Electrophilic and nucleophilic reactions of complexes formed from 2,5-dithiahex-3-yne (MeSC≡CSMe) and tungsten carbonyls *

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Abstract

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


[W] = CpCl(n^2- MeSC≡CSMe)W
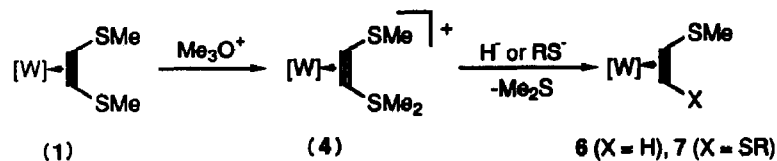
The $Cp(PMe_3)_2Ru^+$ group also adds to a sulfur in 1 to give $\{CpClW(\eta^2\text{-}$ $\text{MeSC}\equiv\text{CSMe})[\eta^2\text{-MeSC}\equiv\text{CS(Me)Ru(PMe}_3)_2Cp]\}BF_4$ (5). Nucleophilic attack by H^- donors and RS^- on 4 displaces Me_2S to yield $CpW(\eta^2\text{-MeSC}\equiv\text{CSMe})(\eta^2\text{-}$ $\text{MeSC}\equiv\text{CX})Cl$ (X = H (6), SC_6H_5 (7a), and $4\text{-}SC_6H_4Me$ (7b)) and Me_2S.

Introduction

It has been noted [1] that π-coordination of acetylenes to transition metals activates the alkyne bond to react 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 $CF_3C\equiv CCF_3$

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* With best wishes to Professor Gordon Stone on the occasion of his 65th birthday.

and $RC\equiv CR'$ in such complexes as $CpM(\eta^2\text{-}CF_3C\equiv CCF_3)_2Cl$ [2–6] (M = Mo and W) and $[Cp\{P(OMe)_3\}_2Mo(\eta^2\text{-}RC\equiv CR')]BF_4$ [7] (R = H, R' = t-Bu, i-Pr; R = Me, R' = Ph).


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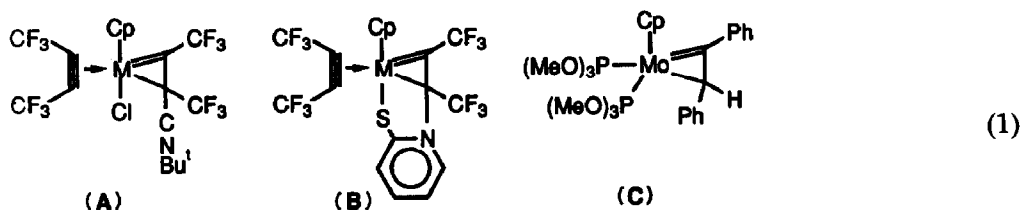
Although much less common [1], electrophiles add to coordinated acetylenes to give σ-vinyl complexes. For example, the complex $RuCl(NO)L_2(\eta^2\text{-}CF_3C\equiv CCF_3)$ [8] (L = PPh_3 and PPh_2Me) when reacted with HSO_3CF_3 gives the cis-vinyl complex (β-Hydrogen cis to the metal center) shown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

$$(2)$$
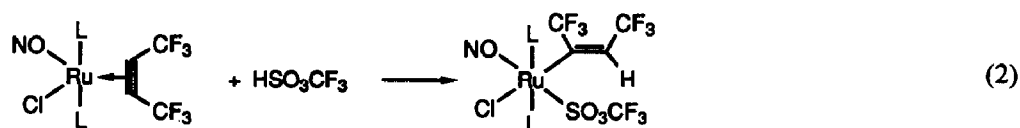
The formation of the vinyl complex was suggested to result from initial addition of the proton to the metal center forming a ruthenium hydride intermediate, followed by proton transfer to the alkyne.

