13}C NMR spectra of 2a, 2b, 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 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. Bases such as $Na[HBEt_3]$, NaOMe, and Na/Hg when reacted with 2a and/or 2b afford only decomposition products.

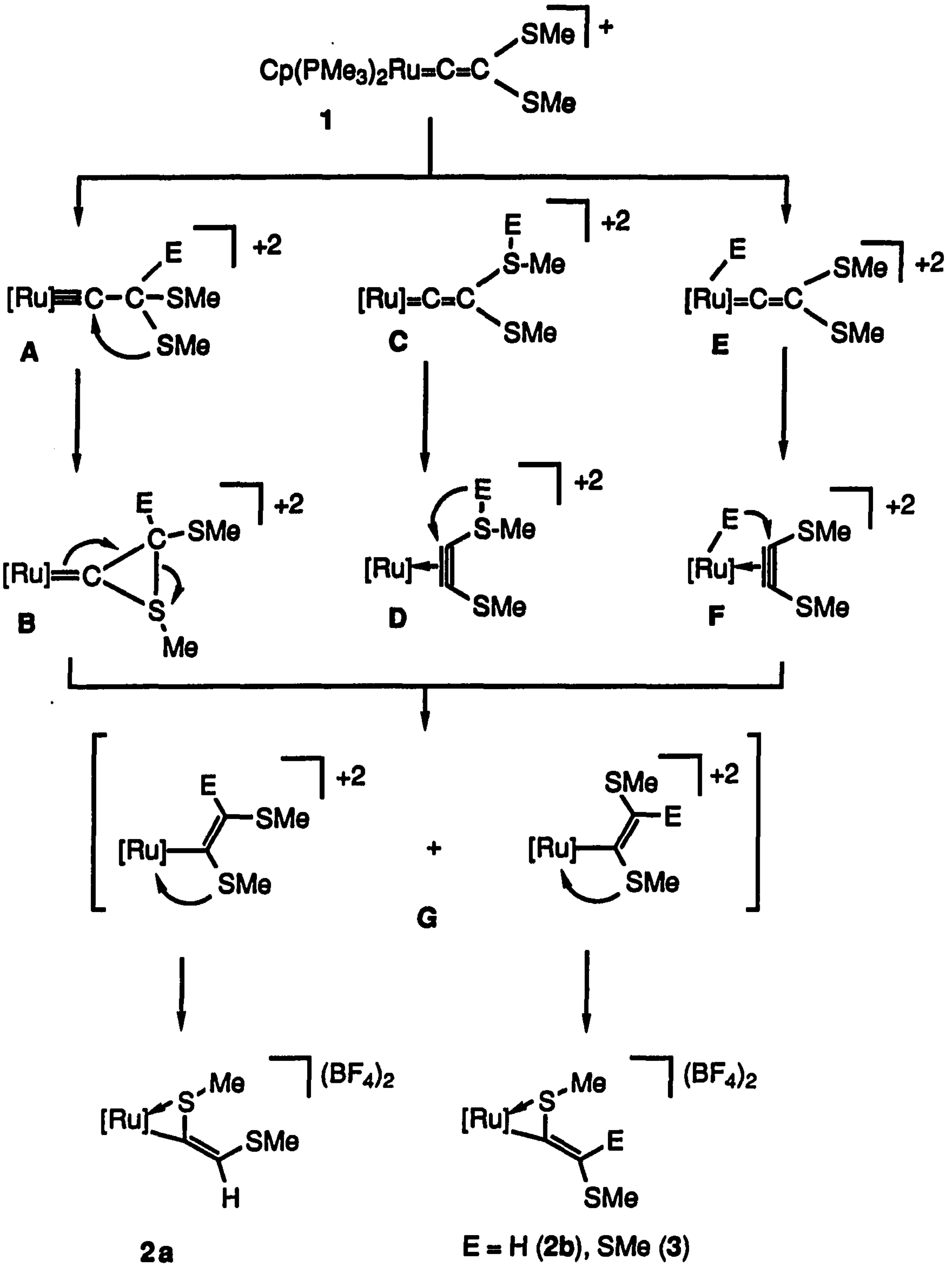
The addition of $[Me_3O]BF_4$ to $[Cp(PMe_3)_2Ru{=}C{=}C(SMe)_2]BF_4$ (1) gives the sulfonium vinylidene $[Cp(PMe_3)_2Ru{=}C{=}C(SMe_2)(SMe)](BF_4)_2$ (4) in 91% yield (Scheme I). Complex 4 was isolated as an air-stable yellow powder and was characterized by its ^1H and ^{13}C NMR spectra, IR, and elemental 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 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 di-cationic vinylidene complexes of $[Cp(PMe_3)_2Ru{=}C{=}C(R)SMe_n](BF_4)_n$ (R = H and Me; n = 1 and 2) have been presented previously.[1]

Mechanisms for the Formation of the Sulfur-Coordinated Vinyl Complexes 2a, 2b, and 3.

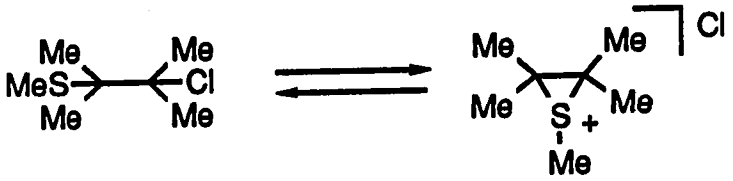
The formation of the sulfur-coordinated vinyl complexes 2a, 2b, and 3 (Scheme II) may be considered to proceed through initial addition of an electrophile to the β-vinylidene carbon of 1 to form a carbyne intermediate (A), to a sulfur of 1 to form a sulfonium vinylidene intermediate (C), or to the ruthenium metal center (E). These possible intermediates could rearrange to give the observed products.

The H^+ and MeS^+ (from $[MeSSMe_2]^+$) electrophiles could add initially to the β-vinylidene carbon of 1 to form a carbyne (A). This addition of electrophiles (such as H^+) to β-vinylidene carbons are well documented for molybdenum and tungsten compounds[16] to give complexes such as $(dppe)(CO)_3W({\equiv}C{-}CH_2Ph)$[16b] and $Cp[P(OMe)_3]_2Mo[{\equiv}C{-}C(H)(t{-}Bu)(SMe)]$.[16c] However, such additions to the β-carbon of



Scheme II

ruthenium vinylidene complexes have not been reported previously. Further rearrangement of the carbyne intermediate (**A**) could proceed when a lone pair of electrons from one of the SMe groups leans over and donates to the carbyne carbon to form a thiiranium-carbene intermediate (**B**). A related thiiranium compound[17] was observed at -60 °C from the ionization of 2,3-dimethyl-3-(methylthio)-2-chlorobutane in SO_2 (eq 5).



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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**, **2b**, 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 a sulfonium-vinylidene 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**,[1] 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**).

A third possible mechanism involves initial addition of

H^+ or MeS^+ to the ruthenium center to form a ruthenium-hydride or ruthenium-sulfide intermediate **E** (Scheme II). In the 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 6.[18]

$$Cp(PMe_3)_2RuCl + XPF_6 \longrightarrow [Cp(PMe_3)_2Ru(Cl)X]PF_6 \qquad 6$$

$$X = H, NO, Cl_2/NH_4PF_6$$

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

X-ray Crystal Structure of
$\{Cp(PMe_3)_2Ru[S(Me)C=C(H)SMe]\}(BF_4)_2 \cdot 1/3CH_3CN$ (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. The distances from the ruthenium to the five carbon atoms of the Cp ring range from 2.19 (1) to 2.28 (1) Å and fall within the range for $[Cp(PMe_3)_2Ru{=}C{=}C(H)(SMe_2)](BF_4)_2$ and several other ruthenium complexes reported in Section II.[1] The Ru-P distances of 2.337 (3) and 2.391 (4) Å are slightly longer than distances

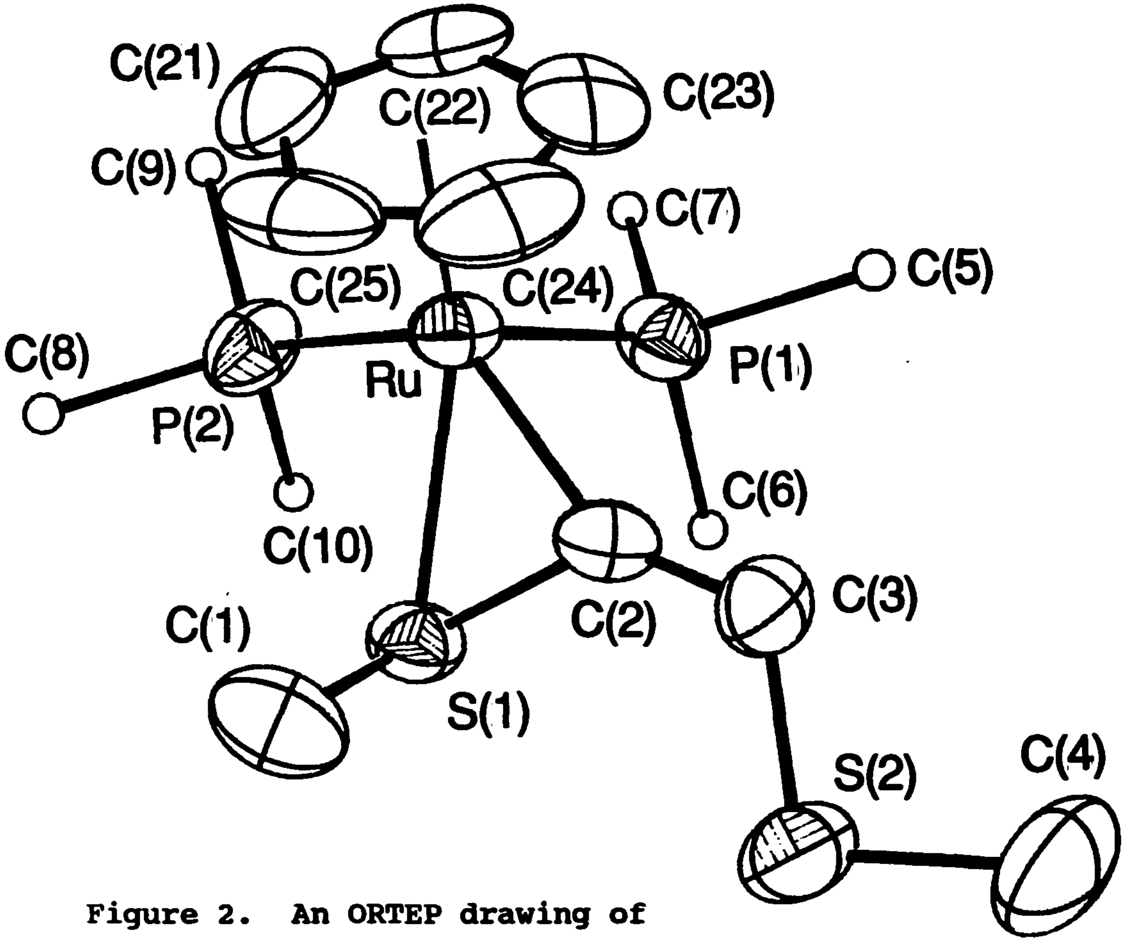

Figure 2. An ORTEP drawing of $\{Cp(PMe_3)_2Ru[S(Me)C{=}C(H)(SMe)](BF_4)_2 \cdot 1/2CH_3CN$ (2a). The phosphine-methyls are shown as arbitrary spheres

