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Reaction Chemistry of a Tungsten Disilene Complex: Net One-Atom Insertion of Chalcogens into $Cp_2W(\eta^2\text{-}Me_2Si{=}SiMe_2)$

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The tungsten disilene complex, $Cp_2W(\eta^2\text{-}Me_2Si{=}SiMe_2)$ (1) reacts with the heavier elemental chalcogens to yield symmetrical insertion products *cyclo*-$Cp_2W(Me_2SiESiMe_2)$ (E = S, Se, Te; **2b–d**). Although 1 does not react cleanly with O_2, the oxygen insertion product *cyclo*-$Cp_2W(Me_2SiOSiMe_2)$ (**2a**) can be prepared by treatment of 1 with trimethylamine *N*-oxide. The four-membered ring compounds **2b,c** are also formed in the reaction of 1 with phosphine chalcogenides, although varying amounts of the unsymmetrical isomers, *cyclo*-$Cp_2W(ESiMe_2SiMe_2)$, are produced. The ratio of symmetrical to unsymmetrical isomers formed is strongly dependent on the size of the phosphine chalcogenide. Thus the unsymmetrical isomer is slightly favored (55:45) with the smallest sulfide examined, $Ph_2MeP{=}S$, and not observed at all in the reaction of 1 with the very hindered $Cy_3P{=}S$ (Cy ≡ cyclohexyl). The molecular structures of **2a** and **2c** were determined by single crystal X-ray diffraction methods. Compound **2a**: monoclinic space group $P2_1/m$, a = 7.639(2) Å, b = 13.877(5) Å, c = 7.974(1) Å, β = 115.71(2)°, V = 761.6(7) Å^3, R_1 = 0.036, R_2 = 0.041. Compound **2c**: orthorhombic space group *Pbca*, a = 17.472(2) Å, b = 17.729(2) Å, c = 21.255(2) Å, V = 6584(2) Å^3, R_1 = 0.042, R_2 = 0.045.

Introduction

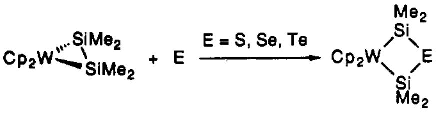
Recent progress over the past few years has clearly established that transition metals are capable of binding and stabilizing reactive unsaturated silicon species in much the same manner as more common organic olefins. Thus, since 1988 stable complexes of disilenes,[2,3] silenes,[4,5] silanimines,[6] and silatrimethylene methanes[7] have been isolated and structurally characterized. Despite the extreme reactivity of the parent silaolefins, these complexes exhibit structural and spectroscopic properties consistent with a bonding scheme which is qualitatively indistinguishable from that well-established for alkenes.

The reactivity observed for silaolefin complexes, however, diverges significantly from established organometallic chemistry. Nowhere is this distinction greater than for the case of disilene complexes, for which a wide variety of reagents have been shown to yield new ring compounds by the net insertion of an atom *between* the two silicon atoms of the silaolefin fragment. This reactivity pattern is observed for both early and late transition metal disilene complexes, but it is almost unprecedented in organometallic chemistry. Continuing in this vein, the present report describes the reactions of the tungsten disilene complex $Cp_2W(\eta^2\text{-}Me_2Si{=}SiMe_2)$ (1), with elemental chalcogens and chalcogen atom transfer agents, and the characterization of the resultant metallacyclic products.

The bonding in silaolefin complexes is best described by the Dewar–Chatt–Duncanson model, in which metal–olefin bonding is bounded by limiting resonance structures involving formal sp^2- or sp^3-hybridization ("olefin complex" vs "metallacyclopropane").[8] The extent of multiple bonding in the olefin complex is inversely proportional to the degree of π-back-bonding from the metal into the LUMO of the olefin. Previous structural and spectroscopic characterization of $Cp_2W(\eta^2\text{-}Me_2Si{=}SiMe_2)$ suggested that partial Si—Si double bond character is maintained in the complexed disilene, but in terms of the chemical reactivity observed in past studies and this report, the disilene complexes are most conveniently viewed as three-membered ring compounds.[2,3] In either extreme, however, the tungsten is an 18-e, coordinatively saturated center, and thus associative or nucleophilic reactions at the metal will tend to be disfavored.

Results and Discussion

Synthesis of *cyclo*-$Cp_2W(Me_2SiESiMe_2)$ (E = O, S, Se, Te; 2a–d). Reactions of 1 with Elemental Chalcogens. Treatment of a benzene solution of the tungsten disilene complex 1 with selenium at 60 °C for 18 h yields the symmetrical insertion product, *cyclo*-$Cp_2W(Me_2SiSeSiMe_2)$ (**2c**), as shown in eq 1. Analysis of the reaction mixture by ^1H NMR indicates that **2c** is the only soluble



(1)

1 **2b,c,d**

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product and the complex has been isolated essentially pure in ca. 80% crude yield (49% following recrystallization). The ^{1}H NMR spectrum of **2c** exhibits a single Cp peak (δ 3.98) and a single methyl resonance (δ 0.98), which clearly establishes the high symmetry of the product. The regiochemistry of the insertion is confirmed by observation of a ^{183}W–^{29}Si coupling constant of 99.2 Hz in the ^{29}Si NMR spectrum (δ −30.5). Tungsten silyl compounds containing one-bond Si–W connections exhibit couplings in the range 50–120 Hz,[2,4,9] whereas two-bonded Si–W couplings are generally too small to be resolved in the silicon NMR. It is possible, therefore, to eliminate alternative symmetrical structures in which selenium atoms are situated between the tungsten and silicon centers. Correct elemental analysis and HRMS confirm that only a single selenium atom has been added to **1**. In addition, the spectroscopic parameters for **2c** are very similar to those observed for $Cp_2Mo(SiMe_2SSiMe_2)$ which has been previously structurally characterized.[2b] Finally, the structure of **2c** has been confirmed by a single crystal X-ray diffraction study (vide infra).