We previously [9] examined the effects of the MeS groups on reactions of $MeSC\equiv CSMe$ with $Cp(PMe_3)_2RuCl$. We 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).

$$(3)$$
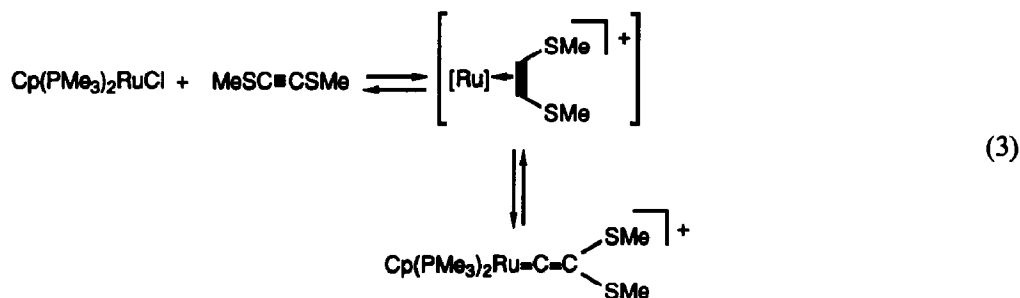
We further discovered that the thiomethyl vinylidene complex reacts with electrophiles (H^+, SMe^+, and Me^+) to give the following complexes (eq. 4) where [Ru] = $Cp(PMe_3)_2Ru$.

$$(4)$$
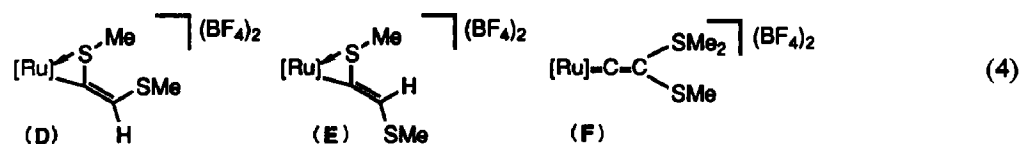
The formation of D and E was suggested to occur as a result of an equilibrium between the vinylidene and π-alkyne complex (eq. 3). Such an equilibrium was

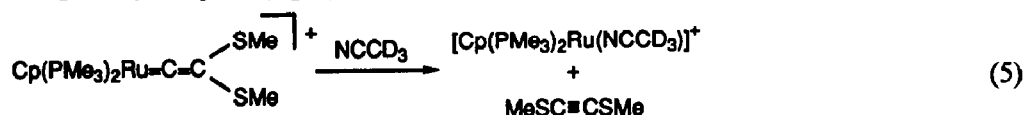supported by the displacement of MeSC≡CSMe from the thiomethyl vinylidene complex by CD_3CN (eq. 5).

$$Cp(PMe_3)_2Ru=C=C\begin{cases}SMe\\SMe\end{cases}\Biggr]^+ \xrightarrow{NCCD_3} \begin{array}{c}[Cp(PMe_3)_2Ru(NCCD_3)]^+ \\ + \\ MeSC≡CSMe\end{array} \qquad (5)$$

Connor and Hudson [10] previously reported the synthesis of mononuclear complexes of MeSC≡CSMe, e.g., $CpM(\eta^2\text{-MeSC≡CSMe})_2Cl$, $M(CO)(\eta^2\text{-MeSC≡CSMe})_3$ (M = Mo and W), $W(CO)(dmpe)(\eta^2\text{-MeSC≡CSMe})_2$, and $W(dmpe)(\eta^2\text{-MeSC≡CSMe})_2$; however, no reactions of the alkyne ligand in these complexes were described. With a view toward expanding our understanding of the chemistry of MeSC≡CSMe, we set out to prepare tungsten complexes of this ligand and to compare and contrast their structures and reactivities with those of the ruthenium complexes.

Experimental

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 position were referenced to the 1601.0 cm^{-1} band of polystyrene. ^{1}H 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 MSL300 (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 (EI-MS) 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 W, 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 = $\eta^5\text{-}C_5H_5$, $W(CO)_3(S_2CNR_2)_2$ (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 higher 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 spectrum showed no tungsten-dimer remaining. The solution was filtered to remove any insoluble products, and the solvents were removed by rotary vacuum evaporation. The resulting powdery residue was dissolved in MeOH (3 × 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): $\nu(CO)$ 2055 m, 1971 vs, 1951 s cm^{-1}.