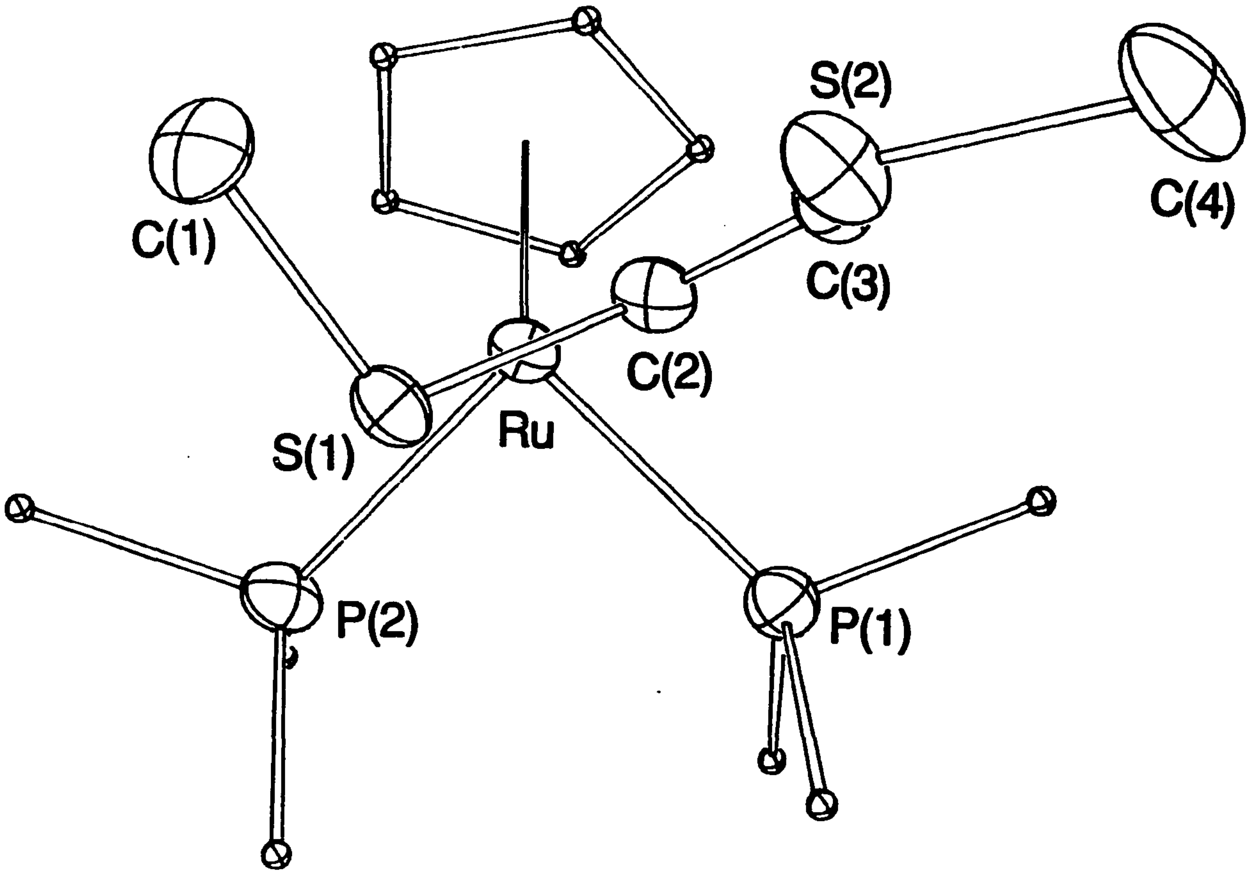

Figure 3. Another view of $[Cp(PMe_3)_2Ru[S(Me)C{=}C(H)(SMe)](BF_4)_2 \cdot 1/2CH_3CN$ (2a). The C_5-ring and phosphine-methyls are shown as arbitrary spheres

Table VI. Bond Distances and Angles for $\{Cp(PMe_3)_2Ru[S(Me)C{=}C(H)(SMe)]\}(BF_4)_2 \cdot 1/2CH_3CN$ (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)			

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[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).

Table VI (continued)

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)				

reported for $[Cp(PMe_3)_2Ru(\eta^2\text{-}CH_2{=}C{=}CH_2)]PF_6$[15] of 2.320 (1) and 2.297 (1) Å and $[Cp(PMe_3)_2Ru{=}C{=}C(H)(SMe_2)](BF_4)_2$[1] of 2.298 (2) and 2.334 (2) Å. The lengthening of the Ru-P bonds my be due to the steric crowding of the two PMe_3 groups caused by the η^2-vinyl sulfide ligand. The P(1)-Ru-P(2) angle at 90.5 (1)° is 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 = $[{=}C{=}C(H)(SMe_2)](BF_4)_2$,[1] 93.08 (7)°; and 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 trans to the sulfur (2.271 (6) Å). These differences were interpreted in terms of a stronger trans-influence for carbon than sulfur.[22,23]

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

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

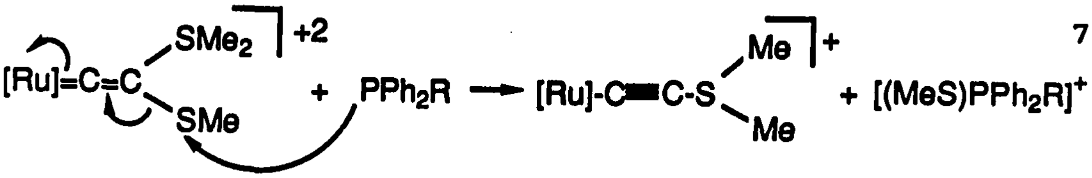
Compound	M-S	M-C	C-S
$\{Cp(PMe_3)_2Ru[S(Me)C{=}C(H)SMe]\}(BF_4)_2$ (2a)	2.380(3)	2.03(1)	1.73(1)
$Cp(CO)_2Mo[S(Me)CH_2]$[25]	2.442(3)	2.24(1)	1.78(1)
$[Me_2Ga(N_2C_3H_3)(OCH_2CH_2NMe_2)](CO)_2Mo[S(Me)CH_2]$[26]	2.475(6)	2.202(3)	1.744(3)
$(HBPz_3)(CO)_2W[S(Me)C(H)PPh_2]$[24]	2.440(9)	2.22(3)	1.80(3)
$(PPh_3)ClPd[S(Me)CH_2]$[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)

distances shown in Table VII; however, the distance is still much longer than the M=C(carbene) distance of 1.93 (2) Å in the metallacyclic carbene $\{(HBPz_3)(CO)_2W[\eta^2\text{-}CH(SMe)]\}$.[28] 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 $Cp(PPh_3)(CO)W(=CS\text{-}Ph)$[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) Å, -0.38 (2) Å, and 0.169 (1) Å, respectively, indicating that the vinyl ligand is relatively planar.

Reactions of 4 with Phosphines and Reducing Agents

The reaction of 4 with PPh_2R (R = Me or Ph) (Scheme I) gives $[Cp(PMe_3)_2Ru\text{-}C\equiv C\text{-}SMe_2]BF_4$ (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,[1] 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$_2$R in CH$_2$Cl$_2$. The resulting colorless oils of [(MeS)PPh$_2$R]Tf were characterized by ^{1}H and ^{31}P NMR, and when R = Me, a FAB mass spectra was also obtained. The [(MeS)PPh$_3$]ClO$_4$ compound was reported[31] previously as exhibiting a ^{1}H NMR methyl resonance at 2.47 ppm (d, J_{PH} = 15 Hz), which is identical to that obtained in our studies (see experimental section). The [(MeS)PPh$_2$Me]Tf compound has not been reported previously. During the reactions of 4 with the phosphines, it was observed that the resonances for [(MeS)PPh$_2$R]$^+$ disappeared with time and new peaks appeared. The new resonances were identified as [MePPh$_2$R]Tf and S=PPh$_2$R by an independent reaction; a solution of [(MeS)PPh$_2$Me]Tf and excess PPh$_2$Me in CH$_2$Cl$_2$ was refluxed for 1 h, and the solution was concentrated under reduced pressure; Et$_2$O was added to precipitate [Me$_2$PPh$_2$]Tf and S=PPh$_2$Me. The compounds were characterized by ^{1}H NMR and GCMS.[32]

Although the vinylidene ligand in its cationic complexes often undergoes 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 7).



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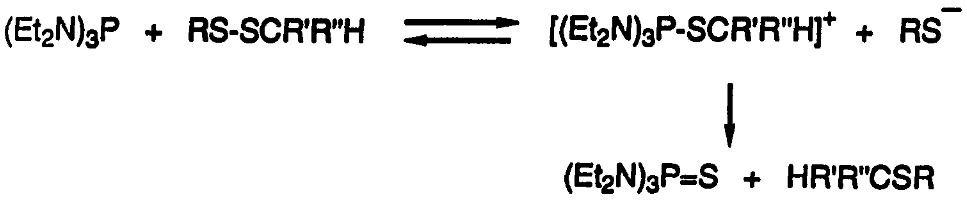
Harpp and Gleason[34] have observed similar phosphine products in the reaction of PR_3 and a disulfide, which gave in the first step a thioalkyltriaminophosphonium and RS^- (eq 8).



$$(Et_2N)_3P + RS\text{-}SCR'R''H \rightleftharpoons [(Et_2N)_3P\text{-}SCR'R''H]^+ + RS^- \downarrow (Et_2N)_3P{=}S + HR'R''CSR$$

8

The RS^- subsequently attacks the carbon adjacent 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 or 2) undergo one- (n = 1) or two-electron (n = 2) reductions to give $Cp(PMe_3)_2Ru\text{-}C{\equiv}C\text{-}Me$. The reactions and mechanisms have been discussed in Section II.[1] Similarly, the reduction of 4 with Na/Hg amalgam gives $Cp(PMe_3)_2Ru\text{-}C{\equiv}C\text{-}SMe$ (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-equivalent aliquots of

Na[HBEt$_3$]. The ^{1}H 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 suggest that this reduction does not favor the one-electron reduction over the two-electron reduction.

Reactions of [Cp(PMe$_3$)$_2$Ru=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 one equivalent of NaSR (R = Me and Et) to 4 gives products 1 and [Cp(PMe$_3$)$_2$Ru=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 ^{1}H and ^{13}C NMR (Tables I and II), IR, FAB mass spectra, and elemental analyses. In the ^{1}H and ^{13}C NMR spectra of 7 the vinylidene resonances are similar to those of 1 and are discussed in detail in Section II.[1] Mercaptides, NaSR, can also act as reducing agents in the reaction with 4. In reactions with an excess (over 2 equivalents) of NaSR, the acetylides Cp(PMe$_3$)$_2$Ru-C≡C-X (X = SMe (5) for R = Me; X = SMe (5) and SEt for R = Et) were observed as side-products in the ^{1}H NMR spectra. The thioethyl acetylide, Cp(PMe$_3$)$_2$Ru-C≡C-SEt, was identified in the ^{1}H NMR spectrum; however, the complex was not successfully separated from 5 which was also present in the reaction mixture.

The reactions of 4-NC_5H_4R (R = H, Et, NMe_2) and SEt_2 with 4 give the dicationic vinylidene complexes 8, 9, 10, and 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 $[Cp(PMe_3)_2Ru{=}C{=}C(SMe_2)(R)](BF_4)_2$:[1] 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 $[Cp(PMe_3)_2Ru{=}C{=}C(NC_5H_5)(SMe)](BF_4)_2$ (8) and a red powder of 1 collected in 57% and 31% yield, 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 coworkers[35] have reported that EtO^- attacks a sulfonium methyl group as shown in eq 9 to give a thioether compound.

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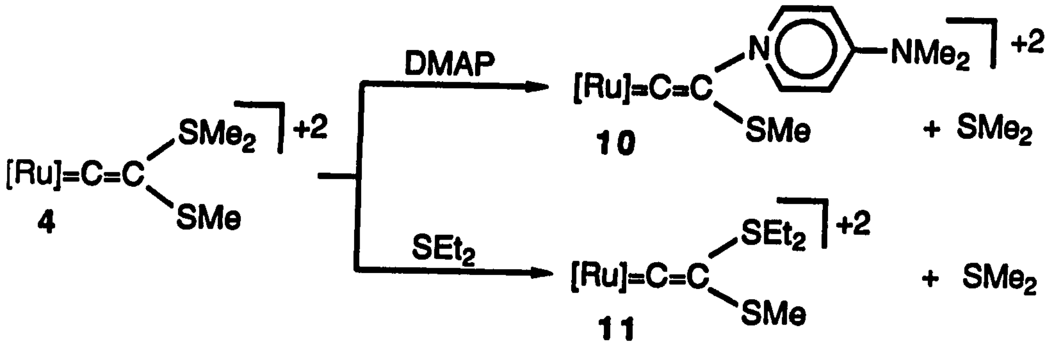
The identification of $[Me\text{-}NC_5H_5]^+$ as a product of the reaction of 4 with pyridine was made by comparing the ^1H NMR spectrum of this reaction run in CD_3CN in an NMR tube with the spectrum of $[Me\text{-}NC_5H_5]Tf$[36] prepared from the reaction of $MeSO_3CF_3$ with pyridine in a 5-mm NMR 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 $4\text{-}NC_5H_4Et$ (0.001 mL, 0.009 mmol) in CD_3CN and heated to 70 °C for 20 h. The ^1H NMR spectrum of this reaction 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 10 and 11 proceed by either a nucleophilic attack or a dissociative mechanism.



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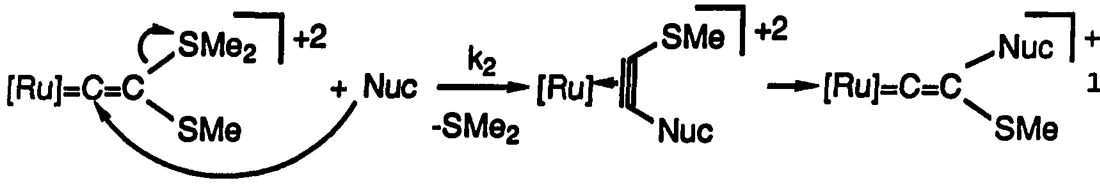
11

Nucleophilic attack would 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 12.