The analogous reaction of **1** with elemental tellurium at 60 °C for 12 h produces *cyclo*-$Cp_2W(Me_2SiTeSiMe_2)$ (**2d**) as the major product, observed by ^{1}H NMR. However, some of the reaction mixture is insoluble in hydrocarbon solvents, and may be due to multiple insertions. Analytically pure **2d** has been obtained in 37% yield following recrystallization of the soluble fraction. The ^{1}H spectrum for **2d** is similar to that found for the selenium complex and indicates an analogous, symmetrical structure. The ^{29}Si NMR spectrum of **2d** exhibits a single peak with large tungsten satellites (δ −61.8, $^1J_{Si-W}$ = 103.1 Hz), again consistent with the proposed structure.

Although one-bond ^{183}W–^{29}Si coupling constants were readily observed in the ^{29}Si NMR spectra of **2c** and **2d**, analogous couplings to the ^{77}Se and ^{125}Te nuclei were not observed. This is presumably due to the lower natural abundance of ^{77}Se (7.50%) and ^{125}Te (7.03%) relative to ^{183}W (14.28%).[10]

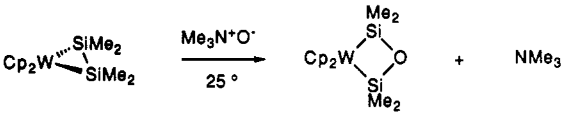
The reactions of **1** with the lighter chalcogens, however, are more complicated than those with selenium and tellurium. Solutions of the tungsten disilene complex **1** react extremely rapidly with O_2 at −78 °C to produce a complex mixture from which no single compound could be cleanly isolated, although, the oxygen insertion product, *cyclo*-$Cp_2W(Me_2SiOSiMe_2)$ (**2a**) was observed in the ^{1}H NMR spectrum of the mixture (ca. 35%). However, **2a** has been isolated by an alternate method, as described below, and fully characterized.

We have previously shown that the molybdenum disilene complex $Cp_2Mo(\eta^2\text{-}Me_2Si{=}SiMe_2)$ reacts readily with elemental sulfur to yield the symmetrical insertion product *cyclo*-$Cp_2Mo(Me_2SiSSiMe_2)$.[2b] Similarly, reaction of the tungsten analog **1** with S_8 yields **2b** as the major product (ca. 50%) within minutes at room temperature. As in the case of **2a**, although **2b** can be readily identified in the ^{1}H NMR spectrum, isolation from the mixture has not proven possible, but **2b** can be cleanly generated by other routes (vide infra).

In addition to our previous studies of the reaction of sulfur with $Cp_2Mo(\eta^2\text{-}Me_2Si{=}SiMe_2)$, precedent for chalcogen insertions into the silicon—silicon bond of a coordinated disilene can be found in West's report of the formation of *cyclo*-$(PR_3)_2Pt(R_2SiOSiR_2)$ from the reaction of oxygen with the corresponding disilene complex.[2b,3b] Potentially relevant analogies are also apparent in the reactions of free disilenes with chalcogens, which initially yield the three-membered Si_2E ring systems,[11-13] and in the reaction of sulfur with siliranes to yield thiasilacyclobutanes (SiC_2S rings).[14]

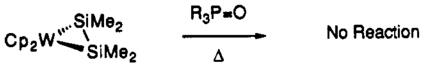
An obvious trend in the reactivity of **1** with chalcogens is the decreasing reactivity going down the group. For example, reaction with oxygen is instantaneous and unselective at room temperature, whereas formation of **2c** and **2d** requires hours at 60 °C. Several factors may give rise to this trend in the apparent reactivity, including the triplet ground electronic state of oxygen, decreasing solubility in organic solvents going down the series, and the trends in Si–E bond strengths and oxidation potentials.

Symmetrical Insertion Products from Reactions of 1 with Group 15 Chalcogenides. The symmetrical insertion products are also formed in the reactions of **1** with other chalcogen atom transfer agents. Thus, although **1** does not react cleanly with O_2, the oxygen insertion product *cyclo*-$Cp_2W(Me_2SiOSiMe_2)$ (**2a**) can be prepared by treatment of the disilene complex with trimethylamine *N*-oxide. Reaction of **1** with trimethylamine *N*-oxide in benzene produces **2a** and trimethylamine within 5 h at 25 °C (eq 2). The reaction rate appears to be limited primarily by the dissolution of Me_3NO in benzene. Compound **2a** has been isolated in 78% yield and the structure assigned on the basis of spectroscopic data, which are similar to those for **2b–d**. In particular, the ^{29}Si NMR spectrum of **2a** exhibits a single resonance (δ 20.6) with tungsten satellites ($^1J_{Si-W}$ = 85.9 Hz). The crystal structure of **2a** has also been determined (vide infra).



(2)

Attempts to synthesize the insertion products **2a–d** from the reaction of **1** with phosphine chalcogenides have been met with varying degrees of success. It has been previously noted that $Ph_3P{=}O$ does not react with $Cp_2Mo(\eta^2\text{-}Me_2Si{=}SiMe_2)$, even at elevated temperatures,[2b] and similarly, there is no reaction upon heating the tungsten complex **1** in with $Ph_3P{=}O$ (eq 3).



(3)

It was also observed that the molybdenum disilene complex reacts with $Ph_3P{=}S$ to form both the symmetrical and asymmetrical insertion products, *cyclo*-$Cp_2Mo(SiMe_2SSiMe_2)$ and *cyclo*-$Cp_2Mo(SSiMe_2SiMe_2)$, in a 1:3 ratio.[2b] Likewise, **1** reacts with $R_3P{=}S$ (R_3P = Ph_2MeP, Ph_3P, and Cy_3P; Cy ≡ cyclohexyl) at 60 °C to yield the two isomeric insertion products, **2b** and *cyclo*-$Cp_2W(SSiMe_2SiMe_2)$, in varying ratios (eq 4).

