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有機小分子在金屬上的化學

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Key words: ketene, thioketene, tungsten

Summary. Treatment of the dinuclear O-coordinated ketene complex $Cp_2(CO)_5W_2(\mu,\eta^1,\eta^2\text{-}CH_2CO)$ (**2**, Cp = $\eta^5\text{-}C_5H_5$) with $PhCH_2NCS$ afforded the dark red bridging thioketene complex $Cp_2(CO)_5W_2(\mu,\eta^3\text{-}SC{=}CH_2)$ (**3**). Reaction of **3** with HBF_4 gave the stable cationic product $[Cp_2(CO)_5W_2(\mu\text{-}SCCH_3)]BF_4$ (**4**) by addition of a proton to the terminal carbon of the thioketene group.

鑰字: 烯酮，硫烯酮，鎢

摘要. 雙核之鎢烯酮化合物 $Cp_2(CO)_5W_2(\mu,\eta^1,\eta^2\text{-}CH_2CO)$ (**2**, Cp = $\eta^5\text{-}C_5H_5$) 與 $PhCH_2NCS$ 反應生成深紅色之鎢硫烯酮化合物 $Cp_2(CO)_5W_2(\mu,\eta^3\text{-}SC{=}CH_2)$ (**3**). **3** 與 HBF_4 反應，氫離子加在硫烯酮基的末端碳上，生成陽離子之化合物 $[Cp_2(CO)_5W_2(\mu\text{-}SCCH_3)]BF_4$ (**4**).

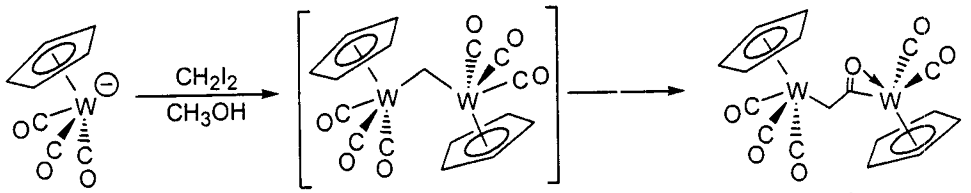
Introduction

Metal complexed ketenes have been prepared by a variety of routes, including coupling of alkylidene and carbonyl moieties,[1] addition of free ketene to unsaturated metal systems[2] and deprotonation of metal acyls.[3] Unlike free ketenes which have been examined for nearly a century,[4] metal complexed ketenes have only recently been investigated. Carbonylation of μ-methylene complexes, **A**, not containing a metal-metal bond has been shown to yield polynuclear ketene complexes.[5] In contrast, dinuclear μ-methylene complexes,[6] **B**, containing a metal-metal bond are not readily carbonylated to μ-ketene complexes due to the stability of the dimetallacyclopropane skeleton.

A

B

Heterobimetallic ketene complexes have been prepared from the acylation of metal anions ML_n^- by $Fp\text{-}CH_2COCl$.[7] We previously reported that reaction of CH_2I_2 with $Cp(CO)_3W^-$ in MeOH affords the dinuclear tungsten complex $Cp_2(CO)_5W_2(\mu,\eta^1,\eta^2\text{-}CH_2CO)$ (**2**), which contains an O-coordinated ketene bridge.[8] Formation of **2** is believed to proceed through carbonylation of the bimetallic methylene intermediate $Cp_2(CO)_6W_2(\mu\text{-}CH_2)$.



2

The ketene oxygen atom of **2** is weakly coordinated to the tungsten metal center and is easily replaced by donor ligands L to give $Cp_2(CO)_5LW_2(\mu,\eta^1,\eta^1\text{-}CH_2CO)$.[9] In the presence of CH_3CN, **2** is converted to the acetylide $Cp_2(CO)_6W_2(\mu\text{-}C{\equiv}C)$. Herein we report the reactions of **2** with various heterocumulenes.