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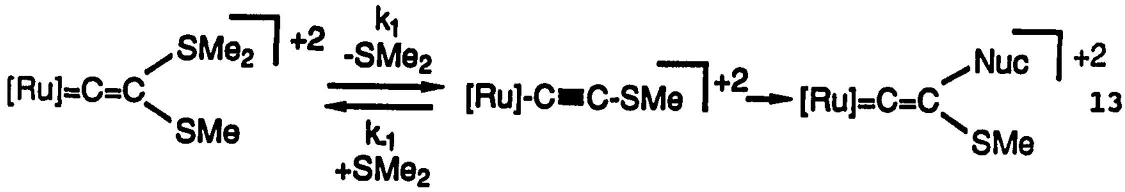
This η^2-acetylene complex could then rearrange via a 1,2-SMe migration to the vinylidene product 10 or 11. Evidence for such 1,2-SMe migration has been obtained for 1 and mechanisms for this rearrangement have been discussed in Section II.[1]

A dissociative mechanism for reactions 10 and 11 would involve initial SMe_2 dissociation to give a 16-electron acetylide intermediate as shown in eq 13.



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Nucleophilic addition of the nucleophile to the β-carbon of the acetylide intermediate would give the observed vinylidene complex.

Rates of reactions 10 and 11 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 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 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 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}

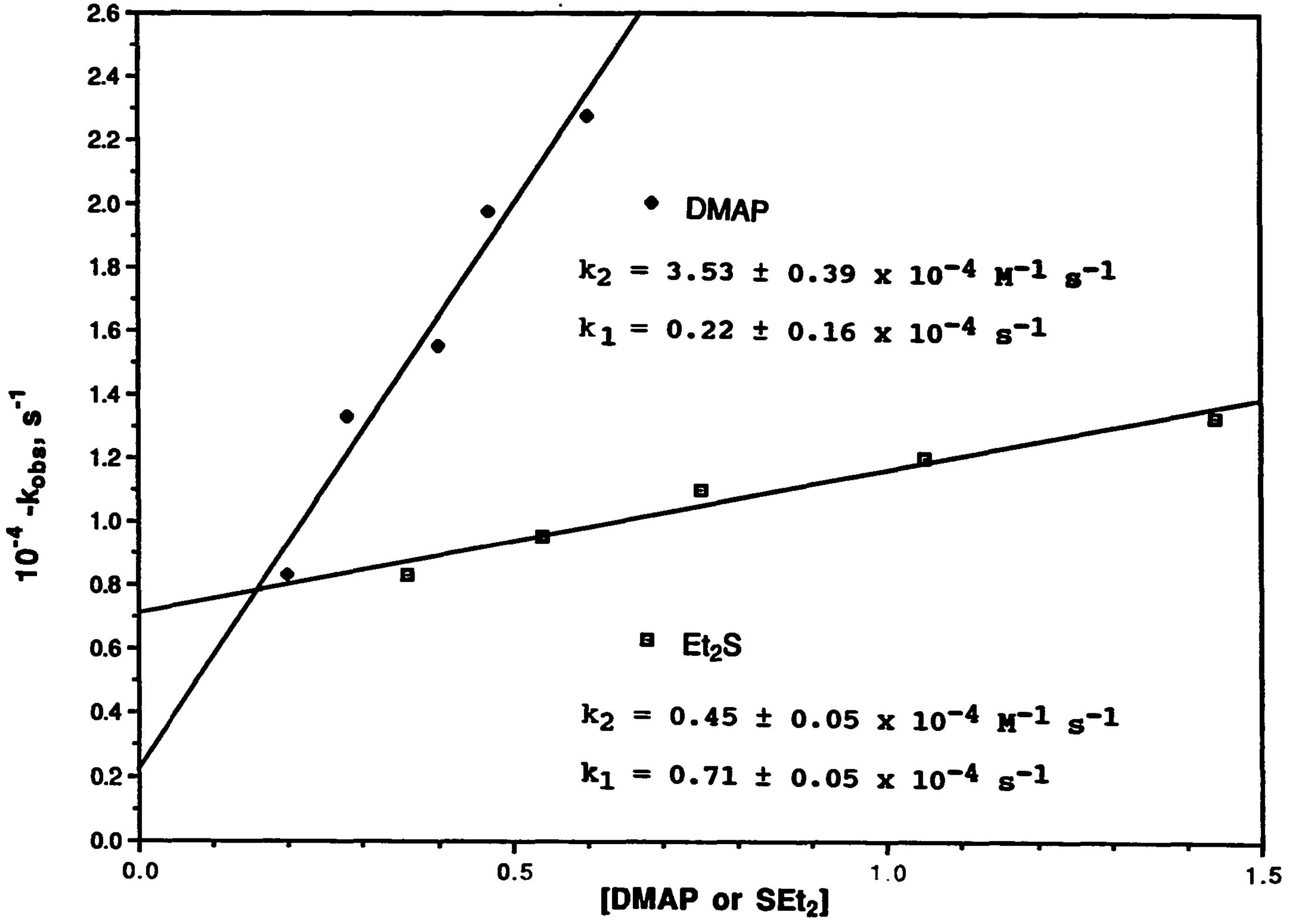

Figure 1. Plot of k_{obs} values versus the concentration of DMAP (at 0 °C) and SEt_2 (at 70 °C) for the reaction shown in eqs 10 and 11

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 pathway, the reaction with the less nucleophilic Et_2S occurs to a significant extent by both the k_2 and a k_1 pathways.

Supporting a nucleophilic attack mechanism (eq 12) 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 than those of the vinylidene complex 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 ^1H NMR Cp resonances 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 pseudo-doublet 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, 2b, 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)[4] upon warming the NMR tube from the 0 °C of the reaction to room temperature. The acetonitrile complex was observed in increasingly higher 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)$(CO)_3W(\equiv C-CH_2Ph)$[16b] or at the metal center to give metal hydride or alkyl complexes. In contrast the thiomethyl vinylidene $[Cp(PMe_3)_2Ru=C=C(SMe)_2]BF_4$ (1) reacts with electrophiles either at a sulfur to give the sulfonium vinylidene complex 4 (Scheme I) or at a vinylidene carbon to give a sulfur-coordinated vinyl complex as in 2a, 2b, 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 sulfonium vinylidene 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 $[Cp(PMe_3)_2Ru-C\equiv C-SMe_2]BF_4$ (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 a 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 the previous studies[1] that the presence of

MeS groups has a major influence on the reactivity of the vinylidene ligand.

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32. ^{1}H NMR (CDCl$_3$): [PPh$_2$Me$_2$]Tf. δ 7.79 (m, 10H), 2.45 (d, J_{PH} = 14.1 Hz, 6H). **S=PPh$_2$Me.** 7.84 (m, 10H), 2.94 (d, J_{PH} = 13.2 Hz, 3H); GCMS, 232 (M^+), 217 (M^+-Me), 200 (M^+-S).

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36. ^{1}H NMR (CD$_3$CN): 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).

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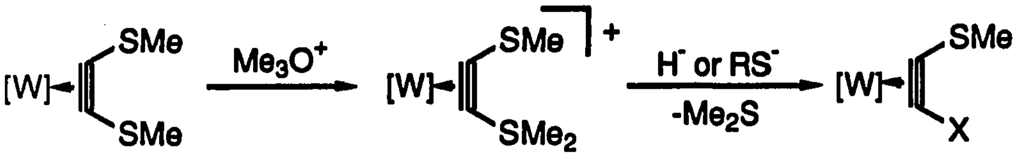
SECTION IV. ELECTROPHILIC AND NUCLEOPHILIC REACTIONS OF COMPLEXES FORMED FROM 2,5-DITHIAHEX-3-YNE (MeSC≡CSMe) AND TUNGSTEN CARBONYLS

ABSTRACT

The alkyne, $MeSC{\equiv}CSMe$, reacts with tungsten(II) carbonyl complexes to yield π-alkyne products, $CpW(MeSC{\equiv}CSMe)_2Cl$ (1), $W(CO)(MeSC{\equiv}CSMe)(S_2CNR_2)_2$ {R = Me (2a) and Et (2b)}, and $W(MeSC{\equiv}CSMe)_2(S_2CNR_2)_2$ {R = Me (3a) and Et (3b)}. The sulfonium complex $[CpClW(MeSC{\equiv}CSMe)(MeSC{\equiv}CSMe_2)]BF_4$ (4) whose structure was established by an X-ray diffraction study, was prepared by the reaction of 1 with Me_3O^+.



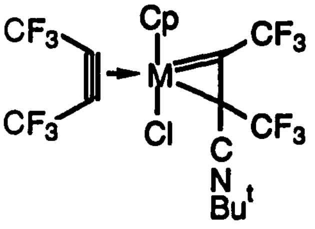
1 4 6 (X = H), 7 (X = SR)

$[W] = CpCl(MeSC{\equiv}CSMe)W$

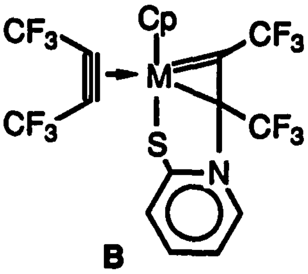
The $Cp(PMe_3)_2Ru^+$ group also adds to a sulfur in 1 to give $[CpClW(MeSC{\equiv}CSMe)(MeSC{\equiv}CS(Me)Ru(PMe_3)_2Cp]BF_4$ (5). Nucleophilic attack by H^- donors and RS^- on 4 displaces Me_2S to yield $CpW(MeSC{\equiv}CSMe)(MeSC{\equiv}CX)Cl$ {R = H (6), SC_6H_5 (7a), and 4-SC_6H_4Me (7b)} and Me_2S.

INTRODUCTION

It has been noted[1] that π-coordination of acetylenes to transition metals activates the alkyne bond towards reactions with nucleophiles. This is particularly pronounced for alkynes with electron-withdrawing CF_3 groups. A variety of novel complexes (eq 1) have been obtained from reactions of nucleophiles with coordinated $CF_3C\equiv CCF_3$ and $RC\equiv CR'$ in such complexes as $CpM(CF_3C\equiv CCF_3)_2Cl$[2-6] (M = Mo and W) and $[Cp\{P(OMe)_3\}_2Mo(RC\equiv CR')]BF_4$[7] (R = H, R' = Bu-t, Pr-i, R = Me, R' = Ph).



A



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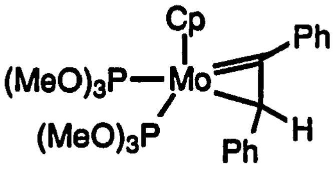
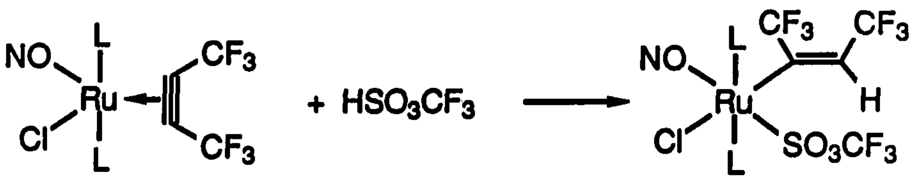


C

1

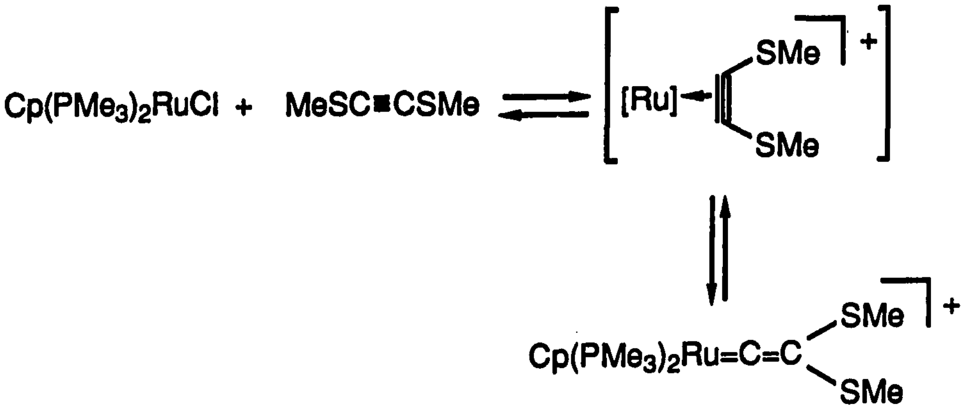
Although much less common,[1] electrophiles add to coordinated acetylenes to give σ-vinyl complexes. For example, the complex $RuCl(NO)L_2(CF_3C\equiv CCF_3)$[8] (L = PPh_3 and PPh_2Me) when reacted with HSO_3CF_3 gives the cis-vinyl complex (β-hydrogen cis to the metal center) shown in eq 2.