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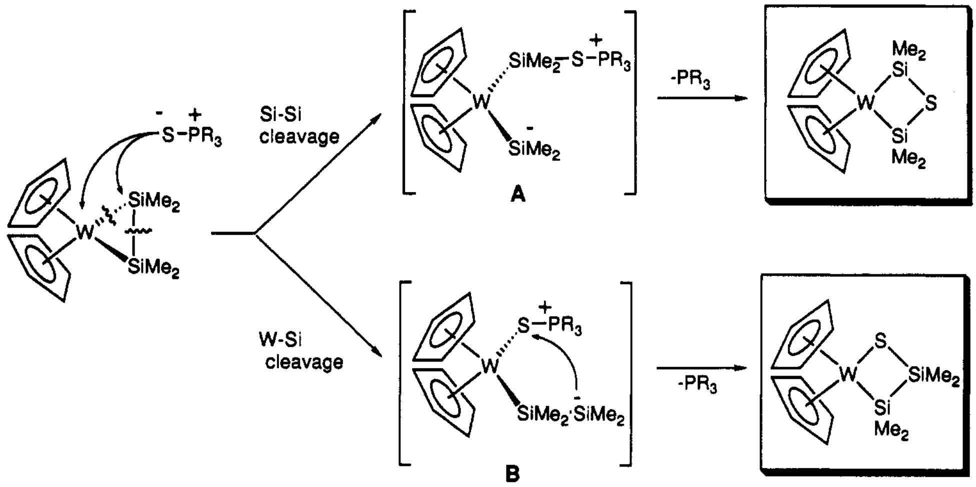
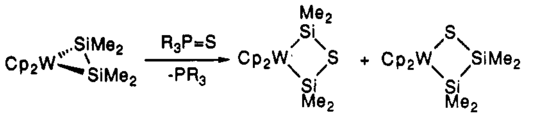
Scheme I




(4)

Ph$_2$MeP=S 45 : 55
Ph$_3$P=S 75 : 25
Cy$_3$P=S 100 : 0

Because **2b** is not cleanly produced in the reaction of 1 with elemental sulfur, the phosphine sulfide reaction was viewed as a potential synthetic route to **2b**. Unfortunately, although reaction of 1 with $Cy_3P{=}S$ quantitatively yields **2b** and PCy_3, attempts to separate pure **2b** from the phosphine by recrystallization and fractional sublimation were not successful. Therefore, all spectroscopic parameters were obtained from the mixture of **2b** and Cy_3P. The unsymmetrical isomer, observed in the reactions of $Ph_3P{=}S$ and $Ph_2MeP{=}S$, also was not isolated, but exhibits a proton NMR spectrum which is virtually identical to that of the structurally characterized unsymmetrical molybdenum analog, $Cp_2Mo(SSiMe_2SiMe_2)$.

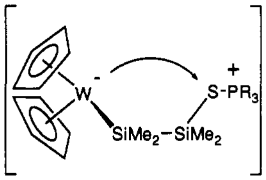
Thermolysis in solution at up to 100 °C does not lead to interconversion of the symmetrical and unsymmetrical isomers, thus it is not possible to establish the relative thermodynamic stabilities of the two forms.

The simplest process for delivery of sulfur to 1 would probably involve nucleophilic attack by the phosphine sulfide. Any proposed mechanism, however, must take into account the formation of both isomers, and the observed dependence of the ratio of isomers on the steric requirements of the phosphine sulfide, as indicated in eq 4. Thus the unsymmetrical isomer is slightly favored with the smallest sulfide examined, $Ph_2MeP{=}S$, and not observed at all in the reaction of 1 with the very hindered $Cy_3P{=}S$. Examination of the molecular structure of 1 suggests that the Si—Si bond is the most sterically accessible, and that the bulk of the Cp rings would tend to hinder approach from along the W—Si bond.

In the proposed mechanism depicted in Scheme I, reaction is initiated by nucleophilic attack by the phosphine sulfide at either a silicon atom, leading to cleavage of a silicon–silicon bond, or at the tungsten center, which would lead to cleavage of a tungsten–silicon bond. Cleavage of the silicon–silicon bond would generate a zwitterionic intermediate, **A**, consisting of a silyl anion and phosphonium cation. Intramolecular nucleophilic displacement of phosphine would then lead to the symmetrical four-membered ring compound. On the other hand, cleavage of a tungsten–silicon bond would result in a different zwitterionic intermediate, **B**, from which intramolecular displacement of phosphine would consequently generate the unsymmetrical ring system. The greater hindrance at the tungsten center would thus disfavor W–Si cleavage, and hence the unsymmetrical isomer, as the size of the phosphine sulfide is increased.

The major drawback to the mechanism in Scheme I is the associative substitution at the 18-e, coordinately saturated metal center required to form **B**. However, nucleophilic attack at tungsten would be more plausible if coupled with a transient change in the Cp ring bonding mode, as has been previously observed in related cyclopentadienyl complexes.[4,15,16]

It is also possible that both isomers arise from initial attack of the phosphine sulfide at silicon. In this alternative sequence, nucleophilic attack at silicon would have two potential outcomes: Si–Si cleavage (as in the top path of Scheme I) or displacement of the W–Si bond to yield a zwitterionic intermediate **C**, consisting of a tungsten anion and a phosphonium cation. Intramolecular displacement of phosphine from **C** would then yield the unsymmetrical isomer. However, in this instance the origins of the steric preference for the symmetrical isomer are not readily apparent, and thus the mechanism shown in Scheme I is preferred.