CpW(η^2-MeSC≡CSMe)$_2$Cl (1). A mixture of $CpW(CO)_3Cl$ (108 mg, 0.30 mmol) and MeSC≡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 × 10 mL), and the extract was chromatographed on alumina (Fisher, 80–200 mesh, 10 × 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. Found: C, 29.68; H, 3.23. $C_{13}H_{17}ClS_4W$ calcd.: C, 29.98; H, 3.29%. ^1H NMR ($CDCl_3$): δ 5.92 (s, Cp), 2.74 (s, SMe); ^{13}C NMR (acetone-d_6): δ 175.20 (C≡C), 106.46 (Cp), 20.04 (SMe); ^{13}C NMR (solid state): δ (175.66, 173.99, 172.04 (C≡C)), 104.48 (Cp), (21.72, 19.79 (SMe)); EI-MS (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)(η^2-MeSC≡CSMe)(S$_2$CNR$_2$)$_2$ (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. Found: C, 22.84; H, 3.45. $C_{11}H_{18}N_2OS_6W$ calcd.: C, 23.16; H, 3.18%. ^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 (C≡C), (40.41, 39.43, 39.38, 39.24 (NMe)), 20.22 (SMe); EI-MS (70 eV): m/e 570 [M^+ not observed], 542 [$M^+ -$ CO], 424 [$M^+ -$ (CO + MeSC≡CSMe)]; IR (CH_2Cl_2): $\nu(CO)$ 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): $\nu(CO)$ 1914 cm^{-1}.

W(η^2-MeSC≡CSMe)$_2$(S$_2$CNR$_2$)$_2$ (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 × 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. Found: C, 25.63; H, 4.08. $C_{14}H_{24}N_2S_8W$ calcd.: C, 25.45; H, 3.66%. ^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$_2$Cl$_2$): δ 2.07.24 (C–N), (178.68, 177.21 (C≡C)), (39.39, 38.83 (NMe)), (20.06, 19.90 (SMe)); EI-MS (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$_3$O]BF$_4$. To a solution of **1** (150 mg, 0.28 mmol) in 10 mL of CH$_3$CN, [Me$_3$O]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$_2$Cl$_2$ (2 × 5 mL) and the resulting solution was filtered through a column of Celite (40 × 5 mm). The solvent was reduced to 3 mL, and 15 mL of Et$_2$O was added to give a yellow precipitate of [CpClW(η^2-MeSC≡CSMe)(η^2-MeSC≡CSMe$_2$)]BF$_4$ (**4**) which was dried and collected in 63% yield (110 mg, 0.18 mmol). Anal. Found: C, 26.91; H, 3.19. $C_{14}H_{20}BClF_4S_4W$ calcd.: C, 27.01; H, 3.24%. ^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 (acetone-d_6): δ (209.81, 191.25, 186.50, 139.36 (C≡C)), 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) (C≡C)), (105.66, 104.34 (Cp)), (28.99, 23.54, 22.59, 20.78 (SMe)); MS (FAB): m/e 535 [M^+], 473 [M^+ – Me$_2$S].

Reaction of 1 with Cp(PMe$_3$)$_2$RuCl. A mixture of **1** (52 mg, 0.10 mmol), Cp(PMe$_3$)$_2$RuCl (36 mg, 0.10 mmol) and NH$_4$BF$_4$ (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$_2$Cl$_2$ (3 × 5 mL), and the solution was passed through a column of Celite (40 × 5 mm). The solvent was reduced to 3 mL, and 20 mL of Et$_2$O was added to give a yellow powder of {CpClW(η^2-MeSC≡CSMe)[η^2-MeSC≡CS(Me)Ru(PMe$_3$)$_2$Cp]}BF$_4$ (**5**) which was dried and collected in 58% yield (54 mg, 0.058 mmol). Anal. Found: C, 31.06; H, 4.49. $C_{24}H_{40}BClF_4P_2RuS_4W$ calcd.: C, 31.13; H, 4.35%. ^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 (C≡C)), 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$_3$)$_2$Ru$^+$].