2

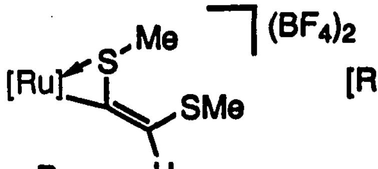
The formation of the vinyl complex was suggested to result from initial addition of the proton to the metal center forming a ruthenium hydride intermediate, followed by proton transfer to the alkyne.

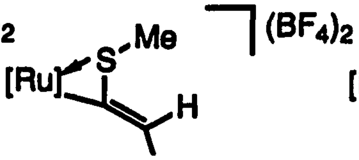
I previously[9] examined the effects of the MeS groups on reactions of $MeSC\equiv CSMe$ with $Cp(PMe_3)_2RuCl$. I noted that this reaction gives the thiomethyl vinylidene $[Cp(PMe_3)_2Ru{=}C{=}C(SMe)_2]BF_4$; this presumably occurs via an η^2-alkyne intermediate which rearranges to the product by a 1,2-SMe migration (eq 3).

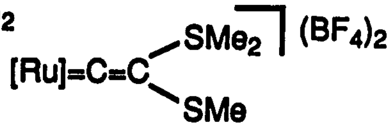


3

I further discovered that the thiomethyl vinylidene complex reacts with electrophiles (H^+, SMe^+, and Me^+) to give the following complexes (eq 4) where [Ru] = $Cp(PMe_3)_2Ru$.

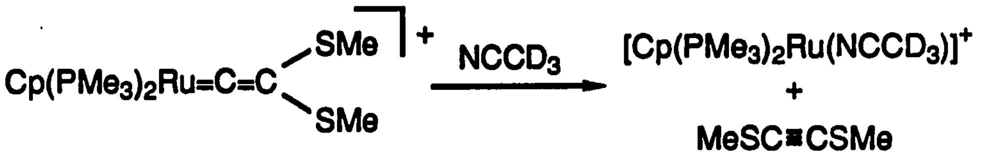

D


E

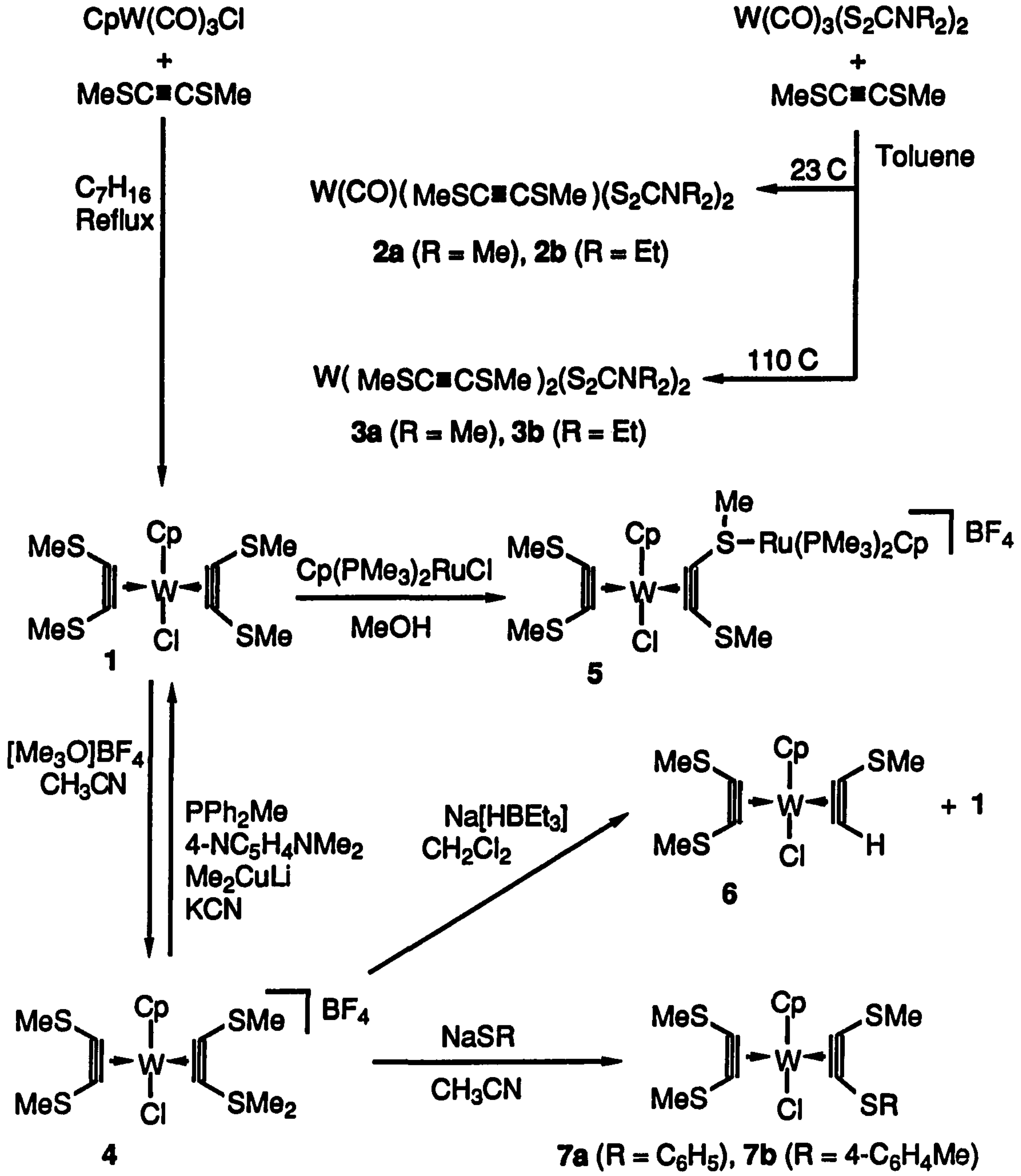

F

4

The formation of D and E was suggested to occur as a result of an equilibrium between the vinylidene and π-alkyne complex (eq 3). Such an equilibrium was supported by the displacement of MeSC≡CSMe from the thiomethyl vinylidene complex by CD_3CN (eq 5).


$$[Cp(PMe_3)_2Ru{=}C{=}C(SMe)_2]^+ \xrightarrow{NCCD_3} [Cp(PMe_3)_2Ru(NCCD_3)]^+ + MeSC{\equiv}CSMe \qquad 5$$

Connor and Hudson[10] previously reported the synthesis of mononuclear complexes of MeSC≡CSMe, e.g., $CpM(MeSC{\equiv}CSMe)_2Cl$, $M(CO)(MeSC{\equiv}CSMe)_3$ (M = Mo and W), $W(CO)(dmpe)(MeSC{\equiv}CSMe)_2$, and $W(dmpe)(MeSC{\equiv}CSMe)_2$; however, no reactions of the alkyne ligand in these complexes were described. With a view toward expanding the understanding of the chemistry of MeSC≡CSMe, I set out to prepare tungsten complexes of this ligand and to compare and contrast their structures and reactivities with those of the ruthenium complexes.


CpW(CO)3Cl
+
MeSC≡CSMe
C7H16
Reflux
W(CO)3(S2CNR2)2
+
MeSC≡CSMe
Toluene
23 C
W(CO)(MeSC≡CSMe)(S2CNR2)2
2a (R = Me), 2b (R = Et)
110 C
W(MeSC≡CSMe)2(S2CNR2)2
3a (R = Me), 3b (R = Et)
MeS
MeS
Cp
W
Cl
SMe
SMe
1
Cp(PMe3)2RuCl
MeOH
Me
S−Ru(PMe3)2Cp
BF4
SMe
5
[Me3O]BF4
CH3CN
PPh2Me
4-NC5H4NMe2
Me2CuLi
KCN
Na[HBEt3]
CH2Cl2
H
+ 1
6
SMe2
BF4
4
NaSR
CH3CN
SR
7a (R = C6H5), 7b (R = 4-C6H4Me)

Scheme I

EXPERIMENTAL SECTION

General Procedures

All reactions, filtrations, distillations, and recrystallizations were carried out under N_2 using standard inert atmosphere and Schlenk techniques.[11] Methylene chloride, hexane, cyclohexane, toluene, 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. Chloroform was dried and stored over molecular sieves (4 Å). Methanol was dried over magnesium methoxide, which was generated from magnesium turnings and iodine in absolute methanol, and distilled under N_2.[12] 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. ^1H NMR spectra were obtained with a Nicolet NT-300 (300 MHz) spectrometer using Me_4Si (TMS) as the internal reference. Proton-decoupled solution ^{13}C NMR spectra were recorded on the Nicolet NT-300 (75.46 MHz) or Bruker WM-200 (50.29 MHz) instruments using the deuteriated solvents as internal references. Proton-decoupled solid state ^{13}C NMR spectra were recorded on a Bruker MSL-300 (75.47 MHz) spectrometer; rotation frequencies were varied between 3.0 and 4.5 kHz to determine the peaks due to spinning side bands. Fast atom bombardment (FAB, 3-nitrobenzyl alcohol matrix) spectra were obtained using a Kratos MS-50 spectrometer. Electron-ionization mass spectra (EIMS) were run on a Finnigan 4000 spectrometer. Photochemical reactions were carried out under N_2 in a quartz tube, using a Canrad-Hanovia medium pressure, 450 Watt, quartz, mercury vapor lamp (40-48% UV, 40-43% visible, the balance is IR). Elemental microanalyses were performed by Galbraith Laboratories Inc., Knoxville, TN.

The compounds $[CpW(CO)_3]_2$[13] (Cp = η^5-C_5H_5), $W(CO)_3(S_2CNR_2)_2$ (R = Me and Et),[14] $Cp(PMe_3)_2RuCl$,[15] and MeSC≡CSMe[16] were prepared by using previously described procedures. All other chemicals were used as received from commercial sources.

Preparation of $CpW(CO)_3Cl$

The preparation of $CpW(CO)_3Cl$ has been reported[17] previously; however, we have found that the following modification was faster and gave higer yields for large scale preparations. A solution of $[CpW(CO)_3]_2$ (2.00 g, 3.00 mmol) in 240 mL of CCl_4 and 60 mL of THF was irradiated for 20 min or until the IR showed no tungsten-dimer remaining. The solution was filtered to remove any insoluble products, and the solvents were removed by rotary evaporation. The resulting powdery residue was dissolved in MeOH (3 x 50 mL) and the solution was filtered to remove any remaining unreacted tungsten dimer. The MeOH was removed by rotary evaporation, and the $CpW(CO)_3Cl$ product was purified by recrystallization from CH_2Cl_2/hexanes at -20 °C. The dark orange crystalline $CpW(CO)_3Cl$ was collected in 50% yield (1.09 g, 3.00 mmol) and identified by its spectra.[17] ^1H NMR ($CDCl_3$): δ 5.77 (s, Cp); IR (hexanes): ν(CO) 2055 m, 1971 vs, 1951 s cm^{-1}.

$CpW(MeSC{\equiv}CSMe)_2Cl$ (1)

A mixture of $CpW(CO)_3Cl$ (108 mg, 0.30 mmol) and $MeSC{\equiv}CSMe$ (100 mg, 0.08 mL, 0.88 mmol) was refluxed in 50 mL of heptane for 4 h under N_2. The resulting yellow-brown solution was evaporated to dryness under vacuum. The residue was extracted with CH_2Cl_2 (3 x 10 mL), and the extract was chromatographed on alumina (Fischer, 80 - 200 mesh, 10 x 150 mm) packed in hexanes. A yellow band which was eluted with CH_2Cl_2 was evaporated to dryness under reduced pressure to give a yellow powder of 1 in 30% yield (47 mg, 0.09 mmol). Anal. Calcd for $C_{13}H_{17}ClS_4W$: C, 29.98; H, 3.29. Found: C, 29.68; H, 3.23. ^1H NMR ($CDCl_3$): δ 5.92 (s, Cp), 2.74 (s, SMe); ^{13}C NMR (d_6-acetone): δ 175.20 (CC), 106.46 (Cp), 20.04 (SMe); ^{13}C NMR (solid state): δ {175.66, 173.99, 172.04 (CC)}, 104.48 (Cp), {21.72, 19.79

(SMe)}; EIMS (70 eV): m/e 520 [M^+], 505 [M^+-Me], 402 [M^+-MeSC=CSMe], 387 [M^+-(Me + MeSC=CSMe)]. Complex 1 has been previously characterized by Connor and Hudson.[10a]

$W(CO)(MeSC{=}CSMe)(S_2CNR_2)_2$
(2a for R = Me, 2b for R = Et)

A solution of $W(CO)_3(S_2CNR_2)_2$ (960 mg, 1.9 mmol for R = Me; 123 mg, 0.23 mmol for R = Et) and MeSC=CSMe (1.3 g, 1.0 mL, 11.0 mmol for R = Me and Et) was stirred in 50 mL of toluene at room temperature for 1 h under N_2. The solution was reduced to 10 mL; addition of 50 mL of cyclohexane caused the green product to separate. After drying under vacuum, a green powder of 2a was collected in 87% yield (943 mg, 1.7 mmol); 2b was obtained as a green oil. 2a. Anal. Calcd for $C_{11}H_{18}N_2OS_6W$: C, 23.16; H, 3.18. Found C, 22.84; H, 3.45. ^1H NMR ($CDCl_3$): δ 3.31 (s, 3 H, NMe), 3.23 (s, 3 H, NMe), 3.22 (s, 6 H, NMe), 2.99 (s, 6 H, SMe); ^{13}C NMR (CD_2Cl_2): δ 244.05 (CO), {212.90, 203.12 (C-N)}, 201.34 (CC), {40.41, 39.43, 39.38, 39.24 (NMe)}, 20.22 (SMe); EIMS (70 eV): m/e 570 [M^+ not observed], 542 [M^+-CO], 424 [M^+-(CO + MeSC=CSMe)]; IR (CH_2Cl_2): ν(CO) 1918 cm^{-1}. 2b. ^1H NMR ($CDCl_3$): δ 3.88 (m, 2 H, NCH_2), 3.63 (m, 6 H, NCH_2), 2.99 (s, 6 H, SMe), 1.31 (t, J_{HH} = 7.2 Hz, 3 H, CH_3), 1.23 (t, 9 H, CH_3); MS (70 eV): m/e 626 [M^+ not observed], 598 [M^+-CO], 480 [M^+-(CO + MeSC=CSMe)]; IR (CH_2Cl_2): 1914 cm^{-1}.