C

The reaction of 1 with $Ph_3P{=}Se$ has also been examined and found to yield the symmetrical **2c** as the only observed product. Interestingly, the reaction is quite rapid at room

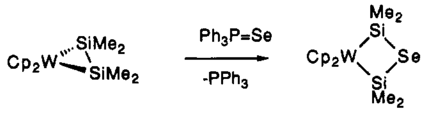

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Table I. Crystallographic Data for the Structure Determinations of 2a and 2c

	2a	**2c**
formula	$C_{14}H_{22}OSi_2W$	$C_{14}H_{22}SeSi_2W$
fw	446.35	509.31
cryst dimens (nm)	0.25 × 0.45 × 0.48	0.10 × 0.23 × 0.40
cryst class	monoclinic	orthorhombic
space group	$P2_1/m$ (No. 11)	*Pbca* (No. 61)
Z	2	16
cell constants		
a (Å)	7.639(2)	17.472(2)
b (Å)	13.877(5)	17.729(2)
c (Å)	7.974(1)	21.255(2)
β (deg)	115.71(2)	
V (Å^3)	761.6(7)	6584(2)
μ (cm^{-1})	78.89	94.87
D_{calc} (g/cm^3)	1.946	2.055
F(000)	432	3872
radiation	Mo K$\bar{\alpha}$ (λ = 0.710 73 Å)	Mo K$\bar{\alpha}$
θ range (deg)	2.0–27.5	2.0–27.5
scan mode	ω–2θ	ω–2θ
linear decay corr (%)	0.6	2.4
transm		
min	37.26	39.74
av	70.20	72.04
max	99.82	99.99
h,k,l collcd	+9,−18,±10	22,23,27
no. of reflns measd	1946	8250
no. of unique reflns	1810	7541
no. of reflns used in refinement	1810 (>3.0σ)	3482 (>3.0σ)
no. of params	89	325
data/param ratio	20.3	10.7
R_1	0.036	0.042
R_2	0.041	0.045
GOF	1.232	1.354

Table II. Selected Bond Distances (Å) in 2a[a]

W–C1	2.285(7)	C3–C3′	1.436(13)
W–C2	2.307(7)	C4–C5	1.412(12)
W–C3	2.325(8)	C5–C6	1.389(14)
W–C4	2.257(10)	C6–C6′	1.411(15)
W–C5	2.301(7)	C7–Si	1.877(9)
W–C6	2.298(7)	C8–Si	1.877(8)
W–Si	2.551(2)	Si–Si′	2.594(3)
C1–C2	1.480(10)	Si–O	1.690(5)
C2–C3	1.399(10)		

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

Table III. Selected Bond Angles (deg) in 2a[a]

Cp1[b]–W–Cp2[b]	141.4	W–Si–Si′	59.4(1)
Si–W–Si′	61.1(1)	W–Si–O	99.3(2)
C2–C1–C2′	106.4(7)	C7–Si–C8	102.1(4)
C1–C2–C3	107.3(7)	C7–Si–Si′	122.8(3)
C2–C3–C3′	109.5(7)	C7–Si–O	105.2(4)
C5–C4–C5′	109.7(10)	C8–Si–Si′	126.9(3)
C4–C5–C6	106.3(9)	C8–Si–O	106.2(3)
C5–C6–C6′	108.8(9)	Si′–Si–O	39.9(2)
W–Si–C7	121.3(2)	Si–O–Si′	100.2(4)
W–Si–C8	120.9(3)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits. [b] Cp1 and Cp2 refer to the C_5H_5 ring centroids.

Table IV. Selected Bond Distances (Å) in 2c[a]

molecule A		molecule B	
W–Si1	2.547(4)	W′–Si1′	2.544(4)
W–Si2	2.559(4)	W′–Si2′	2.565(4)
Si1–Se	2.325(5)	Si1′–Se′	2.313(5)
Si1–C11	1.878(17)	Si1′–C11′	1.842(18)
Si1–C12	1.880(17)	Si1′–C12′	1.891(18)
Si2–Se	2.309(5)	Si2′–Se′	2.335(5)
Si2–C13	1.855(17)	Si2′–C13′	1.899(16)
Si2–C14	1.876(18)	Si2′–C14′	1.875(19)
C1–C2	1.386(21)	C1′–C2′	1.347(20)
C1–C5	1.400(21)	C1′–C5′	1.431(21)
C2–C3	1.436(21)	C2′–C3′	1.430(22)
C3–C4	1.399(21)	C3′–C4′	1.418(21)
C4–C5	1.420(20)	C4′–C5′	1.400(20)
C6–C7	1.429(21)	C6′–C7′	1.385(22)
C6–C10	1.407(22)	C6′–C10′	1.444(22)
C7–C8	1.426(22)	C7′–C8′	1.373(22)
C8–C9	1.432(22)	C8′–C9′	1.363(21)
C9–C10	1.421(21)	C9′–C10′	1.377(21)

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

Table V. Selected Bond Angles (deg) in 2c[a]

molecule A		molecule B	
Cp1[b]–W–Cp2[b]	140.2	Cp1′[b]–W′–Cp2′[b]	140.0
Si1–W–Si2	71.2(1)	Si1′–W′–Si2′	70.8(1)
W–Si1–Se	104.5(2)	W′–Si1′–Se′	104.4(2)
W–Si1–C11	120.9(6)	W′–Si1′–C11′	122.0(5)
W–Si1–C12	119.8(6)	W′–Si1′–C12′	120.3(6)
Se–Si1–C11	105.1(6)	Se′–Si1′–C11′	103.6(6)
Se–Si1–C12	105.3(5)	Se′–Si1′–C12′	103.4(6)
C11–Si1–C12	99.6(8)	C11′–Si1′–C12′	100.7(8)
W–Si2–Se	104.5(2)	W′–Si2′–Se′	103.1(2)
W–Si2–C13	122.0(6)	W′–Si2′–C13′	122.2(6)
W–Si2–C14	121.0(7)	W′–Si2′–C14′	119.6(6)
Se–Si2–C13	103.7(6)	Se′–Si2′–C13′	102.3(6)
Se–Si2–C14	104.6(6)	Se′–Si2′–C14′	105.5(6)
C13–Si2–C14	98.8(10)	C13′–Si2′–C14′	101.8(8)
Si1–Se–Si2	79.8(2)	Si1′–Se′–Si2′	79.1(2)
C2–C1–C5	108.1(13)	C2′–C1′–C5′	109.9(14)
C1–C2–C3	110.2(13)	C1′–C2′–C3′	107.9(13)
C2–C3–C4	104.4(13)	C2′–C3′–C4′	107.6(13)
C3–C4–C5	110.6(12)	C3′–C4′–C5′	107.6(13)
C1–C5–C4	106.7(12)	C1′–C5′–C4′	107.0(13)
C7–C6–C10	107.4(13)	C7′–C6′–C10′	104.6(13)
C6–C7–C8	109.3(13)	C6′–C7′–C8′	110.1(13)
C7–C8–C9	105.9(13)	C7′–C8′–C9′	108.7(13)
C8–C9–C10	109.1(13)	C8′–C9′–C10′	108.4(14)
C6–C10–C9	108.3(13)	C6′–C10′–C9′	108.2(1)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits. [b] Cp1 and Cp2 refer to the C_5H_5 ring centroids.