Reaction of 4 with Na[HBEt$_3$]. To a solution of **4** (46 mg, 0.074 mmol) in 8 mL of CH$_2$Cl$_2$, 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$_2$O (3 × 5 mL), and the solution was filtered through a small column of alumina (Fisher, 80–200 mesh, 40 × 5 mm). The solvent was removed from the resulting yellow solution under reduced pressure to give a yellow powder of a mixture of CpW(η^2-MeSC≡CSMe)(η^2-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. ^{1}H NMR (CD$_3$CN): δ 9.23 (s, 1 H, $\equiv$CH), 5.79 (s, 5 H, Cp), 2.73 (s, 6 H, SMe), 2.65 (s, 3 H, SMe); ^{13}C NMR (CD$_3$CN): δ (176.54, 176.47, 160.29 (C$\equiv$C)), 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$\equiv$CH], 387 [$M^+ -$ (Me + MeSC$\equiv$CH)].

Reactions of 4 with NaS-4-C$_6$H$_4$R (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$_6$H$_4$R (10 mg, 0.076 mmol for R = H; 14 mg, 0.096 mmol for R = Me) in 8 mL of CH$_3$CN 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$_2$Cl$_2$ (3 $\times$ 5 mL) and chromatographed on alumina (Fisher, 5% water, 80–200 mesh, 40 $\times$ 10 mm) packed in hexanes. A single yellow band was eluted with CH$_2$Cl$_2$. The solvent was removed from the resulting yellow solution under vacuum to give yellow oils of CpW(η^2-MeSC$\equiv$CSMe)(η^2-MeSC$\equiv$CSC$_6$H$_5$)Cl (**7a**) in 79% yield (18 mg, 0.031 mmol) and of CpW(η^2-MeSC$\equiv$CSMe)(η^2-MeSC$\equiv$CS-4-C$_6$H$_4$Me)Cl (**7b**) in 84% yield (13 mg, 0.022 mmol). **7a**. Anal. Found: C, 37.03; H, 3.39 C$_{18}$H$_{19}$ClS$_4$W calcd.: C, 37.09; H, 3.29%. ^{1}H NMR (CDCl$_3$): δ 7.45 (m, 2 H, Ph), 7.34 (m, 3 H, Ph), 5.89 (s, 5 H,

Table 1

Crystal and data collection parameters for [CpClW(η^2-MeSC$\equiv$CSMe)(η^2-MeSC$\equiv$CSMe$_2$)]BF$_4$·1.5CH$_2$Cl$_2$ (**4**)

Formula	WCl$_4$S$_4$C$_{15.5}$F$_4$BH$_{23}$
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$\times$0.15$\times$0.60
μ(Mo-K_α), cm^{-1}	53.1
Data collection instrument	Enraf-Nonius CAD4
Radiation (monochromated incident beam)	Mo-K_α (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, °	4–50
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 $= [\Sigma w (| F_o | - | F_c |)^2 / (N_{obs} - N_{parameters})]^{1/2}$.

Cp), 2.78 (s, 6 H, SMe), 2.39 (s, 3 H, SMe); ^{13} H NMR (CD$_3$CN): δ 176.13 (C≡C), 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)); EI-MS (70 eV): m/e 582 $[M^+]$, 473 $[M^+ - \text{SPh}]$. **7b.** ^{1}H 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(η^2-MeSC≡CSMe)(η^2-MeSC≡CSMe$_2$)] BF$_4$ · 1.5CH$_2$Cl$_2$ (4). Yellow crystals of **4** were grown from a CH$_2$Cl$_2$/hexanes solution at $-80\,^\circ$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 $-100\,^\circ$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 1.