$W(MeSC{\equiv}CSMe)_2(S_2CNR_2)_2$
(3a for R = Me, 3b for R = Et)

A solution of $W(CO)_3(S_2CNR_2)_2$ (0.220 g, 0.43 mmol for R = Me; 830 mg, 1.5 mmol for R = Et) and MeSC≡CSMe (260 mg, 0.20 mL, 2.2 mmol for R = Me; 870 mg, 0.70 mL, 7.4 mmol for R = Et) were refluxed in 50 mL of toluene for 1 h under N_2. The solvent was removed from the resulting yellow-brown solution under vacuum. The residue was extracted with 5 mL of CH_2Cl_2, and the extract was chromatographed on alumina (Fisher, 80 - 200 mesh, 10 x 40 mm) packed in hexanes. A single yellow band was eluted with toluene. The collected toluene solution was reduced under vacuum to 5 mL, and 30 mL of cyclohexane was added producing a bright yellow precipitate of the product which was collected and dried under vacuum. Yellow powders of 3a and 3b were collected in 35% (101 mg, 0.15 mmol) and 31% yields (333 mg, 0.47 mmol), respectively. 3a. Anal. Calcd for $C_{14}H_{24}N_2S_8W$: C, 25.45; H, 3.66. Found: C, 25.63; H, 4.08. ^1H NMR ($CDCl_3$): δ 3.36 (s, 6 H, NMe), 3.14 (s, 6 H, NMe), 2.76 (s, 6 H, SMe), 2.74 (s, 6 H, SMe); ^{13}C NMR (CD_2Cl_2): δ 207.24 (C-N), {178.68, 177.21 (CC)}, {39.39, 38.83 (NMe)}, {20.06, 19.90 (SMe)}; EIMS (70 eV): m/e 660 [M^+], 542 [M^+-MeSC≡CSMe], 424 [M^+-2 MeSC≡CSMe]. 3b. ^1H NMR ($CDCl_3$): δ 3.97 (m, 2 H, NCH_2), 3.65 (m, 4 H, NCH_2), 3.51 (m, 2 H, NCH_2), 2.75 (s, 12 H, SMe), 1.36 (t, J_{HH} = 6.9 Hz, 6 H, CH_3), 1.19 (t, J_{HH} =

6.9 Hz, 6 H, CH_3); MS (70 eV): m/e 716 [M^+], 598 [M^+-MeSC≡CSMe], 480 [M^+-2 MeSC≡CSMe].

Reaction of 1 with $[Me_3O]BF_4$

To a solution of 1 (150 mg, 0.28 mmol) in 10 mL of CH_3CN, $[Me_3O]BF_4$ (69 mg, 0.47 mmol) was added. The solution was stirred for 5 h, and the solvent was removed under reduced pressure. The residue was dissolved in CH_2Cl_2 (2 x 5 mL) and the resulting solution was filtered through a column of Celite (40 x 5 mm). The solvent was reduced to 3 mL, and 15 mL of Et_2O was added to give a yellow precipitate of $[CpClW(MeSC{\equiv}CSMe)(MeSC{\equiv}CSMe_2)]BF_4$ (4) which was dried and collected in 63% yield (110 mg, 0.18 mmol). Anal. Calcd for $C_{14}H_{20}BClF_4S_4W$: C, 27.01; H, 3.24. Found: C, 26.91; H, 3.19. ^1H NMR ($CDCl_3$): δ 6.03 (s, Cp), 3.40 (s, 3 H, SMe_2), 3.15 (s, 3 H, SMe_2), 2.86 (s, 3 H, SMe), 2.83 (s, 6 H, SMe); ^{13}C NMR (d_6-acetone): δ {209.81, 191.25, 186.50, 139.36 (CC)}, 106.80 (Cp), {69.22, 29.67, 21.81, 20.43 (SMe)}; ^{13}C NMR (solid state): δ {[192.86, 190.49, 188.41, 182.61, 180.76, 178.47], [142.55, 139.72, 137.35] (CC)}, {105.66, 104.34 (Cp)}, {28.99, 23.54, 22.59, 20.78 (SMe)}; MS (FAB): m/e 535 [M^+], 473 [M^+-Me_2S].

Reaction of 1 with $Cp(PMe_3)_2RuCl$

A mixture of 1 (52 mg, 0.10 mmol), $Cp(PMe_3)_2RuCl$ (36 mg, 0.10 mmol) and NH_4BF_4 (42 mg, 0.40 mmol) in 20 mL of MeOH was stirred for 10 h under N_2. The solvent was removed under vacuum. The yellow residue was dissolved in CH_2Cl_2 (3 x 5 mL), and the solution was passed through a column of Celite (40 x 5 mm). The solvent was reduced to 3 mL, and 20 mL of Et_2O was added to give a yellow powder of $[CpClW(MeSC{=}CSMe)(MeSC{=}CS(Me)Ru(PMe_3)_2Cp]BF_4$ (5) which was dried and collected in 58% yield (54 mg, 0.058 mmol). Anal. Calcd for $C_{24}H_{40}BClF_4P_2RuS_4W$: C, 31.13; H, 4.35. Found: C, 31.06; H, 4.49. ^1H NMR ($CDCl_3$): δ 5.92 (s, 5 H, CpW), 4.84 (s, 5 H, CpRu), 2.97 (s, 3 H, SMe), 2.79 (s, 3 H, SMe), 2.78 (s, 6 H, SMe), 1.52 (d, J_{PH} = 8.3 Hz, 9 H, PMe_3), 1.42 (d, J_{PH} = 8.3 Hz, 9 H, PMe_3); ^{13}C NMR ($CDCl_3$): δ {180.54, 174.20, 105.35 (CC)}, 104.34 (CpW), 82.43 (CpRu), 33.09 (S(Me)Ru), 22.54 (t, J_{PC} = 6.0 Hz, PMe_3), 22.03 (t, J_{PC} = 6.0 Hz, PMe_3), {20.79, 19.75 (SMe)}; MS (FAB): m/e 839 [M^+], 319 [$Cp(PMe_3)_2Ru^+$].

Reaction of 4 with $Na[HBEt_3]$

To a solution of 4 (46 mg, 0.074 mmol) in 8 mL of CH_2Cl_2, $Na[HBEt_3]$ (0.15 mL, 0.15 mmol) was added under N_2. The solution was stirred for 10 min and the solvent removed under reduced pressure. The yellow residue was dissolved in

Et_2O (3 x 5 mL), and the solution was filtered through a small column of alumina (Fisher, 80 - 200 mesh, 40 x 5 mm). The solvent was removed from the resulting yellow solution under reduced pressure to give a yellow powder of a mixture of CpW(MeSC≡CSMe)(MeSC≡CH)Cl (6) and 1 in a 1:1 ratio, as determined by the ^1H NMR spectrum. The mixture of 1 and 6 was collected in approximately 98% yield (38 mg, 0.072 mmol). Even after several attempts to separate the mixture by chromatography, a pure sample of 6 could not be obtained; it was characterized by its spectra. ^1H NMR (CD_3CN): δ 9.23 (s, 1 H, ≡CH), 5.79 (s, 5 H, Cp), 2.73 (s, 6 H, SMe), 2.65 (s, 3 H, SMe); ^{13}C NMR (CD_3CN): δ {176.54, 176.47, 160.29 (CC)}, 104.63 (Cp), {23.17, 20.12, 20.05 (SMe)}; EIMS (70 eV): m/e 474 [M^+], 459 [M^+-Me], 427 [M^+-SMe], 402 [M^+-MeSC≡CH], 387 [M^+-(Me + MeSC≡CH)].

Reactions of 4 with NaS-4-C_6H_4R
(7a for R = H, 7b for R = Me)

A mixture of 4 (24 mg, 0.039 mmol for R = H; 16 mg, 0.026 mmol for R = Me) and NaS-4-C_6H_4R (10 mg, 0.076 mmol for R = H; 14 mg, 0.096 mmol for R = Me) in 8 mL of CH_3CN was stirred for 10 h under N_2. The solvent was removed from the yellow solution under reduced pressure. The resulting residue was dissolved in CH_2Cl_2 (3 x 5 mL) and chromatographed on alumina (Fisher, 5% water, 80 - 200 mesh, 10 x 40 mm) packed in hexanes. A single yellow band was eluted with CH_2Cl_2. The solvent was removed from the resulting yellow solution under vacuum to give yellow oils of $CpW(MeSC{\equiv}CSMe)(MeSC{\equiv}CSC_6H_5)Cl$ (7a) in 79% yield (18 mg, 0.031 mmol) and of $CpW(MeSC{\equiv}CSMe)(MeSC{\equiv}CS\text{-}4\text{-}C_6H_4Me)Cl$ (7b) in 84% yield (13 mg, 0.022 mmol). 7a. Anal. Calcd for $C_{18}H_{19}ClS_4W$: C, 37.09; H, 3.29. Found: C, 37.03; H, 3.39. ^1H NMR ($CDCl_3$): δ 7.45 (m, 2 H, Ph), 7.34 (m, 3 H, Ph), 5.89 (s, 5 H, Cp), 2.78 (s, 6 H, SMe), 2.39 (s, 3 H, SMe); ^{13}C NMR (CD_3CN): δ 176.13 (CC), 136.76 (1-C), 133.25 (3,5-C), 129.79 (2,6-C), 129.23 (4-C), 106.05 (Cp), {20.32, 19.77 (SMe)}; EIMS (70 eV): m/e 582 [M^+], 473 [M^+-SPh]. 7b. ^1H NMR ($CDCl_3$): δ 7.36 (d, J_{HH} = 8.12 Hz, 2 H, 3,5-H), 7.16 (d, J_{HH} = 8.10 Hz, 2 H, 2,6-H), 5.89 (s, 5 H, Cp), 2.78 (s, 6 H, SMe), 2.39 (s, 3 H, Me or SMe), 2.38 (s, 3 H, Me or SMe).

X-ray Structure Determination of $[CpClW(MeSC{\equiv}CSMe)(MeSC{\equiv}CSMe_2)]BF_4 \cdot 1.5CH_2Cl_2$ (4)

Data collection and reduction

Yellow crystals of 4 were grown from a CH_2Cl_2/hexanes solution at -80 °C. After the selected crystal was mounted on the end of a glass fiber, it was then immediately moved to the diffractometer and cooled to -100 °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 I.

A total of 4917 reflections were collected in the +h, ±k, ±l hemisphere, of which 4547 were unique. The agreement factor for the averaging of 696 observed reflections was 1.5% (based on intensity). The intensities of three standards, checked hourly over the course of the data collection, indicated only random variations within the errors of the measurements. Lorentz and polarization corrections were applied. An absorption correction based on a series of psi-scans was made.