temperature, in contrast to that of **1** with $Ph_3P{=}S$, which requires days to reach completion. The trend in relative reactivity of the phosphine chalcogenides with **1** is opposite to that found for the free chalcogens, in which the lighter analogs react faster.

Crystal Structures of *cyclo*-$Cp_2W(SiMe_2ESiMe_2)$ (2a and 2c). The structures of the oxygen and selenium metallacycles $Cp_2W(SiMe_2ESiMe_2)$ (**2a** and **2c**) were confirmed by single crystal X-ray diffraction methods. Crystallographic details are summarized in Table I, and bond distances and angles are listed in Tables II–V. An ORTEP drawing of **2a** is shown in Figure 1. The tungsten center in **2a** lies on a crystallographic mirror plane, which bisects the two Cp rings and the WSi_2O ring. The WSi_2O ring is nearly planar, the oxygen atom lies only 0.063 Å above the WSi_2 plane, and the dihedral angle formed by the WSi_2 and Si_2O planes does not differ significantly from zero (3 ± 3°).

In contrast, **2c** crystallizes with two unique molecules in the unit cell (**A** and **B**), as shown in Figures 2 and 3. Structural parameters for the two independent molecules are virtually identical, except for the planarity of the WSi_2Se ring. The four-membered ring in molecule **A** is essentially planar; the Se atom lies only 0.070 Å above the WSi_2 plane and the dihedral angle formed by the WSi_2 and Si_2Se planes is only 2 ± 3°. However, the ring in molecule **B** is fairly puckered, with the selenium atom 0.464 Å above the WSi_2 plane and a corresponding dihedral angle of 15.0 ± 0.5°.

Compound **2c** is isomorphous with the molybdenum/

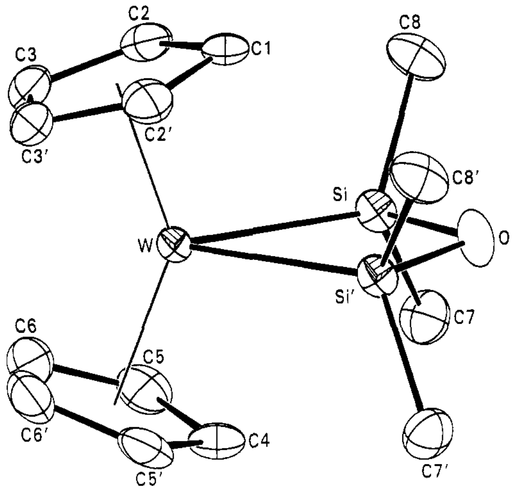


Figure 1. ORTEP drawing of *cyclo*-$Cp_2W(Me_2SiOSiMe_2)$ (**2a**) showing 30% thermal ellipsoids.

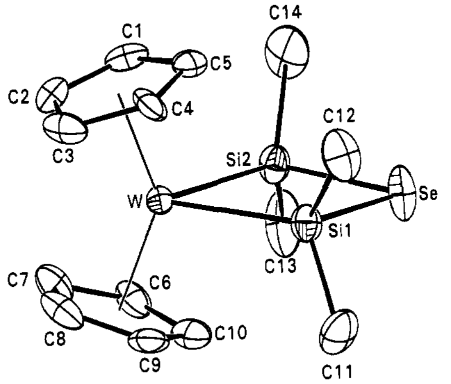


Figure 2. ORTEP drawing of *cyclo*-$Cp_2W(Me_2SiSeSiMe_2)$ (**2c**), molecule **A**, showing 30% thermal ellipsoids.

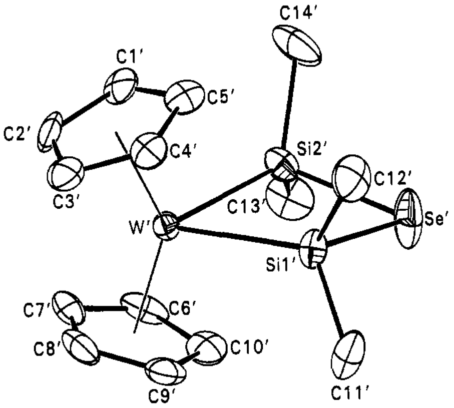


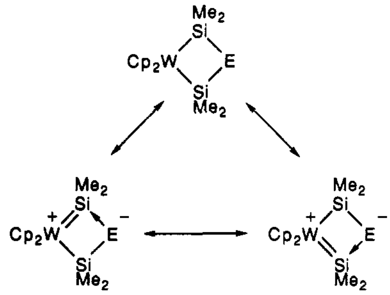
Figure 3. ORTEP drawing of *cyclo*-$Cp_2W(Me_2SiSeSiMe_2)$ (**2c**), molecule **B**, showing 30% thermal ellipsoids.

sulfur analog $Cp_2Mo(\eta^2\text{-}Me_2Si{=}SiMe_2)$[2b] crystallizing in the same space group and with similar cell parameters. The molybdenum complex also crystallizes with two independent molecules, one of which has a planar Mo—Si_2—S ring and one of which is puckered. It is clear that minor distortion of the MSi_2E rings in these systems does not require much energy and that crystal packing forces have more influence on ring conformation in the solid state than minor variations in M or E.