Table 2

Positional and thermal parameters for [CpClW(η^2-MeSC≡CSMe)(η^2-MeSC≡CSMe$_2$)]BF$_4$·1.5CH$_2$Cl$_2$ (4)

Atom	x	y	z	$B(\text{Å}^2)$ [a]
W	0.23155(2)	0.43315(1)	0.29487(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)
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)
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]

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

A total of 4917 reflections were collected in the $+h$, $\pm k$, $\pm l$ 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.

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 positions 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

Table 3

Bond distances (Å) for $[CpClW(\eta^2\text{-MeSC≡CSMe})(\eta^2\text{-MeSC≡CSMe}_2)]BF_4 \cdot 1.5CH_2Cl_2$ (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 4

Bond angles (°) for [CpClW(η^2-MeSC≡CSMe)(η^2-MeSC≡CSMe$_2$)]BF$_4$·1.5CH$_2$Cl$_2$ (4)

Cl(1)–W–C(2)	121.8(2) [a]	Cl(1)–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)
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]		

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

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 2. Selected bond lengths and angles are presented in Tables 3 and 4, respectively; an ORTEP drawing of 4 is given in Fig. 1.

Results and discussion

Synthesis of η^2-MeSC≡CSMe tungsten complexes 1, 2, and 3. The reaction of CpW(CO)$_3$Cl with MeSC≡CSMe in refluxing heptane forms a yellow air-stable
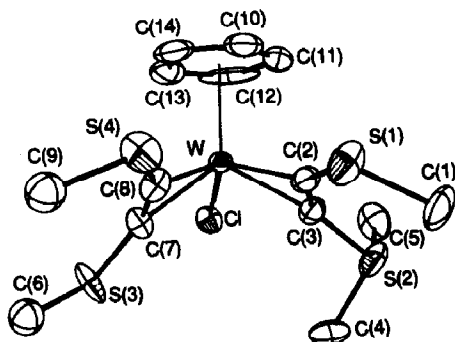
Fig. 1. An ORTEP drawing of CpClW(η^2-MeSC≡CSMe)(η^2-MeSC=CSMe$_2$)]BF$_4$·1.5CH$_2$Cl$_2$ (4).
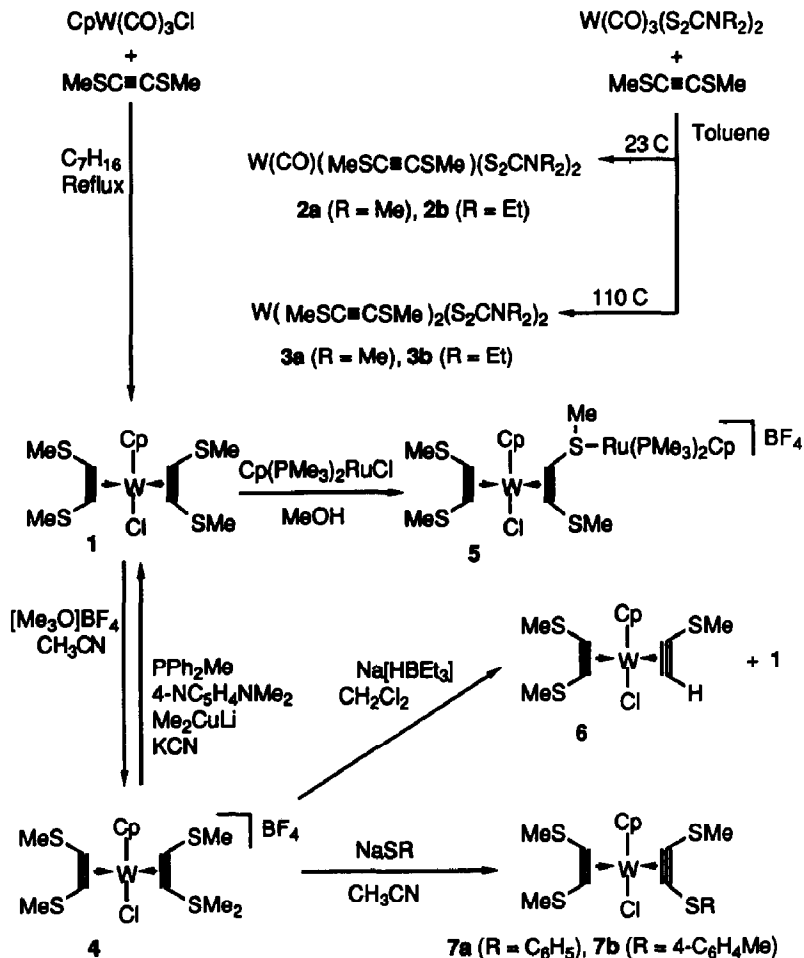
Scheme 1