Results and Discussion

Reactions of 2 with Isothiocynate. Treatment of the O-coordinated ketene bridged complex **2** with $C_6H_5CH_2NCS$ in CH_2Cl_2 at room temperature for 30 mins affords a dark red C,S-coordinated thioketene complex $Cp_2(CO)_5W_2(\mu\text{-}SC{=}CH_2)$ (**3**) in moderate yield (Scheme 1).[9] The thioketene bridges the two W metal centers in a μ,η^1,η^2-bonding mode with the CS portion behaving as a four-electron-donor ligand. Use of other organic isothiocyanate in this reaction led to the same product. The Cp' analogue **3'** (Cp' = C_5H_4Me) was also prepared. In the ^1H NMR spectrum of **3**, two doublet resonances at δ 5.93 and 6.32 with $J_{H\text{-}H}$ = 0.88 Hz are assigned to the terminal protons of the thioketene ligand. These resonances are down field relative to those in the ketene ligand of **2** (δ 3.41) and are characteristic of olefinic $=CH_2$ methylene protons. The two ^{13}C resonances of the thioketene ligand occur at δ 117.9 (terminal carbon) and 166.5, and show $^1J_{C\text{-}H}$ and $^2J_{C\text{-}H}$ coupling with the olefinic protons; assignments were made via two dimensional HMQC and HMBC NMR techniques.[10]

In order to establish the structure, complex **3** was characterized by an X-ray diffraction analysis. The thioketene ligand bridges the two metal centers with the sulfur atom in a bonding mode that differs from that seen in the O-coordinated ketene complex **2**. This may be attributed to higher affinity of tungsten for sulfur. The W(1)-S and W(2)-S bond distances are 2.530(6) and 2.466(6) Å, respectively, and the W(2)-C(6) distance is 2.07(2) Å. The C(6)-C(7) bond distance (1.31(4) Å) is typical of a carbon-carbon double bond and is consistent with the NMR data. This type of coordination differs from that of the bimetallic Mo S-bridging thioketene complex $Cp_2(CO)_4Mo_2(\mu\text{-}SC{=}CR_2)$ which contains a metal-metal bond. This Mo complex was prepared from reaction of cyclohexene sulfide with the bridging vinylidene complex $Cp_2(CO)_4Mo_2(\mu\text{-}C{=}CR_2)$.[11] No sturcture data was provided for the Mo complex. Unlike the weakly coordinated oxygen in **2**, the bridging thio ligand in **3** is much more strongly coordinated to the tungsten metal centers. No reaction was observed between **3** and PPh_3. It has been reported that the reaction of $Cp(CO)_3WH$ with $S(NMe_2)_2$ affords the dinuclear S-bridging tungsten complex $[Cp(CO)_3W]_2(\mu\text{-}S)$ which, upon reacting with CH_2N_2, gives the thioformaldehyde complex $[Cp(CO)_2W]_2(\mu\text{-}CH_2S)$.[12]

Conversion of **2** to **3** involves substitution of the ketene oxygen with sulfur and a change of coordination mode. A possible mechanism for the formation of **3** is depicted in Scheme 1. The reaction is suggested to proceed via a [2+2] cycloaddition of the CS group of the RNCS with the CO unit with concomitant generation of RNCO and/or $(RNH)_2CO$. It is less likely that the thioisocyanate coordinates to the metal center followed by migration of S to ketene because the reaction of CS_2 with **2** (described below) does not involve loss of the oxygen atom.

Protonation of 3. Protonation of **3** with HBF_4 takes place at the terminal carbon of the thioketene ligand affording $[Cp_2(CO)_5W_2(\mu\text{-}SCCH_3)]BF_4$ (**4**). The IR spectrum of **4** displays absorption bands at 2051, 2031, 1970 and 1945 cm^{-1}, much higher than those (2036, 1947, 1916 and 1813 cm^{-1}) of the neutral complex **3**, indicating a cationic character of the complex. In the ^1H NMR spectrum of **4**, three singlet resonances at δ 5.88, 5.86 and 2.96 are assigned to the two cyclopentadienyl and the methyl groups, respectively. In the ^{13}C NMR spectrum, a down-field resonance at δ 256.6 is attributed to the carbene (or carbocation) carbon center of the CS group. The FAB mass spectrum of **4** shows parent peaks assignable to the cation at m/e = 697. Protonation of **3** with CF_3COOH gave the product $[Cp_2(CO)_5W_2(\mu\text{-}SC(O_2CCF_3)CH_3)]$ which displayed parent peak at m/e = 810 in its FAB mass spectrum indicating that the trifluoroacetate moiety is bound. The protonation reaction is reversible; addition of triethylamine converts **4** to **3**. Protonation of the mononuclear Co complex $Cp(PMe_3)Co(\eta^2\text{-}SC{=}CR_2)$ also occurs at the terminal carbon of the η^2-coordinated thioketene ligand to give a thioacyl complex.[13]