Structure solution and refinement

The triclinic space group $P\bar{1}$ was chosen for the initial solution. The positions of the W, S, and Cl atoms of the cation were taken from a direct-methods E-map.[18] The major positions of the remaining carbon atoms of the cation and the positions of the atoms of the BF_4 and CH_2Cl_2 moieties were found in subsequent difference Fourier maps. A later difference map indicated disorder of the MeSC≡CSMe ligand. In the disordered model, the minor S atoms and one of the methyl groups were slightly displaced from the major orientation, and the S(4) - C(9) group was rotated almost 180 ° about the S(4) - C(8) bond. At this point a change to the acentric group P1 was made, and the structure was generated from difference maps, starting with the position of the W atoms. However, the disorder was not resolved, so the switch back to the centric space group was made. The relative occupancies of the two disordered ligands refined to 0.808(6) for the major orientation and 0.192(6) for the minor orientation. One molecule of CH_2Cl_2 was found on a general position in the lattice, and another disordered about a center of inversion. The two Cl atoms of the disordered solvent molecule were positioned so that they represented both of the possible orientations, and the central carbon atom had two possible positions on either side of the inversion center. In the later stages of refinement, all of the atoms were refined with anisotropic thermal parameters except for the disordered methyl atoms, atom S(3′), and the carbon atom of the disordered solvent molecule. The final cycle of refinement included 277 variable parameters and converged to $R = 0.030$ and $R_w = 0.048$.[19]

Refinement of the structure was carried out using the SHELX-76 programs.[20] The final positional and thermal parameters are listed in Table II. Selected bond lengths and angles are presented in Tables III and IV, respectively; an ORTEP drawing of 4 is given in Figure 1.

Table I. Crystal and Data Collection Parameters for $[CpClW(MeSC{\equiv}CSMe)(MeSC{\equiv}CSMe_2)]BF_4 \cdot 1.5CH_2Cl_2$ (4)

Formula	$WCl_4S_4C_{15.5}F_4BH_{23}$
Formula weight	738.06
Space Group	$P\bar{1}$
a, Å	7.697(3)
b, Å	11.668(1)
c, Å	15.740(3)
α, deg	107.34(1)
β, deg	99.56(3)
γ , deg	99.47(1)
V, $Å^3$	1296(4)
Z	2
d_{calc}, g/cm^3	1.91
Crystal size, mm	0.10 x 0.15 x 0.60
u(MoKα), cm^{-1}	53.1
Data collection instrument	Enraf-Nonius CAD4
Radiation (monochromated in incident beam)	MoKα (λ = 0.71073 Å)
Orientation reflections, number, range (2θ)	25, 17.6 - 31.9°
Temperature, °C	-100
Scan method	θ - 2θ
Data col. range, 2θ, deg	4 - 50

Table I (continued)

No. unique data, total:	4547
with $F_o^2 > 3\sigma(F_o^2)$:	4246
Number of parameters refined	277
R^a	0.0299
R_w^b	0.0475
Quality-of-fit indicator[c]	1.60
Largest shift/esd, final cycle	0.01
Largest peak, e/Å^3	1.13

[a] $R = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$.

[b] $R_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w|F_o|^2]^{1/2}$; $w = 1 / [\sigma^2(|F_o|) + 0.001|F_o|^2]$.

[c] Quality-of-fit $= [\Sigma w(|F_o| - |F_c|)^2 / (N_{obs} - N_{parameters})]^{1/2}$.

Table II. Positional and Thermal Parameters for $[CpClW(MeSC{\equiv}CSMe)(MeSC{\equiv}CSMe_2)]BF_4 \cdot 1.5CH_2Cl_2$ (4)

Atom	x	y	z	$B(Å^2)$[a]
W	0.23155(2)	0.43315(1)	0.2948(1)	1.659(7)
Cl(1)	0.5034(2)	0.3605(1)	0.33789(8)	2.32(3)
S(1)	-0.1018(2)	0.3805(2)	0.0903(1)	3.91(4)
S(2)	0.2336(2)	0.1632(2)	0.0999(1)	3.47(4)
S(3)	0.6479(3)	0.6405(2)	0.3313(3)	3.16(6)
S(3')	0.652(3)	0.648(2)	0.340(3)	10.1(9)[b]
S(4)	0.1079(3)	0.6832(2)	0.2478(1)	3.37(6)
S(4')	0.223(1)	0.7350(7)	0.2497(6)	2.8(2)
C(1)	-0.138(1)	0.2471(6)	-0.0117(4)	4.1(2)
C(2)	0.0691(7)	0.3614(5)	0.1628(3)	2.4(1)
C(3)	0.1871(7)	0.2945(5)	0.1713(3)	2.3(1)
C(4)	0.464(1)	0.2174(7)	0.0991(5)	4.6(2)

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[a] Estimated standard deviations are given in parentheses. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3) * [a^2*B(1,1) + b^2*B(2,2) + c^2*B(3,3) + ab(\cos \gamma)*B(1,2) + ac(\cos \beta)*B(1,3) + bc(\cos \alpha)*B(2,3)]$.

[b] Atoms refined isotropically.

Table II (continued)

Atom	x	y	z	B(Å^2)^a
C(5)	0.257(1)	0.0724(6)	0.1722(6)	4.3(2)
C(6)	0.679(1)	0.7876(7)	0.3116(6)	3.5(2)^b
C(6′)	0.660(5)	0.806(3)	0.347(3)	3.5(2)^b
C(7)	0.4189(7)	0.5845(5)	0.3047(4)	2.5(1)
C(8)	0.2565(8)	0.6015(5)	0.2776(4)	2.6(1)
C(9)	0.241(1)	0.8371(7)	0.2731(6)	3.7(1)^b
C(9′)	-0.020(3)	0.692(3)	0.208(2)	3.7(1)^b
C(10)	-0.0543(8)	0.4248(7)	0.3303(4)	3.9(2)
C(11)	-0.013(1)	0.3164(6)	0.3332(5)	4.4(2)
C(12)	0.145(1)	0.3493(9)	0.4064(6)	5.9(3)
C(13)	0.1922(9)	0.4810(7)	0.4436(4)	4.1(2)
C(14)	0.0661(9)	0.5236(7)	0.3983(4)	4.0(2)
B	0.2617(9)	0.0368(6)	-0.1495(5)	3.1(2)
F(1)	0.2218(8)	-0.0381(4)	-0.0982(4)	6.4(2)
F(2)	0.1659(8)	0.1265(5)	-0.1305(5)	8.1(2)
F(3)	0.4385(7)	0.0885(6)	-0.1313(6)	10.1(3)
F(4)	0.219(1)	-0.0267(6)	-0.2356(4)	15.2(4)
Cl(2)	-0.1275(3)	0.1184(2)	0.4863(1)	5.07(5)
Cl(3)	-0.4986(4)	0.1474(3)	0.4716(2)	8.0(1)
Cl(4)	0.3725(4)	0.5076(3)	0.0567(2)	8.0(1)

Table II (continued)

Atom	x	y	z	B(Å^2)^a
C(15)	-0.320(1)	0.1400(7)	0.4179(5)	4.6(2)
C(16)	0.393(2)	0.418(1)	-0.0652(9)	3.7(2)^b

RESULTS AND DISCUSSION

Synthesis of η^2-MeSC≡CSMe Tungsten Complexes 1, 2, and 3

The reaction of $CpW(CO)_3Cl$ with MeSC≡CSMe in refluxing heptane forms a yellow air-stable complex $CpW(MeSC{\equiv}CSMe)_2Cl$ (1) in 30% yield (Scheme I). Complex 1 is characterized by ^1H and ^{13}C NMR spectra, EIMS, and elemental analyses; complex 1 was previously reported by Connor and Hudson.[10a] Similarly, reactions of $W(CO)_3(S_2CNR_2)_2$ (R = Me and Et) with excess MeSC≡CSMe in toluene solution gives at room temperature green complexes of $W(CO)(MeSC{\equiv}CSMe)(S_2CNR_2)_2$ (2a for R = Me, 2b for R = Et); the same reactions at refluxing temperatures cause complete decarbonylation to give yellow air-stable complexes $W(MeSC{\equiv}CSMe)_2(S_2CNR_2)_2$ (3a for R = Me, 3b for R = Et) in 30 - 35% yield (Scheme I). Complexes 2a and 2b exhibit a strong ν(CO) absorption at 1918 and 1914 cm^{-1}, respectively. The position of this band is similar to that reported for other $W(CO)(acetylene)(S_2CNR_2)_2$ complexes for which ν(CO) bands are observed at 1878 and 1881 cm^{-1} for cyclooctyne (R = Me and Et),[21] at 1960 (KBr)[22] and 1925 cm^{-1} (toluene)[23] for HC≡CH (R = Et), and at 1920 cm^{-1} for $Ph_2PC{\equiv}CPPh_2$ (R = Et).[23]

Complexes 1, 2, and 3 show no evidence of sulfur coordination by the ligand, MeSC≡CSMe, to the tungsten. This is supported by their ^1H and ^{13}C NMR spectra. The ^1H

NMR spectra of 1, 2, and 3b each show only one ^{1}H NMR SMe signal which occurs in the range from 2.74 to 2.99 ppm. The ^{1}H NMR alkyne-methyl resonances of similar complexes such as $W(CO)(MeC\equiv CMe)(S_2CNEt_2)_2$,[23] $W(CO)_2(dppe)(MeO_2CC\equiv CCO_2Me)_2$,[24] and $WI_2(CO)_2(MeC\equiv CMe)_2$[25] also occur as singlets at 3.18, 3.58, and 3.0 ppm, respectively. The equivalence of both groups on the alkyne indicates rapid rotation of the alkyne ligand. On the other hand, 3a shows two ^{1}H NMR SMe resonances of equal intensity.

Inequivalent ^{1}H NMR methyl resonances are also reported for the π-alkyne in $[CpW(CO)(MeC\equiv CMe)_2]PF_6$[26] where the two methyls give rise to singlets at 3.06 and 2.83 ppm. Previous dynamic NMR studies[27-29] for a number of molybdenum(II)- and tungsten(II)-alkyne derivatives, e.g., $Mo(CO)(MeC\equiv CMe)(PEt_3)_2Br_2$[27b] and $Mo(CO)(PhC\equiv CH)(S_2CNMe_2)_2$[27d] reveal barriers of rotation in the range of 35 - 80 kJ mol^{-1}. The ^{1}H NMR spectra suggest that rotation does not occur in 3a at ambient temperature on the NMR time-scale; whereas, in the other complexes 1, 2, and 3b, the $MeSC\equiv CSMe$ rotates rapidly under the same conditions. It is not clear why the rotation rates are different in these complexes.

Templeton and others[30] have suggested that involvement of both π-orbitals on the alkyne in bonding with a metal leads to pronounced downfield shifts of the ^{13}C NMR resonances of the alkyne carbons.[28] Thus, alkyne ^{13}C chemical shifts vary over 100 ppm for molybdenum(II)- and tungsten(II)-alkyne complexes (Table V).[24,30a] Carbon chemical shifts of alkynes which act as four-electron donors range from 190 to 250 ppm; those of three-electron donor alkynes occur in the range of 130 to 180 ppm; the same shifts for two-electron donor alkynes occur from 100 to 120 ppm. The ^{13}C NMR alkyne resonances for 1 (175.20 ppm) and 3a (178.69 and 177.21 ppm) suggest that the MeSC≡CSMe ligand functions as a three-electron donor; complex 2a exhibits its alkyne resonance at 201.34 ppm which suggests that it acts as a four-electron donor alkyne. Thus, all of the complexes 1, 2, and 3a achieve a formal 18-electron count. The solid state ^{13}C NMR chemical shifts of 1 are very similar to these obtained in the solution ^{13}C NMR spectrum; however, three resonances (175.66, 173.99, and 172.04 ppm) are observed for the alkyne-carbons and two resonances (21.72 and 19.79 ppm) for the SMe groups. These additional signals indicate that the alkyne ligands are not rotating in the solid state.

Reactions of $CpW(MeSC{\equiv}CSMe)_2Cl$ (1)

The addition of electrophiles to coordinated acetylenes frequently leads to cis-vinyl complexes via initial addition to the metal center, as shown in eq 2. Complex 1 reacts (Scheme I) with $[Me_3O]BF_4$ in CH_3CN to form the dimethylsulfonium complex $[CpClW(MeSC{\equiv}CSMe)(MeSC{\equiv}CSMe_2)]BF_4$

Table V. Carbon-13 Chemical Shifts of Alkyne Carbons π-bound to Molybdenum(II) and Tungsten(II) Centers

Complex	C≡C	N[a]	Ref.
$[CpW(PMe_3)_2(MeC{\equiv}COMe)]BF_4$	227.9, 200.5	4	33
$W(CO)(\eta 2\text{-}C_8H_{12})(S_2CNMe_2)_2$	215.2	4	21
$CpW(CO)(MeC{\equiv}CMe)COEt$	193.7	4	31
$Mo(EtC{\equiv}CEt)_2(S_2CNMe_2)_2$	183.8, 181.3	3	30e
$Mo(PhC{\equiv}CH)_2(S_2CNEt_2)_2$	183.2, 177.1	3	30a
$WI_2(CO)_2(MeC{\equiv}CMe)_2$	151.9	3	25
$[CpW(CO)(MeC{\equiv}CMe)_2]PF_6$	160.4, 142.2	3	26
$Cp_2Mo(HC{\equiv}CH)$	117.7	2	32
$Cp_2Mo(MeC{\equiv}CMe)$	115.3	2	30a

[a] N = Number of electrons formally donated by each alkyne to the metal.