complex CpW(η^2-MeSC≡CSMe)$_2$Cl (1) in 30% yield (Scheme 1). Complex 1 is characterized by ^{1}H NMR and ^{13}C NMR spectra, EI-MS, and elemental analyses; complex 1 was previously reported by Connor and Hudson [10a]. Similarly, reactions of W(CO)$_3$(S$_2$CNR$_2$)$_2$ (R = Me and Et) with excess MeSC≡CSMe in toluene solution give at room temperature green complexes of W(CO)(η^2-MeSC≡CSMe)(S$_2$CNR$_2$)$_2$ (2a for R = Me, 2b for R = Et); the same reactions at refluxing temperatures cause complete decarbonylation to give yellow air-stable complexes W(η^2-MeSC≡CSMe)$_2$(S$_2$CNR$_2$)$_2$ (3a for R = Me, 3b for R = Et) in 30–35% yield (Scheme 1). 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)(η^2-acetylene)(S$_2$CNR$_2$)$_2$ 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$_2$PC≡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 ^{1}H and ^{13}C NMR spectra. The ^{1}H NMR spectra of 1, 2, and 3b show only one ^{1}H NMR SMe signal; it occurs

Table 5

Carbon-13 chemical shifts of alkyne carbons π-bound to molybdenum(II) and tungsten(II) centers

Complex	C≡C	N^a	Ref.
[CpW(PMe₃)₂(η^2-MeC≡COMe)]BF₄	227.9, 200.5	4	45
W(CO)(η^2-C₈H₁₂)(S₂CNMe₂)₂	215.2	4	21
CpW(CO)(η^2-MeC≡CMe)COEt	193.7, 192.5	4	42
Mo(η^2-EtC≡CEt)₂(S₂CNMe₂)₂	183.8, 181.3	3	30e
Mo(η^2-PhC≡CH)₂(S₂CNEt₂)₂	183.2, 177.1	3	30a
WI₂(CO)₂(η^2-MeC≡CMe)₂	151.9	3	25
[CpW(CO)(η^2-MeC≡CMe)₂]PF₆	160.4, 142.2	3	26
Cp₂Mo(η^2-HC≡CH)	117.7	2	43
Cp₂Mo(η^2-MeC≡CMe)	115.3	2	30a

^{a} N = Number of electrons formally donated by each alkyne to the metal.

in the range from 2.74 to 2.99 ppm. The ^{1}H NMR alkyne-methyl resonances of similar complexes such as W(CO)(η^2-MeC≡CMe)(S₂CNEt₂)₂ [23], W(CO)₂(dppe) (η^2-MeO₂CC≡CCO₂Me)₂ [24], and WI₂(CO)₂(η^2-MeC≡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 Me resonances are also reported for the π-alkyne in [CpW(CO)(η^2-MeC≡CMe)₂]PF₆ [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)(η^2-MeC≡CMe)(PEt₃)₂Br₂ [27b] and Mo(CO)(η^2-PhC≡CH)(S₂CNMe₂)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≡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 5) [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(η^2-MeSC≡CSMe)₂Cl (1). The addition of electrophiles to coordinated acetylenes is known to give *cis*-vinyl complexes, presumably via initial addition to the metal center, as shown in eq. 2. In contrast, complex **1** reacts

(Scheme 1) with [Me$_3$O]BF$_4$ in CH$_3$CN to form the dimethyl-sulfonium complex [CpClW(η^2-MeSC≡CSMe)(η^2-MeSC≡CSMe$_2$)]BF$_4$ (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≡CSMe$_2^+$ ligand is stabilized in 4 since the free sulfonium-alkyne [PhC≡CS(Me)Et](picrate) [31] is reported to be unstable.