Reaction of 2 with CS_2. Treatment of a red dichloromethane solution of **2** with excess CS_2 for 30 mins at room temperature afforded a scarlet red solution from which the dinuclear thiocarbonyl complex $Cp_2(CO)_5(CS)W_2(\mu\text{-}CH_2COS)$ (**5**) was isolated in 93% yield. The product is air stable and can be stored at room temperature. ^1H NMR analysis of the crude reaction mixture indicated that there were two products in a ratio of 4:1. In the ^1H NMR spectrum of the crude product, the two Cp resonances at δ 5.76, 5.52 and the singlet methylene resonance at δ 2.83 with a pair of tungsten satellites ($J_{W\text{-}H}$ = 5.4 Hz) are assigned to the major product. Two singlet resonances at δ 5.69, 5.54 and resonances with an AB pattern centered at δ 2.88 are assigned to the minor product. Both sets display a relative intensity ratio of 5:5:2. The resonances with an AB pattern centered at δ 2.88 assignable to the diastereotopic CH_2 group of the minor product implies asymmetry at the neighboring metal center. The singlet resonance at δ 2.83 assignable to the CH_2 group of the major product indicates the trans disposition of the CS ligand. In the ^{13}C NMR spectrum, the resonances at δ 1.5 and 0.9 are attributed to the methylene carbon atoms of the two isomers and the resonances at δ 228.8 and 228.9 are assigned to the bridging COS groups. The two isomers are inseparable by recrystallization and the FAB mass spectrum of the mixture gave a parent peak at m/z = 756 with fragmentation peaks due to consecutive losses of CO groups. The Cp' ($\eta^5\text{-}C_5H_4Me$) analogue of **5** was also prepared as a mixture of isomers with the same ratio (4:1). In the ^{13}C NMR spectrum of **5'**, two down-field resonances at δ 348.2 and 332.8

assignable to the CS ligands are comparable to that of many thiocarbonyl complexes.[14] On the basis of these spectroscopic data, we conclude that the two products are a mixture of *cis* and *trans*-isomers.

Single crystals of **5'** were grown by careful addition hexane to a CH_2Cl_2 solution. An X-ray diffraction study gave the structure. Co-crystallization of the cis and trans isomers causes disorder of the CS and CO ligands. The two W atoms are connected by a μ-CH_2COS bridge with one W atom bound to the methylene carbon and the other W atom bound to the S atom. The W(1)-C(7) and W(2)-S(1) bond distances are 2.32(2) and 2.489(4) Å, respectively, with the W(1)-C(7)-C(8) and W(2)-S(1)-C(8) bond angles being 114.8(10) and 107.0(5)°, respectively. All the bond distances and angles of the CH_2COS bridge are normal. The thiocarbonyl CS ligand is bound to W(2), which is also bonded to the S(1) atom of the S-C(O)-CH_2 bridge. The *cis-trans* ratio is 33:67 for **5'** in crystal form, slightly different from that observed by NMR (20:80). This assignment gives reasonable thermal parameters and bond distances. The two metal centers exist as mutually independent mononuclear states and no evidence for metal-metal interaction is detected.

Complex **5** is stable in $CDCl_3$ and C_6D_6, even at the refluxing temperatures. The CS ligand is not replaced under 1 atm of CO pressure. However, thermolysis of **5** in CH_3CN caused cleavage of the C-S bond of the bridging ligand to give the mononuclear complex $Cp(CO)_3WCH_2COOH$ in high yield.[9] Nucleophilic attack of water at the central carbon atom of the CH_2COS bridge took place in the presence of trace water in CH_3CN. The other half of **5**, namely $Cp(CO)_2(CS)WS$, decomposed at the refluxing temperature of CH_3CN to give an unidentified mixture. Reactivity of **5'** is similar to that of **5**.