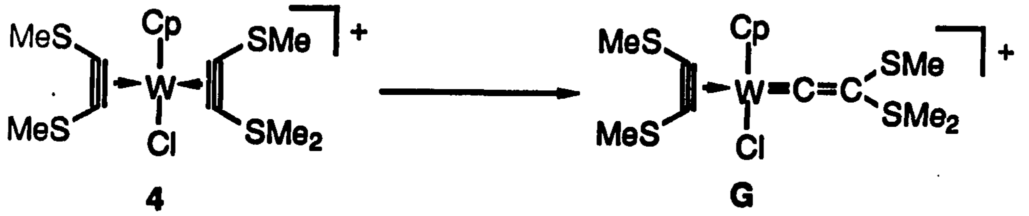
(4) via direct addition to a sulfur atom of the thioalkyne ligand. Complex 4 is isolated as an air-stable yellow crystalline product in 63% yield. Addition of the methyl to the sulfur is established by an X-ray determination of 4 which will be discussed later. It is interesting that the sulfonium alkyne $MeSC{\equiv}CSMe_2^+$ ligand is stabilized in 4 since the free sulfonium-alkyne $[PhC{\equiv}CS(Me)Et](picrate)$[34] is reported to be unstable.

Complex 1 also reacts with $Cp(PMe_3)_2RuCl$ and NH_4BF_4 in methanol solution to give the ruthenium-methyl-sulfonium complex $[CpW(MeSC{\equiv}CSMe)(MeSC{\equiv}CS(Me)Ru(PMe_3)_2Cp]BF_4$ (5) as an air-stable yellow powder in 58% yield. The addition of the $Cp(PMe_3)_2Ru^+$ to the sulfur is supported by the ^1H NMR Cp-ruthenium chemical shift at 4.84 ppm which is nearly identical to the Cp resonance (4.86 ppm) for the S-coordinated $\{Cp(PMe_3)_2Ru[S(Me)C{\equiv}CSMe]\}BF_4$.[9]

The ^1H NMR resonances of the diastereotopic methyls in the SMe_2 sulfonium group in 4 are observed at 3.40 and 3.15 ppm; in 5 the Ru-coordinated SMe is observed at 2.97 ppm. The downfield shifts of these signals as compared with that (2.74 ppm) in 1 is expected for cationic sulfonium groups. Similar downfield shifts are observed for -SMe and $-SMe_2^+$ groups in pairs of complexes such as $Cp(PPh_3)(NO)ReCH_2SMe$ (2.01 ppm) and $[Cp(PPh_3)(NO)ReCH_2SMe_2]PF_6$ (2.60 ppm),[35] as well as $[Cp(PMe_3)_2Ru=C=C(Me)(SMe)]I$ (2.20 ppm) and $[Cp(PMe_3)_2Ru=C=C(Me)(SMe_2)](BF_4)_2$ (2.83 ppm).[9] The SMe and Cp signals in complexes 4 and 5 move only slightly downfield as compared to those in 1.

The solid state ^{13}C NMR spectrum of 4 shows nine alkyne carbon signals in two groups which range from 192.86 to 178.47 ppm and 142.55 to 137.35 ppm. An X-ray determination of 4 (discussed in the next section) identifies the structure as a bis-π-alkyne complex. The large number of signals observed in the solid state ^{13}C spectrum are probably due, at least in part, to the lack of rotation of the π-alkyne ligands. This is in contrast to only four alkyne-carbon signals observed in the solution ^{13}C NMR spectrum. Even though the signals in the solid state range from 192.86 to 137.35 ppm they still lie within the range of a 3-electron donor alkyne (Table V), making 4 an 18-electron complex. The rather broad range of alkyne carbon signals in the bis-alkyne complexes $[CpW(MeC=CMe)_2L]BF_4$[36] (L = CO and NCMe) at 146.2 and 165.1 ppm (L = CO), and 161.9 and 181.7 ppm (L = NCMe) is consistent with 4 having a bis-alkyne structure.

The ^{13}C NMR chemical shifts of 4 in solution are somewhat different than observed in the solid state. This chemical shift difference may suggest that a π-alkyne to vinylidene rearrangement occurs in solution (eq 6) similar to the 1,2-SMe migration proposed for the ruthenium complex shown in eq 3.



6

The π-alkyne-vinylidene complex G would also be an 18-electron complex if the π-alkyne were to donate 4-electrons to the tungsten center. The ^{13}C NMR alkyne carbon signals of 4 in d_6-acetone at 209.81, 191.25, 186.50, and 137.35 ppm could suggest that two of the three downfield resonances are due to a π-alkyne which is a 4-electron donor (Table V); the remaining downfield resonance may be due to the vinylidene α-carbon and the signal at 137.35 could be due to the β-carbon. However, in known vinylidene complexes of Mo, the α- and β-carbon vinylidene resonances are observed at 326.4 and 132.7 ppm in $CpMoI[P(OMe)_3]_2{=}C{=}C(H)(t\text{-}Bu)$[37] and at 348.6 and 141.3 ppm in $CpMo[P(OMe)_3](N_2C_6H_4F\text{-}4){=}C{=}C(H)(t\text{-}Bu)$,[37] respectively. The characteristic far downfield α-carbon resonance at 325 - 350 ppm is not observed in the solution ^{13}C NMR spectrum of 4 which indicates that this complex does not have the vinylidene structure G and probably retains the bis-alkyne structure found in the solid state.

Although nucleophiles are known to attack certain alkyne ligands as in eq 1, complex 1 does not react at all with the following nucleophiles: PPh_3, CNBu-t, CO, AgCN, NaSPh, $Na[S_2CNMe_2]$, NaH, and $Na[HBEt_3]$.

Crystal Structure of $[CpClW(MeSC{\equiv}CSMe)(MeSC{\equiv}CSMe_2)]BF_4{\cdot}1.5CH_2Cl_2$ (4)

The geometry about the tungsten center is nearly octahedral, one face of the octahedron being occupied by the Cp group and the opposite face by the chloride and two alkyne ligands (Figure 1). The $C{\equiv}C$ bonds of the two coordinated alkynes lie approximately parallel to the $W{\rightarrow}Cl$ vector with carbon atoms C(2) and C(8) tilted towards each other. The angles between the $C(2){\rightarrow}C(3)$ and $W{\rightarrow}Cl$ vectors and the $C(7){\rightarrow}C(8)$ and $W{\rightarrow}Cl$ vectors are 15.2 ° and 10.9 °, respectively.

The tungsten carbon distances to the Cp ring range from 2.323 (6) to 2.405 (8) Å (Table III). These distances are very similar to the corresponding distances (2.29 (3) to 2.38 (3) Å) in $CpW(CF_3C{\equiv}CCF_3)_2Cl$[38] and those (2.338 (4) to 2.409 (4) Å) in the cationic complex $[CpMo(MeC{\equiv}CMe)_2(CO)]BF_4$.[36] The W-Cl distance (2.452 (1) Å) is slightly longer than those in $CpW(CF_3C{\equiv}CCF_3)_2Cl$[38] (2.417 (3) Å) and $CpWCl(CF_3C{\equiv}CCF_3)(CF_3CC(CF_3)CNBu\text{-}t)$[3] (2.416 (3) Å).

The tungsten-alkyne carbon distances to the $MeSC{\equiv}CSMe$ ligand (W-C(7) (2.036 (5) Å) and W-C(8) (2.044 (6) Å)) are

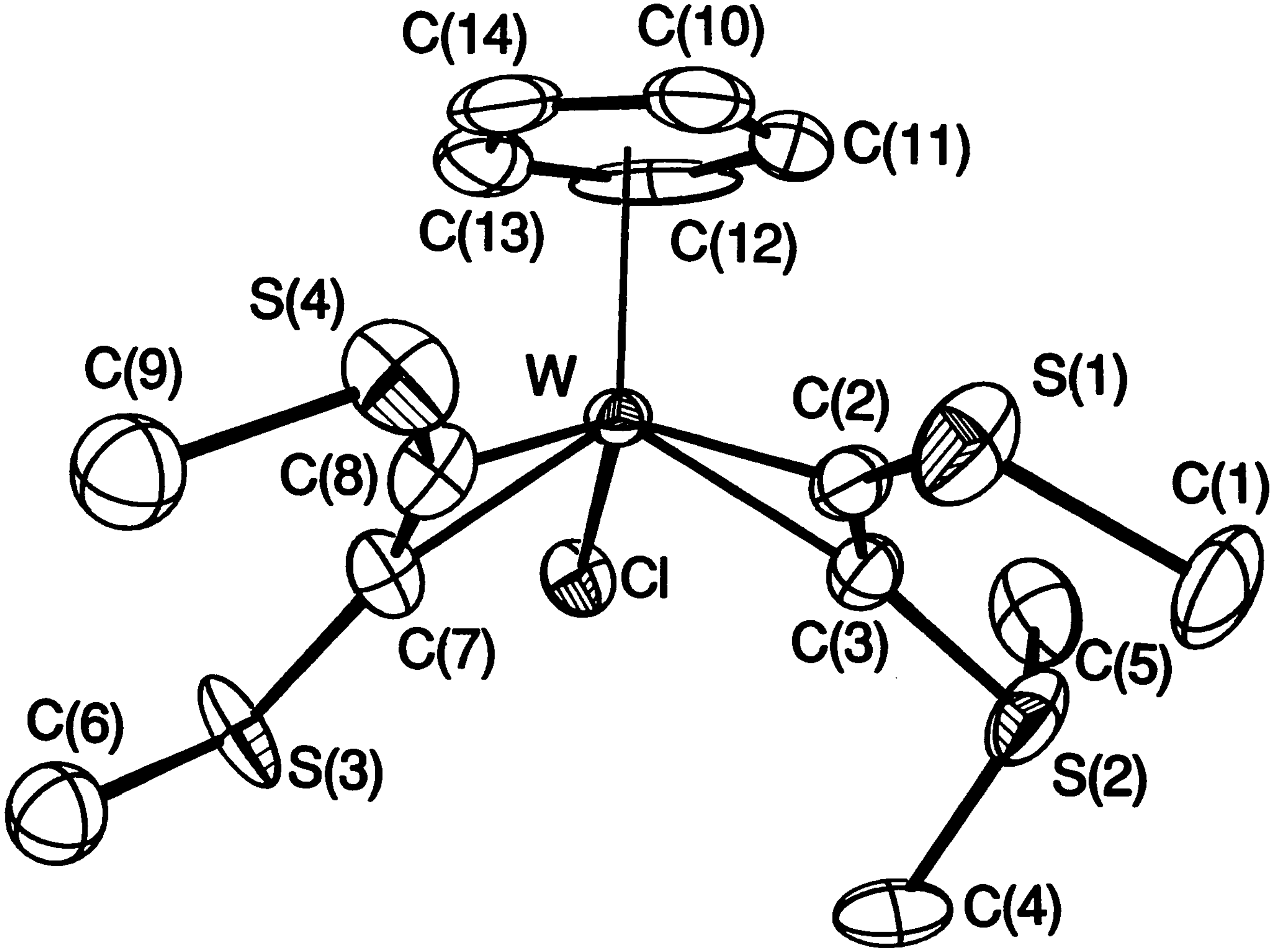


Figure 1. An ORTEP drawing of

$[CpClW(MeSC{\equiv}CSMe)(MeSC{\equiv}CSMe_2]BF_4\cdot 1.5\ CH_2Cl_2$ (4)

Table III. Bond Distances (Å) for $[CpClW(MeSC{\equiv}CSMe)(MeSC{\equiv}CSMe_2)]BF_4{\cdot}1.5CH_2Cl_2$ (4)

W	Cl(1)	2.452(1)[a]	S(4)	C(8)	1.699(7)
W	C(2)	2.084(4)	S(4)	C(9)	1.809(8)
W	C(3)	2.058(5)	S(4′)	C(8)	1.79(1)
W	C(7)	2.036(5)	S(4′)	C(9′)	1.81(2)
W	C(8)	2.044(6)	C(2)	C(3)	1.307(8)
W	C(10)	2.352(7)	C(7)	C(8)	1.319(8)
W	C(11)	2.405(8)	C(10)	C(11)	1.37(1)
W	C(12)	2.38(1)	C(10)	C(14)	1.385(8)
W	C(13)	2.323(6)	C(11)	C(12)	1.44(1)
W	C(14)	2.344(7)	C(12)	C(13)	1.43(1)
S(1)	C(1)	1.816(6)	C(13)	C(14)	1.36(1)
S(1)	C(2)	1.683(6)	S(2)	C(3)	1.741(5)
S(2)	C(4)	1.789(8)	S(2)	C(5)	1.778(9)
S(3)	C(6)	1.82(1)	S(3)	C(7)	1.710(5)
S(3′)	C(6′)	1.80(5)	S(3′)	C(7)	1.75(2)
B	F(1)	1.39(1)	C(15)	Cl(2)	1.781(9)[b]
B	F(2)	1.37(1)	C(15)	Cl(3)	1.728(9)[b]
B	F(3)	1.340(8)	C(16)	Cl(4)	1.94(1)[b]
B	F(4)	1.291(8)			

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

[b] Methylene chloride molecules.