The unique W–Si distance in **2a** (2.551(2) Å) is essentially identical to the average of 2.554 Å for the four W–Si distances in **2c**, which range from 2.544(4) to 2.565(4) Å. Both are quite comparable to the metal–silicon distances observed in the molybdenum/sulfur analog (2.558 Å average) and are similar to those in other tungsten and molybdenum silyls.[2,4,17]

The silicon–chalcogen distances in the ring compounds are slightly longer than might be expected. The Si–O distance in **2a** is 1.690(5) Å, compared with the 1.61–1.65 Å found in unstrained six-membered and larger cyclic siloxanes. However, similar Si–O elongation has been seen in strained cyclic disiloxanes,[18] as well as in related $IrSi_2O$[19] and $PtSi_2O$[3b] ring systems. Similarly, the Si–Se distances in **2b** (2.332 Å average) are longer than in acyclic Si–Se–Si compounds.[20] The sum of the covalent radii of silicon and selenium is 2.28 Å, and a value of 2.27 Å was determined for *D*(Si–Se) in $Se(SiH_3)$ from both gas phase and crystal diffraction studies.[20a,21] Even the highly strained disilaselenirane *cyclo*-$Mes_2SiSeSiMes_2$ exhibits an average Si–Se distance of just 2.306(2) Å.[13] Only in the Si_2Se_3 propellane core of a 2,4,5-triselena-1,3-disilabicyclo[1.1.1]pentane[20d] is the Si–Se distance (2.340 Å) comparable to that found in **2b**.

The relatively long silicon chalcogen distances in **2a** and **2c** are probably the result of the strain in the four-membered ring systems. However, the lengthening may also be due to some degree of π-back-bonding from tungsten into the Si–E σ* orbitals ("hyperconjugation"). Population of this antibonding orbital would lead to strengthening of the W–Si bonds at the expense of the Si–E bond, as illustrated by the minor resonance structures in I.



I

This type of interaction is clearly present in the interesting base-stabilized silylene silyl complex described by Ogino and co-workers recently, as shown in II.[22] In this complex the ring system includes a methoxy group, not a bare oxygen atom as in **2a**; thus electron counting considerations mandate some silylene character. Accordingly, the ring Si–O distances in the iron complex are

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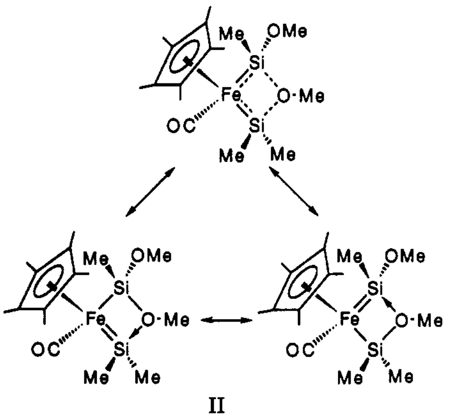

II

extremely long (ca. 1.79 Å). Evidence against a large degree of π-back-bonding in **2a–d** includes the normal length of the W–Si bonds and the invariance of the metal–silicon bond length as a function of the chalcogen in the O, S, and Se derivatives.

Another structural parameter to be addressed is the transannular Si–Si distance. Although this interaction is formally nonbonding, Tessier-Youngs and Youngs have prepared and examined a series of Pt_2Si_2 complexes in which short 1,3-contacts appear to be the result of Si–Si bonding across the four-membered ring.[23] A strong case has been made for viewing these compounds as bridging disilene complexes, with two metals bonded to opposite faces of the silaolefin. Significantly, short Si–Si contacts are not observed in all cases, indicating the interaction is fairly weak and can be disrupted by small changes in the sterics of the complexes. Transannular Si–Si bonding has also been suggested as a possibility by West and Pham in the $PtSi_2O$ ring system described above, although the question arises whether the Si–Si interaction results from favorable bonding energetics or is merely a nonbonded contact enforced by geometrical constraints of the small rings.[3b] The structures of **2a**, **2c**, and the previously reported $MoSi_2S$ derivative allow examination of the Si–Si contact as a function of chalcogen. Indeed, the transannular Si–Si distance in the oxygen adduct **2a** is 2.595 Å, similar to those in the platinum[3b] (2.549 Å) and iridium[19] (2.567 Å) complexes. Although quite long compared with a normal Si–Si single bond (2.34 Å),[24] these values do fall within the observed range in strained ring compounds (2.70 Å maximum). However, the Si–Si contact lengthens substantially to 2.888 Å in the $MoSi_2S$ analog and is even greater (2.971 Å) in the WSi_2Se ring. There is no compelling reason to view these latter two distances as anything other than nonbonding. This trend is consistent with the short 1,3-Si–Si contact in the oxygen derivatives being due principally to simple geometric considerations; the M–Si bond length is essentially invariant in all three derivatives; thus a smaller chalcogen requires a smaller Si–M–Si angle and a closer 1,3-Si–Si contact to permit normal Si–E bond lengths. This is illustrated in Figure 4, which shows a scale representation of the superposition of the WSi_2O and WSi_2Se rings.

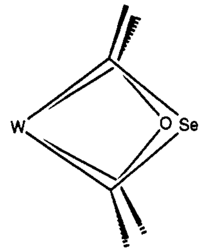

Figure 4. Superposition of WSi_2O (**2a**) and WSi_2Se (**2c**, planar ring only) metallacycles.