Reaction of 2 with Trithiocarbonate. Treatment of **2** with trithiocarbonate $S{=}C(SCH_2)_2$ afforded the dithiocarbene complex[15] $Cp_2(CO)_5[C(SCH_2)_2]W_2(\mu\text{-}CH_2COS)$ (**6**) in 51 % yield. In the ^{13}C NMR spectrum of **6**, a resonance at δ 266.3 assignable to the dithiocarbene carbon atom is observed far downfield from the resonance (δ 228.0) of the corresponding carbon atom in free ethylene trithiocarbonate, and the resonance at δ 229.6 assignable to the bridging COS functionality is consistent with that (δ 228.8 and 228.9) of **5**. The assignment was confirmed by a 2D NMR HMBC experiment in which long range $^3J_{C\text{-}H}$ coupling was seen between the resonances at δ 266.3 (^{13}C) and δ 3.38 (^1H NMR resonance) for the $M{=}C(SCH_2)_2$ ligand and between the resonances at δ 229.6 (^{13}C) and δ 2.83 (^1H) for the CH_2COS group. The FAB mass spectrum of **6** displays a parent peak at m/e = 817 as well as fragmentations attributed to successive losses of three CO ligands.

We believe that opening of the weakly coordinated ketene oxygen atom along with a π-coordination of the S=C bond of CS_2 or $S{=}C(SCH_2)_2$ to form an adduct (Scheme 2) may occur in the first stage, in analogy to the case of phosphine addition.[9] Subsequent cleavage of the coordinated C=S bond along with coordination of the CS moiety (as in the reaction of CS_2) or coordination of the carbene unit (in the reaction of trithiocarbonate) and insertion of S atom to the W-O bond accounts for the product. The η^2-CS_2 adduct has been reported for $CpCo(PMe_3)(\eta^2\text{-}CS_2)$[16] and several Pt complexes.[17] Cleavage of one of the C=S bonds of CS_2 either by a metal cluster or in the process of forming a metal cluster has been previously observed.[18] In the reaction of $Os_3(CO)_{12}$ with CS_2, the thiocarbonyl cluster $Os_3(CO)_{10}(CS)(S)$ was obtained.[19] Thermolysis of $CpCo(CO)_2$ in the presence of CS_2 affords the thiocarbonyl sulfide cluster $Cp_3Co_3(\mu_3\text{-}CS)(\mu_3\text{-}S)$.[20] While there are previous examples of C=S bond cleavage, S insertion into the metal-oxygen bond is the first example of this type.[21] Carbon disulfide is an unsaturated electrophile with an extensive organic and organometallic chemistry.[22] Typically, CS_2 reacts with metal alkyls or hydrides by insertion, forming dithiocarboxylate or dithioformate complexes.

Reaction of 2 with Allene. Reaction of gaseous allene with **2** readily occurred at room tempertaure to yield the dinuclear allylic complex $Cp_2(CO)_5W_2[\mu,\eta^1,\eta^3\text{-}CH_2COC(CH_2)_2]$ (7) in 92% yield. The reaction likely follows the same route as do other donors reacting with **2** to form, in this case, a π-allene-acyl intermediate. Subsequent coupling of the allene and acyl ligands gives the observed product. Coupling of the metal coordinated σ-allenyl group with another ligand coordinated to the same metal generally occurs at the α-carbon atom but coupling of the π-allene ligand occurs at the central-carbon atom.[23] This may be due to the proximity of the ligands.