Table IV. Bond Angles (deg) for

$[CpClW(MeSC{\equiv}CSMe)(MeSC{\equiv}CSMe_2)]BF_4 \cdot 1.5CH_2Cl_2$ (4)

Cl(1)	W	C(2)	121.8(2)	Cl(1)[a]	W	C(3)	85.5(2)
Cl(1)	W	C(7)	82.1(2)	Cl(1)	W	C(8)	119.8(2)
C(2)	W	C(3)	36.8(2)	C(2)	W	C(7)	108.9(2)
C(2)	W	C(8)	86.4(2)	C(3)	W	C(7)	112.4(2)
C(3)	W	C(8)	110.9(2)	C(7)	W	C(8)	37.7(2)
C(1)	S(1)	C(2)	103.2(3)	C(3)	S(2)	C(4)	101.7(3)
C(3)	S(2)	C(5)	102.0(3)	C(4)	S(2)	C(5)	101.5(4)
C(6)	S(3)	C(7)	105.0(4)	C(6′)	S(3)	C(7)	101.(1)
C(6′)	S(3′)	C(7)	101.(2)	C(8)	S(4)	C(9)	105.5(3)
C(8)	S(4′)	C(9′)	99.(1)	W	C(2)	S(1)	144.6(3)
W	C(2)	C(3)	70.6(3)	S(1)	C(2)	C(3)	144.8(4)
W	C(3)	S(2)	152.3(3)	W	C(3)	C(2)	72.7(3)
S(2)	C(3)	C(2)	135.0(4)	W	C(7)	S(3)	140.8(4)
W	C(7)	S(3′)	141.(1)	W	C(7)	C(8)	71.5(3)
S(3)	C(7)	C(8)	147.7(5)	S(3′)	C(7)	C(8)	147.(1)
W	C(8)	S(4)	134.5(3)	W	C(8)	S(4′)	166.5(4)
W	C(8)	C(7)	70.8(4)	S(4)	C(8)	C(7)	154.6(5)
S(4′)	C(8)	C(7)	122.4(5)	F(1)	B	F(2)	107.2(7)
F(1)	B	F(3)	113.0(7)	F(1)	B	F(4)	110.6(6)

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

Table IV (continued)

F(2)	B	F(3)	109.9(6)	F(2)	B	F(4)	110.9(7)
F(3)	B	F(4)	105.4(8)	Cl(2)	C(15)	Cl(3)	112.0(5)[b]
Cl(4)	C(16)	Cl(4)	98.3(5)[b]				

[b] Methylene chloride molecules.

essentially the same but somewhat shorter than the W-C(2) (2.084 (4) Å) and W-C(3) (2.058 (5) Å) distances to the $MeSC{\equiv}CSMe_2^+$ ligand. Similar Mo- and W-η^2-alkyne carbon distances range from 2.049 (18) to 2.071 (15) Å for $CpW(CF_3C{\equiv}CCF_3)_2Cl$,[38] from 2.061 (4) to 2.124 (4) Å for $[CpMo(MeC{\equiv}CMe)_2(CO)]BF_4$,[36] and are 2.032 (6) and 2.038 (6) Å for $CpW(CO)\{C(4\text{-}C_6H_4Me)CO\}(MeC{\equiv}CNEt_2)$.[39] The fact that the W-C(3) bond (2.058 (5) Å) is shorter than the W-C(2) distance (2.084 (4) Å) may suggest partial η^2-vinyl type bonding in the $MeSC{\equiv}CSMe_2^+$ ligand. However, W-C(3) is not as short as the η^2-vinyl W=C distance (1.894 (8) Å) and W-C(2) is not as long as the W-C distance (2.304 (10) Å) in $CpWCl(CF_3C{\equiv}CCF_3)(\eta^2\text{-}CF_3CC(CF_3)CNBu\text{-}t)$[3] (A in eq 1); the same is true for the corresponding distances (1.951 (3) Å and 2.301 (3) Å) in $Cp\{P(OMe)_3\}_2Mo(\eta^2\text{-}PhCC(H)Ph)$.[7] Thus, the $MeSC{\equiv}CSMe_2^+$ is most accurately described as a π-alkyne ligand.

The alkyne C(2)-C(3) (1.307 (8) Å) and C(7)-C(8) (1.319 (8) Å) distances are similar to other π-alkyne distances which range from 1.266 (9) Å in exo-$CpW\{E\text{-}\eta^3\text{-}SC(CF_3){=}C(CF_3)H\}(CF_3C{\equiv}CCF_3)$[40] to 1.267 (6) and 1.277 (5) Å in $[CpMo(MeC{\equiv}CMe)_2(CO)]BF_4$[36] and to 1.339 (8) Å in $CpW(CO)\{C(4\text{-}C_6H_4Me)CO\}(MeC{\equiv}CNEt_2)$.[39] The C(sp)-SMe distances in 4 range from 1.683 (6) to 1.710 (5) Å which are typical of C(sp)-S single bond distances found in

$Cp(PPh_3)(CO)W(\equiv C\text{-}SPh)$[41] (1.716 (10) Å), $[HB(pz)_3](MeS)_2W(\equiv C\text{-}SMe)$[42] (1.700 (7) Å), and $MeSC\equiv CSMe$[16b] (1.671 (2) Å). The C(sp)-S(2) sulfonium distance at 1.741 (5) Å suggests a single bond. No comparative C(sp)-S(sulfonium) distances have been reported; however, it is much longer than full $C(sp^2){=}S$ double bond distances found in $[Cp(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}C{=}S)$[43] (1.596 (9) Å) and $(CO)_2(PPh_3)_2(H)Os[C(=S)SMe]$[44] (1.648 (4) Å). These comparisons therefore suggest that there is no significant C(sp)-S multiple bonding in 4.

Reactions of $[CpClW(MeSC\equiv CSMe)(MeSC\equiv CSMe_2)]BF_4$ (4)

The reactions of 4 in CH_3CN at room temperature with the nucleophiles PPh_2Me, 4-$NC_5H_4NMe_2$, Me_2CuLi, KCN, and Et_4NBr give complex 1 quantitatively, as indicated by ^1H NMR spectra of the product (Scheme I). The formation of 1 presumably occurs by attack of the nucleophile on one of the sulfonium methyl carbons. A similar attack was previously observed in the reaction of $[Cp(PMe_3)_2Ru{=}C{=}C(SMe)(SMe_2)](BF_4)_2$ with 4-NC_5H_4R (R = H and Et) to give $[Cp(PMe_3)_2Ru{=}C{=}C(SMe)_2]BF_4$ and $[Me\text{-}NC_5H_4R]^+$.[9]

In addition to attacking the methyl carbon, nucleophiles may add to the alkyne carbon with displacement of the SMe_2 group. Thus, the reaction of $Na[HBEt_3]$ with 4 gives a yellow powder containing a 1:1 mixture of

CpW(MeSC≡CSMe)(MeSC≡CH)Cl (6) and 1 obtained in an overall yield of 98% (Scheme I). The ^1H NMR spectrum of the reaction mixture shows the presence of free SMe_2 when the reaction is performed in CD_3CN in an NMR tube. Complex 6 is characterized by its ^1H and ^{13}C NMR spectra, and mass spectrum. The singlet resonance at 9.23 ppm in the ^1H NMR spectrum of 6 is assigned to the alkyne proton. Such far downfield protons have been observed in other π-bound 1-alkyne complexes, CpW(CO)(PhC≡CH)COEt[31] (12.82 ppm) and $Cp_2Mo(MeC≡CH)$[32] (7.05 ppm).

The reaction of 4 with mercaptides, NaSR (R = C_6H_5 and 4-C_6H_4Me), gives only Me_2S-displaced products CpW(MeSC≡CSMe)(MeSC≡CSR)Cl (7a for R = C_6H_5, 7b for R = 4-C_6H_4Me) which are isolated as yellow oils in approximately 80% yield (Scheme I). Complex 7a is characterized by ^1H and ^{13}C NMR spectra, elemental analyses, and its mass spectrum. The ^{13}C NMR spectrum of 7a shows a single chemical shift for the alkyne carbons at 176.13 ppm which is nearly identical to that of the alkyne-carbon resonances observed for 1.

The reactions of 4 with mercaptides presumably occur by nucleophilic attack on the alkyne-carbon adjacent to the sulfonium unit. Similar nucleophilic additions, without displacement of a leaving group give the η^2-vinyl complexes shown in eq 1. Also, phosphines and phosphites attack the alkyne in $[M(PhC≡CH)(ma)(S_2CNR_2)_2]$[45] (M = Mo or W, R =

Me; M = W, R = Et; ma = maleic anhydride) to give η^2-vinyl complexes $[M\{C(Ph)C(H)(PR_3)\}(ma)(S_2CNR_2)_2$.

CONCLUSIONS

In contrast to $Cp(PMe_3)_2RuCl$ which reacts with $MeSC\equiv CSMe$to give the thiomethyl vinylidene $[Cp(PMe_3)_2Ru=C=C(SMe)_2]^+$ via a 1,2-SMe migration (eq 3),[9] the tungsten(II) carbonyls $CpW(CO)_3Cl$ and $W(CO)_3(S_2CNR_2)_2$ (R = Me and Et) give the π-alkyne complexes 1, 2, and 3. Similar to the reaction of the electrophile Me^+ which adds to the sulfur atom of $[Cp(PMe_3)_2Ru=C=C(SMe)_2]^+$ to give F (eq 4), the electrophiles Me^+ and $Cp(PMe_3)_2Ru^+$ also add to a sulfur atom of 1 to give the π-alkyne-sulfonium complexes 4 and 5. Rearrangement from a π-alkyne to a vinylidene complex, as occurs in the ruthenium complexes, is not observed in these tungsten(II) complexes. This is a major difference in reactivity of $MeSC\equiv CSMe$ in the ruthenium and tungsten systems. The reason for the lack of rearrangement on a tungsten(II) center is not totally clear, however, it has been noted[7] that the rearrangement of π-bound 1-alkynes are not observed on d^4 metals whereas the rearrangement is common for octahedral d^6 complexes. It is also possible that the strongly electron-withdrawing vinylidene ligand is stabilized to a greater extent by the more electron-rich $Cp(PMe_3)_2Ru^+$ group.

As the sulfonium-vinylidene complex $[Cp(PMe_3)_2Ru=C=C(SMe_2)(SMe)]^{+2}$ reacts with nucleophiles (Nuc

= SEt_2, NC_5H_5, and NaSEt) to give substituted vinylidene $[Cp(PMe_3)_2Ru=C=C(Nuc)(SMe)]^+$(1 or 2) complexes and SMe_2, the sulfonium alkyne tungsten complex 4 reacts with the nucleophiles H^- and $^-S-4-C_6H_4R$ (R = H and Me) to give the π-alkyne complexes 6 and 7 and SMe_2 (Scheme I). Thus, in both the tungsten sulfonium alkyne complex 4 and the ruthenium sulfonium vinylidene complex the Me_2S group is readily displaced by nucleophiles.

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GENERAL SUMMARY

The research described in this dissertation shows that the thioalkyne, MeSC≡CSMe, can initially react with a ruthenium(II) compound to give a S-coordinated complex. This S-coordinated complex readily rearranges to a vinylidene complex via a 1,2-SMe migration, the likely intermediate is a π-thioalkyne complex. In contrast, the thioalkyne reacts with tungsten(II) centers to give only mono- and bis-π-alkyne complexes.

It is also demonstrated that the ruthenium(II)- and tungsten(II)-thioalkyne complexes can be methylated at the sulfur atom to give mono- and dicationic sulfonium complexes. Other electrophiles, e.g., H^+ and MeS^+, react with several ruthenium(II)-thioalkyne complexes to give three-member metallacyclic complexes as well as a number of vinylidene derivatives. In addition, nucleophiles react with several of these thioalkyne-metal complexes to give in one case nucleophilic substituted complexes via the loss of Me_2S and in another case a methyl-sulfur cleavage.

Finally the complexes $[Cp(PMe_3)_2Ru{=}C{=}C(R)(SMe_n)]^{+n}$ (n = 1 or 2) undergo one- or two-electron reductions to give the ruthenium-acetylide complexes and MeSSMe or Me_2S.

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