Complex 1 also reacts with Cp(PMe$_3$)$_2$RuCl and NH$_4$BF$_4$ in methanol solution to give the ruthenium-methyl-sulfonium complex {CpW(η^2-MeSC≡CSMe)[η^2-MeSC≡CS(Me)Ru(PMe$_3$)$_2$Cp]}BF$_4$ (5) as an air-stable yellow powder in 58% yield. The addition of the Cp(PMe$_3$)$_2$Ru$^+$ to the sulfur is supported by the ^{1}H 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$_3$)$_2$Ru[S(Me)C≡CSMe]}BF$_4$ [9].

The ^{1}H NMR resonances of the diastereotopic methyls in the SMe$_2$ sulfonium 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)Re (CH$_2$SMe) (2.01 ppm) and [Cp(PPh$_3$)(NO)Re(CH$_2$SMe$_2$)]PF$_6$ (2.60 ppm) [32], as well as [Cp(PMe$_3$)$_2$Ru=C=C(Me)(SMe)]I (2.20 ppm) and [Cp(PMe$_3$)$_2$Ru=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 5), making 4 an 18-electron complex. The rather broad range of alkyne carbon signals in the bis-alkyne complexes [CpW(η^2-MeC≡CMe)$_2$L]BF$_4$ [34] 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.

$$\begin{array}{ccc} \text{MeS} & \text{Cp} & \text{SMe} \\ \text{} & | & \\ \text{W} & & \\ \text{MeS} & | & \text{SMe}_2 \\ & \text{Cl} & \end{array}^+ \longrightarrow \begin{array}{ccc} \text{MeS} & \text{Cp} & \text{SMe} \\ & | & \\ \text{W=C=C} & \\ \text{MeS} & | & \text{SMe}_2 \\ & \text{Cl} & \end{array}^+ \quad (6)$$

(4)   (G)

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 acetone-d_6 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 5); 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 CpMo[P(OMe)$_3$]$_2$=C=C(H)-(t-Bu) [33] and at 348.6 and 141.3 ppm in CpMo[P(OMe)$_3$](N$_2$C$_6$H$_4$F-4)=C=C(H)(t-Bu) [33] 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 room temperature with the following nucleophiles: PPh$_3$, CNt-Bu, CO, AgCN, NaSPh, Na[S$_2$CNMe$_2$], NaH, and Na[HBEt$_3$].

Crystal structure of [CpClW(η²-MeSC≡CSMe)(η²-MeSC≡CSMe$_2$)]BF$_4$ · 1.5CH$_2$Cl$_2$ (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 (Fig. 1). The C≡C bonds of the two coordinated alkynes lie approximately parallel to the W → Cl vector with carbon atoms C(2) and C(8) tilted towards each other. The angles between the C(2) → C(3) and W → Cl vectors and the C(7) → C(8) and W → 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 3). These distances are very similar to the corresponding distances (2.29(3) to 2.38(3) Å) in CpW(η²-CF$_3$C≡CCF$_3$)$_2$Cl [35] and those (2.338(4) to 2.409(4) Å) in the cationic complex [CpMo(η²-MeC≡CMe)$_2$(CO)]BF$_4$ [34]. The W–Cl distance (2.452(1) Å) is slightly longer than those in CpW(η²-CF$_3$C≡CCF$_3$)$_2$Cl [35] (2.417(3) Å) and CpWCl(η²-CF$_3$C≡CCF$_3$)(η²-CF$_3$CC(CF$_3$)CN^{t}Bu) [3] (2.416(3) Å).