At room temperature, complex **7** displays fluxionality on the allylic part of the molecule, namely, the allylic ligand undergoes interconversion between endo and exo forms. Thus, in the ^{13}C NMR spectrum obtained at room tempaerature, sharp resonances at δ 92.4 (Cp) and -10.4 (CH_2) are assigned to the $Cp(CO)_3WCH_2$ part of **7**, and broad resonances at δ 87.9 and 25.9 are assigned to the $Cp(CO)_2W(allyl)$ part of **7**. In the ^1H NMR spectrum the resonance of the methylene group of the ketene unit appears at δ 2.25 and that of the *syn* and *anti* protons of the allylic group at δ 3.08 and 1.58, respectively. These assignments have been confirmed by two-dimensional NMR HMBC and HMQC experiments. The ^1H NMR spectrum of **7** at -10°C displays resonances at δ 2.99, 2.18 and 1.60, assignable to the allylic *anti* proton, WCH_2 and allylic *syn* proton, respectively, of the *endo* isomer. The corresponding resonances for the *exo* isomer appear at δ 3.10, 2.10 and 1.15. The *endo:exo* ratio is ca. 10:1. And in the ^{13}C NMR spectrum the broad Cp resonance at δ 87.9 resolves into two sharp resonances also with a ration of 10:1. Since **7** is a β-substituted allylic complex, the major isomer is expected to have an *endo* conformation. No attempt was made to assign the ^{13}C resonances of the minor isomer. The fluxionality is similar to that seen in $Cp_2(CO)_5W_2[\mu,\eta^1,\eta^2\text{-}COC(CH_2)_2]$ prepared from the reaction of $Cp(CO)_3W^-$ with $Cp(CO)_2W\text{-}(C(CH_2)_2COCl)$.[24]

Suitable crystals of **7** for X-ray diffraction analysis were obtained by recrystallization from hexane. The two W metal centers are bridged by a β-substituted allylic unit with the allylic unit in an *endo* conformation. The three W(1)-C(allyl) bond distances (2.29(1), 2.27(1) and 2.29(1) Å, for W(1)-C(6) W(1)-C(7) and W(1)-C(8), respectively) and the W(2)-

C(10) bond distance (2.35(1) Å) are in keeping with the literature for W-η^3-C_3H_5 allyl derivatives and W-C single bond, respectively. The W-CO bond lengths and the W-Cp distances are all normal for both metal centers. The allyl unit is approximately coplanar with the neighboring carbonyl group.

In the presence of $Fe(CO)_5$, allenes and aldehydes give the substituted trimethylenemethane complexes whose formation has been proposed to proceed via coupling of the carbonyl carbon of the aldehyde with the central carbon of the allene followed by elimination of CO_2.[25] Recently, migratory insertion of allene into alkyl and acetyl palladium complexes leading to stable η^3-allylic compounds has been reported.[26] The acetyl group gives a rapid allene insertion, but the alkyl ligand requires poorly coordinating ligand such as BF_4 to give the same insertion. The allene insertion proceeds considerably faster than the insertion of alkenes.

Concluding Remark We studied chemical reactivity of the bimetallic tungsten complex **2** containing a μ,η^1,η^2-ketene bridge; particularly chemical reactions with various heterocumulenes. From the reaction of **2** with isothiocyanate, the bridging thioketene complex **3** was isolated which displayed dissimilar bridging mode from the bridging ketene in complex **2**. The reaction of **2** with CS_2 induced S-insertion reaction and afforded the thiocarbonyl complex **5**. In the case of allene as an incoming ligand, coordination of the allene ligand is followed by a subsequent ketene-allene coupling at the central carbon atom of the coordinated-allene to yield the allylic product **7**.

Experimental Section:

General Procedures. All manipulations were performed under nitrogen using vacuum line, drybox and standard Schlenk techniques. NMR spectra were recorded on a Bruker AM-300WB spectrometer and are reported in units of ppm with residual protons in the solvent as an internal standard ($CDCl_3$, δ 7.24). IR spectra were measured on a Bruker Vector-22 instrument and frequencies (cm^{-1}) were assigned relative to a polystyrene standard. FAB mass spectra were recorded on a JEOL SX-102A spectrometer. Diethyl ether was distilled from CaH_2 and stored over molecular sieves prior to use. Benzene and CH_2Cl_2 were distilled from LAH and CaH_2, respectively. THF used were distilled from sodium-benzophenone. All other solvents and reagents were reagent grade and used without further purification. $W(CO)_6$ was purchased from Strem Chemical and dicyclopentadiene, CS_2 and CH_2I_2 were purchased from Merck. Complexes $[CpW(CO)_3]_2$,[27] $CpW(CO)_3^-$ (**1**)[28] and $Cp_2(CO)_5W_2(\mu,\eta^1,\eta^2\text{-}CH_2CO)$, (**2**) and the Cp' analogue **2'**[8] were prepared according to the literature methods.