Table VI. ^{29}Si NMR Data for *cyclo*-$Cp_2W(SiMe_2ESiMe_2)$

E	δ (ppm)	$^1J_{Si-W}$ (Hz)
O	20.6	85.9
S	−17.8	96.4
Se	−30.5	99.2
Te	−68.1	103.1

Trends in the ^{29}Si NMR Parameters of the Chalcogenide Insertion Products. Two primary trends are apparent in the ^{29}Si NMR data for the symmetrical complexes **2a–d** (Table VI). First of all, the ^{29}Si chemical shifts exhibit a pronounced upfield trend moving down the series, from δ 20.6 in **2a** to δ −60.8 in **2d**. This behavior is identical to that observed for the analogous disilyl chalcogenides, $(Me_3Si)_2E$, and has been attributed to more effective shielding of silicon by the larger chalcogens.[25],[26]

The second clear trend in the ^{29}Si NMR spectra of **2a–d** is the increase in the one-bond ^{29}Si–^{183}W coupling constants going down the series. This trend, which indicates there is greater s-orbital character in the Si–W bonds of the heavier chalcogenide derivatives, can have several possible origins. However, the trend cannot be simply explained on the basis of electronegativity, as Bent's rule would predict the greatest p-orbital character in the Si–E bonds (and thus greatest s-orbital character in the W–Si bonds) of the most electronegative analog, **2a**. This prediction is opposite of the observed trend. The W–Si bond distances, which are nearly identical for **2a** and **2c**, are also not a source of the trend in the W–Si coupling constants. However, coupling constants are extremely sensitive to the geometry at the atoms involved, and it is likely that the trend in $^1J_{Si-W}$ reflects the W–Si–E and Si–W–Si angles, both of which increase steadily going down the series.

Conclusions

Symmetrical four-membered ring compounds *cyclo*-$Cp_2W(SiMe_2ESiMe_2)$ have been prepared from the reactions of elemental chalcogens or group 15 chalcogenides with a tungsten disilene complex. The insertion of chalcogen between the two silicon atoms is consistent with a high degree of metallacyclopropane character in the starting silene complex. Varying amounts of the unsymmetrical isomers are also formed in the reaction of phosphine sulfides with 1, and the variation of the isomer ratio with size of the phosphine is most consistent with competitive attack of the sulfide at silicon and tungsten. As observed in previous MSi_2O ring systems, the crystal

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structure of the oxygen analog, **2a**, exhibits a relatively short transannular Si–Si contact, although structure of the selenium analog does not. This is most likely due to the geometrical constraints imposed by the great difference in lengths of the W–Si and Si–O bonds which define the strained four-membered ring.

Experimental Section

General Procedures. All manipulations were carried out under dry nitrogen using high vacuum-line or Schlenk techniques or in a Vacuum Atmospheres glovebox. Glassware was oven-dried before use. Petroleum ether (boiling range 35–65 °C), toluene, benzene, tetrahydrofuran (THF), and diethyl ether were freshly distilled from sodium benzophenone ketyl. IR spectra were measured on a Perkin-Elmer 1430 spectrophotometer. ^{29}Si NMR spectra were measured on an IBM-Bruker AM 200 spectrometer using the DEPT pulse sequence. Elemental analyses were performed by Robertson Microlit Laboratories. High resolution mass spectral analyses were performed on a VG Instruments ZAB-E spectrometer.

Synthesis of $\mathrm{Cp_2W(Cl)(SiMe_2SiMe_2Cl)}$. To a suspension of $\mathrm{(Cp_2WHLi)_4}$ (2.50 g, 1.89 mmol) was added $\mathrm{ClSiMe_2SiMe_2Cl}$ (ca. 13 equiv/W) in dimethoxyethane at −196 °C. The mixture was warmed to −50 °C and allowed to warm slowly to room temperature while stirring for 12 h. The volatiles were removed in vacuo. The yellow solid was extracted with toluene and filtered. Treatment of the solute with excess $\mathrm{CCl_4}$ (10 mL) for 5 min at 25 °C resulted in a color change from orange to burgundy, upon which the volatiles were removed. The solid was extracted with toluene, filtered, and recrystallized from toluene/petroleum ether to yield 2.78 g (71%) of burgundy product. ^{1}H NMR: δ 4.26 (s, 10H), 0.60 (s, 6H), 0.56 (s, 6H). ^{29}Si NMR (DEPT): δ 35.5, −29.1 ($^1J_{\mathrm{Si-W}}$ = 83.0 Hz).

Synthesis of $\mathrm{Cp_2W(\eta^2\text{-}SiMe_2SiMe_2)}$ (1). To $\mathrm{Cp_2W(Cl)(SiMe_2SiMe_2Cl)}$ (0.778 g, 1.55 mmol) and Rieke magnesium[27] (3.82 mmol) was added dimethoxyethane (150 mL) at −196 °C. The mixture was warmed to −50 °C and stirred for 12 h, at which time the volatiles were removed in vacuo. The solid was extracted with toluene and recrystallized from toluene/petroleum ether to yield 0.39 g (59%) of fine orange plates. ^{1}H NMR: δ 3.86 (s, 10H), 0.62 (s, 12H). ^{29}Si NMR (DEPT): δ −48.1 ($^1J_{\mathrm{Si-W}}$ = 50.7 Hz).

Synthesis of *cyclo*-$\mathrm{Cp_2W(SiMe_2OSiMe_2)}$ (2a). A solution of **1** (51 mg, 0.12 mmol) and trimethylamine *N*-oxide hydrate (9 mg, 0.1 mmol) in 25 mL of benzene was stirred for 4 h at 25 °C. Solvent was removed in vacuo, yielding 41 mg (78%) of a yellow solid. The crude material is essentially pure by ^{1}H NMR but can be recrystallized from tetrahydrofuran/diethyl ether. ^{1}H NMR: δ 3.96 (s, 10H, *Cp*), 0.53 (s, 12H, Si*Me*$_2$). ^{13}C NMR: δ 75.0 (*Cp*), 8.6 (Si*Me*$_2$). ^{29}Si NMR (DEPT): δ 20.6 ($^1J_{\mathrm{Si-W}}$ = 85.9 Hz). Anal. Calcd for $\mathrm{C_{14}H_{22}OSi_2W}$: C, 37.67; H, 4.97. Found: C, 36.90; H, 4.42.