The tungsten-alkyne carbon distances to the MeSC≡CSMe ligand (W–C(7) (2.036(5) Å) and W–C(8) (2.044(6) Å)) are 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≡CSMe$_2^+$ ligand. Similar Mo- and W-η²-alkyne carbon distances range from 2.049(18) to 2.071(15) Å for CpW(η²-CF$_3$C≡CCF$_3$)$_2$Cl [35], from 2.061(4) to 2.124(4) Å for [CpMo(η²-MeC≡CMe)$_2$(CO)]BF$_4$ [34] and from 2.032(6) to 2.038(6) Å for CpW(CO){C(4-C$_6$H$_4$Me)CO}(η²-MeC≡CNEt$_2$) [36]. 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 η²-vinyl type bonding in the MeSC≡CSMe$_2^+$ ligand. However, W–C(3) is not as short as the η²-vinyl W=C distance (1.894(8) Å) and W–C(2) is not as long as the other W–C distance (2.304(10) Å) in CpWCl(η²-CF$_3$C≡CCF$_3$)(η²-CF$_3$CC(CF$_3$) CN^{t}Bu) [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)$_3$}$_2$Mo(η²-PhCC(H)Ph) [7]. Thus, the MeSC≡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) in exo-CpW{E-η³-SC(CF$_3$)=C(CF$_3$)H}(η²-CF$_3$C≡CCF$_3$) [37] to 1.267(6) and 1.277(5) Å in [CpMo(η²-MeC≡CMe)$_2$(CO)]BF$_4$ [34] and to 1.339(8) Å in CpW(CO){C(4-C$_6$H$_4$Me)CO}(η²-MeC≡CNEt$_2$) [36]. 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(≡C-SPh) [38] (1.716(10 Å), [HB(pz)$_3$](MeS)$_2$W(≡C–SMe) [39] (1.700(7) Å), and MeSC≡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 $[Cp(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}C=S)$ [40] (1.596(9) Å) and $(CO)_2(PPh_3)_2(H)Os$ $[C(=S)SMe]$ [41] (1.648(4) Å). These comparisons therefore suggest that there is no significant $C(sp)$–S multiple bonding in 4.

Reactions of $[CpClW(\eta^2\text{-}MeSC\equiv CSMe)(\eta^2\text{-}MeSC\equiv CSMe_2)]BF_4$ *(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 1). 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 $[Cp(PMe_3)_2\text{-}Ru=C=C(SMe)(SMe_2)](BF_4)_2$ with 4-NC_5H_4R (R = H and Et) to give $[Cp(PMe_3)_2\text{-}Ru=C=C(SMe)_2]BF_4$ 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 $CpW(\eta^2\text{-}MeSC\equiv CSMe)(\eta^2\text{-}MeSC\equiv CH)Cl$ (6) and 1 obtained in an overall yield of 98% (Scheme 1). 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, $CpW(CO)(\eta^2\text{-}PhC\equiv CH)COEt$ [42] (12.82 ppm) and $Cp_2Mo(\eta^2\text{-}MeC\equiv CH)$ [43] (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 $CpW(\eta^2\text{-}MeSC\equiv CSMe)(\eta^2\text{-}MeSC\equiv CSR)Cl$ (7a for R = C_6H_5, 7b for R = 4-C_6H_4Me) which are isolated as yellow oils in approximately 80% yield (Scheme 1). 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 $[M(\eta^2\text{-}PhC\equiv CH)(ma)(S_2CNR_2)_2]$ [44] (M = Mo or W, R = Me; M = W, R = Et; ma = maleic anhydride) to give η^2-vinyl complexes $M\{\eta^2\text{-}C(Ph)C(H)(PR_3)\}(ma)(S_2CNR_2)_2$.

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 to vinylidenes is not observed on d^4 metals whereas this 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 1). Thus, in both the tungsten sulfonium alkyne complex **4** and the ruthenium sulfonium vinylidene complex the Me_2S group is readily displaced by nucleophiles.

Acknowledgments

Supplementary material available. Tables containing displacement parameters (2 pages) and structure factors (22 pages) are available from R.J. Angelici.

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