Reaction of 2 with $PhCH_2NCS$ at room temperature. A solution of complex **2** (1.20 g, 1.76 mmol) in 20.0 mL of CH_2Cl_2 under nitrogen was treated with $PhCH_2NCS$ (0.28 g, 1.88 mmol) and the resulting solution was stirred for 30 mins while the solution turned from red to dark red. Then the solvent was removed under vacuum, and the residual red oil was redissolved in 5 mL of CH_2Cl_2. Addition of 20 mL of hexane to the solution caused precipitation of a dark red product which was filtered and washed with 2 × 10 mL of hexane to give $Cp_2(CO)_5W_2(\mu\text{-}SC{=}CH_2)$ (**3**, 0.47 g) in 38% yield. Spectroscopic data of **3** are as follows. IR, cm^{-1}, $CHCl_3$: 2036(vs), 1947(vs), 1916(sh), 1813(m) ν(CO). ^1H NMR, $CDCl_3$: δ 6.32 (d, $J_{H\text{-}H}$ = 0.88, $J_{W\text{-}H}$ = 6.90 Hz, 1H, =CH); 5.93 (d, $J_{H\text{-}H}$ = 0.88 Hz, 1H, =CH); 5.53, 5.42 (s, Cps). ^{13}C NMR, $CDCl_3$: 242.1, 224.6, 214.2 (CO); 166.5 (CS); 117.9 (CH_2); 94.7, 92.5 (2 Cps). MS, FAB m/e: 696 (M^+), 668 (M^+-CO). Anal. data for $C_{17}H_{12}O_5SW_2$: Calcd. C, 29.34; H, 1.74; found: C, 29.48; H, 1.68. Complex $Cp'_2(CO)_5W_2(\mu\text{-}SC{=}CH_2)$, (**3'**, Cp' = η^5-C_5H_4Me) was prepared from **2'** and $PhCH_2NCS$ in 33% yield using the same procedure. Spectroscopic data of **3'** are as follows. IR, cm^{-1}, $CHCl_3$: 2033(vs), 1943(vs), 1913(sh), 1816(m) ν(CO). ^1H NMR, $CDCl_3$: δ 6.25 (d, $J_{H\text{-}H}$ = 0.66 Hz, 1H, =CH); 5.86 ($J_{H\text{-}H}$ = 0.66 Hz, 1H, =CH); 5.53-5.14 (m, 8H, C_5H_4); 2.18, 1.95 (s, Me). MS, FAB m/e: 724 (M^+), 696 (M^+-CO), 668 (M^+-3CO). Anal. data for $C_{19}H_{16}O_5SW_2$: Calcd. C, 31.52; H, 2.23; found: C, 31.68; H, 2.33.