Preparation of *cyclo*-$\mathrm{Cp_2W(SiMe_2SSiMe_2)}$ (2b). A solution of **1** (87 mg, 0.20 mmol) and $\mathrm{Cy_3P{=}S}$ (63 mg, 0.20 mmol) in toluene was stirred at 25 °C for 12 h, solvent was removed in vacuo, and the mixture of **2b** and $\mathrm{Cy_3P{=}S}$ was collected. Compound **2b** was the only $\mathrm{Cp_2W}$ complex observed in the ^{1}H NMR spectrum of the mixture. Attempts to remove $\mathrm{Cy_3P{-}S}$ by recrystallization and fractional sublimation were not successful; thus spectroscopic measurements were made on the mixture. ^{1}H NMR: δ 4.00 (s, 10H, *Cp*), 0.73 (s, 12H, Si*Me*$_2$). ^{13}C NMR: δ 77.6 (*Cp*), 12.0 (Si*Me*$_2$). ^{29}Si NMR: δ −30.5 ($^1J_{\mathrm{Si-W}}$ = 96.4 Hz).

Synthesis of *cyclo*-$\mathrm{Cp_2W(SiMe_2SeSiMe_2)}$ (2c). A slurry of selenium powder (35 mg, 0.44 mmol) in a solution of **1** (71 mg, 0.16 mmol) in 50 mL of benzene was heated at 50 °C for 18 h, solvent was removed in vacuo and the product was extracted with 25 mL of toluene. Recrystallization from toluene at −30 °C yielded 41 mg (49%) of yellow solid. ^{1}H NMR: δ 3.98 (s, 10H, *Cp*), 0.89 (s, 12H, Si*Me*$_2$). ^{13}C NMR: δ 78.1 (*Cp*), 12.0 (Si*Me*$_2$). ^{29}Si NMR: δ −30.5 ($^1J_{\mathrm{Si-W}}$ = 99.2 Hz). Anal. Calcd for $\mathrm{C_{14}H_{22}SeSi_2W}$: C, 33.02; H, 4.35. Found: C, 32.65; H, 4.41.

Synthesis of *cyclo*-$\mathrm{Cp_2W(SiMe_2TeSiMe_2)}$ (2d). A slurry of tellurium powder (48 mg, 38 mmol) in a solution of **1** (135 mg, 31 mmol) in 50 mL of benzene was heated at 50 °C for 12 h, solvent was removed in vacuo, and the product was extracted with 25 mL of toluene. Recrystallization from toluene at −80 °C yielded 62 mg (37%). ^{1}H NMR δ 3.99 (s, 10H, *Cp*), 1.00 (s, 12H, Si*Me*$_2$). ^{13}C NMR: δ 79.4 (*Cp*), 11.1 (Si*Me*$_2$). ^{29}Si NMR: δ −61.8 ($^1J_{\mathrm{Si-W}}$ = 103.1 Hz). Anal. Calcd for $\mathrm{C_{14}H_{22}Si_2TeW}$: C, 30.12; H, 3.97. Found: C, 30.75; H, 3.91.

Structure Determinations of 2c. Single crystals of suitable size were grown from toluene/hexanes at −35 °C, sealed in 0.5-mm thin-walled Pyrex capillary in the glovebox, and the capillary was mounted on the diffractometer. Refined cell dimensions and their standard deviations were obtained from least-squares refinement of 25 accurately centered reflections with $2\theta > 25°$. Crystal data are summarized in Table I.

Diffraction data were collected at 295 K on an Enraf-Nonius CAD-4 diffractometer employing Mo K$\bar{\alpha}$ radiation filtered through a highly oriented graphite crystal monochromator. A linear correction for decay was applied on the basis of the intensities of three standard reflections measured at intervals of 3500 s of X-ray exposure. The raw intensities were corrected for Lorentz and polarization effects by using the program BEGIN from the SDP+ package.[28] Empirical absorption corrections based on ψ-scans were also applied.

All calculations were performed on a DEC MicroVax 3100 computer using the SDP+ software package.[28] The full-matrix least squares refinement was based on F, and the function minimized was $\sum w(|F_o| - |F_c|)^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes. The weights (w) were taken as $1/\sigma^2(F_o)$. Atomic scattering factors and complex anomalous dispersion corrections were taken from refs 29–31. Agreement factors are defined as $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_2 = [\sum w||F_o| - |F_c||^2/\sum w|F_o|^2]^{1/2}$. The goodness-of-fit is defined as $\mathrm{GOF} = [\sum w(|F_o| - |F_c|)^2/(N_o - N_p)]^{1/2}$, where N_o and N_p are the number of observations and parameters.

The coordinates of the tungsten, silicon, and selenium atoms were obtained from three-dimensional Patterson maps. Analysis of subsequent difference Fourier maps led to location of the remaining heavy atoms. Refinement using anisotropic Gaussian amplitudes followed by difference Fourier synthesis resulted in the location of most of the Cp hydrogens and at least one hydrogen on each methyl group. All remaining hydrogen atoms were placed at idealized locations, and the positions of all hydrogens were optimized by using the program HYDRO.[28] Final refinements included anisotropic Gaussian amplitudes for all non-hydrogen atoms and fixed positions and fixed isotropic parameters for the hydrogen atoms. Structure refinement is summarized in Table I. Final positional parameters for **2a** and **2c** are included in the supplementary material.

Acknowledgment. Financial support of this work by the National Science Foundation (Grant Nos. CHE-9014625 and DMR-9120668) is gratefully acknowledged.

Supplementary Material Available: Tables of positional parameters, anisotropic thermal parameters, and intramolecular distances and angles for **2a** and **2c** (15 pages). Ordering information is given on any current masthead page.

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