Reaction of 3 with HBF_4. To a solution of **3** (0.20 g, 0.03 mmol) dissolved in 0.50 mL of $CDCl_3$ under nitrogen, HBF_4 (54% in ether, 0.30 mmol) was added. Color of the solution changed from dark red to orange immediately. The solvent was removed under vacuum, and the red oil was redissolved in 5 mL of CH_2Cl_2. Addition of 20 mL of hexane to the solution caused precipitation of a dark red product which was filtered and washed with 2×10 mL of hexane to give $[Cp_2(CO)_5W_2(\mu\text{-}SCCH_3)]BF_4$ (**4**, 0.21 g) in 95% total yield. Spectroscopic data of **4** are as follows. IR, cm^{-1}, $CHCl_3$: 2048(vs), 2029(s), 1968(s), 1944(vs), ν(CO). ^1H NMR, $CDCl_3$: δ 5.95 (s, 5H, Cp); 5.93 (s, 5H, Cp), 2.99 (s, 3H, CH_3). ^{13}C NMR, $CDCl_3$: δ 256.6 (CS); 220.3, 215.9, 215.8, 214.8, 210.0 (CO); 94.5, 94.0 (2 Cps), 35.5 (CH_3). MS, FAB m/e: 697 (M^+), 669 (M^+-CO), 641 (M^+-2CO). Anal. data for $C_{17}H_{13}BF_4O_5SW_2$: Calcd. C, 26.04; H, 1.67; found: C, 26.29; H, 1.82. Protonation reaction using CF_3COOH using the same procedure afforded a similar product $[Cp_2(CO)_5W_2(\mu\text{-}SC(O_2CCF_3)CH_3)]$. The parent peak of this complex in the FAB mass spectrum appeared at m/e = 810. The ^1H NMR spectrum of this product is essentially the same as that of **4**. Spectroscopic data of this complex are as follows. IR, cm^{-1}, $CHCl_3$: 2051(vs), 2031(s), 1970(s), 1945(vs) 1787(vs), ν(CO). ^1H NMR, $CDCl_3$: δ 5.88 (s, 5H, Cp); 5.86 (s, 5H, Cp), 2.96 (s, 3H, CH_3). MS, FAB m/e: 810 (M^+), 782 (M^+-CO), 754 (M^+-2CO), 697 (M^+-CF_3COO). Anal. data for $C_{19}H_{13}F_3O_7SW_2$: Calcd. C, 28.17; H, 1.62; found: C, 28.44; H, 1.74. If CF_3COOD is used, a ^1H multiplet resonance at δ 2.94 ($J_{H\text{-}D}$ = 4.91 Hz) was observed indicating protonation at the methylene group. By addition of Et_3N to the solution of **4**, complex **3** was recovered in greater than 90% NMR yield.

Reaction of 2 with CS_2. To a solution of **2** (1.20 g, 1.76 mmol) in 20.0 mL of CH_2Cl_2, CS_2 (0.16 g, 2.11 mmol) was added under nitrogen. The resulting solution was stirred for 30 mins while the solution turned to scarlet red. The solvent and excess CS_2 were removed under vacuum to leave a red oily residue, which was redissolved in 5 mL of CH_2Cl_2. Addition of 20 mL of hexane to the resulting solution caused precipitation of a red product which was filtered and washed with 2×10 mL of hexane to give an isomeric mixture of *cis* and *trans*-$Cp_2(CO)_5(CS)W_2(CH_2COS)$ (**5**, 1.24 g) in 93% total yield. Spectroscopic data of **5** are as follows. IR, cm^{-1}, $CHCl_3$: 2024(vs), 1927(vs), 1594(w) ν(CO and CS). ^1H NMR, $CDCl_3$: *trans*-isomer: δ 5.79, 5.54 (s, Cps); 2.86 (s, $J_{W\text{-}H}$ = 5.2 Hz, 2H, CH_2); *cis*-isomer: δ 5.71, 5.57 (s, Cps); 2.91 (AB pattern, $J_{H\text{-}H}$ = 3.3 Hz, 2H, CH_2). ^{13}C NMR, $CDCl_3$: δ 228.8, 224.8, 217.1, 216.8, 216.6, 215.1, 210.8, 210.3, 209.1 (CO); *trans*-isomer: 343.7 (CS); 228.9 ($CH_2\underline{C}O$); 96.2, 91.8 (2 Cps); 1.5 (CH_2); *cis*-isomer: 330.2 (CS); 228.4 ($CH_2\underline{C}O$); 95.0, 91.8 (2 Cps); 0.9 (CH_2). MS, FAB m/e: 756 (M^+), 728 (M^+-CO), 700 (M^+-2CO), 628 (M^+-3CO,CS), 616 (M^+-5CO), 600 (M^+-4CO,CS). Anal. data for $C_{18}H_{12}O_6S_2W_2$: Calcd. C, 28.59; H, 1.60; found: C, 28.31; H, 1.41. A mixture of *cis*- and *trans*-isomers of complex $Cp'_2(CO)_5(CS)W_2(\mu\text{-}CH_2COS)$ (**5'**) in 90% total yield could be similarly prepared. Single crystals of **5'** containing both isomers were grown by careful addition of hexane to a CH_2Cl_2 solution of **5'**. Spectroscopic data of **5'** are as follows. IR, cm^{-1}, $CHCl_3$: 2021(vs), 1923(vs), 1593(w) ν(CO and CS). ^1H NMR, $CDCl_3$: *trans*-isomer: δ 5.69-5.43 (m, 8H, 2 C_5H_4); 2.84 (s, $J_{W\text{-}H}$ = 5.4 Hz, 2H, CH_2), 2.17 (s, 3H, Me), 2.11 (s, 3H, Me); *cis*-isomer: δ 5.69-5.48 (m, 8H, 2 C_5H_4); 2.88 (AB pattern, $J_{H\text{-}H}$ = 5.6 Hz, 2H, CH_2), 2.17 (s, 3H, Me), 2.15 (s, 3H, Me). ^{13}C NMR, $CDCl_3$: δ 230.1, 225.3, 218.3, 218.0, 217.7, 215.7, 210.8, 210.5, 209.0 (CO); *trans*-isomer: 348.2 (CS); 230.2 ($CH_2\underline{C}O$); 115.2 (CMe), 107.4 (CMe), 95.2-92.0 (C_5H_4), 13.9, 13.5 (2Me), 2.2 (CH_2); *cis*-isomer: 332.8 (CS); 229.9 ($CH_2\underline{C}O$); 114.1 (CMe), 108.2 (CMe), 96.2-91.2 (C_5H_4); 13.7, 13.3 (2Me), 1.7 (CH_2). MS, FAB m/e: 784 (M^+), 756 (M^+-CO), 728 (M^+-2CO), 656 (M^+-3CO,CS), 644 (M^+-5CO), 628 (M^+-4CO,CS). Anal. data for $C_{20}H_{16}O_6S_2W_2$: Calcd. C, 30.63; H, 2.06; found: C, 30.41; H, 1.84.

Reaction of 2 with $S{=}C(SCH_2)_2$. To a solution of complex **2** (0.70 g, 1.03 mmol) in 20 mL of CH_2Cl_2 under nitrogen, $SC(SCH_2)_2$ (0.21 g, 1.05 mmol melt at 45°C) was added through a micro-syringe. The resulting solution was stirred for 30 mins while the solution turned to dark yellow. Then the solvent was removed under vacuum yielding oily residue, which was washed with 2×10 mL of hexane to give the product. The crude product was re-crystallized from a mixture of CH_2Cl_2/hexane (1:5) to give $Cp(CO)_3WCH_2COS\text{-}W(CO)_2[C(SCH_2)_2]Cp$ (**6**, 0.51 g) in 61% yield. Spectroscopic data of **6** are as follows. IR, cm^{-1}, CH_2Cl_2: 2021(vs), 1981(m), 1925(s), 1903(s) ν(CO). ^1H NMR, $CDCl_3$: δ 5.70, 5.57 (s, Cps); 3.38 (s, 4H, SCH_2); 2.83 (s, 2H, CH_2). ^{13}C NMR, $CDCl_3$: δ 266.3 (M=C); 229.6, 216.9, 216.8, 210.3 (CO & CSs); 97.5, 91.9 (2 Cps); 44.9 (SCH_2); 2.1 (CH_2CO). MS, FAB m/e: 817 (M^++1), 788 (M^+-CO), 759 (M^+-2CO), 732 (M^+-3CO). Anal. data for $C_{20}H_{16}O_6S_3W_2$: Calcd. C, 29.43; H, 1.98; found: C, 30.01; H, 1.81.

Reaction of 2 with $H_2C{=}C{=}CH_2$. Gaseous allene was slowly bubbled through the deep red solution of **2** (2.30 g, 3.38 mmol) in 30.0 mL of CH_2Cl_2 at room temperature for 35 mins until the solution turned light yellow. Then the solvent was removed under vacuum to yield yellow oil which was further purified by recrystallization from a mixture of CH_2Cl_2/hexane (2:3) at -20°C to give $Cp_2(CO)_5W_2(\mu\text{-}CH_2CO[C(CH_2)_2])$ (**7**, 2.24 g) in 92% yield. Spectroscopic data of **7**: IR, cm^{-1}, CH_2Cl_2: 2022(m), 1957(w, sh), 1918(vs), 1613(m) ν(CO). ^1H NMR, $CDCl_3$, -10°C: *endo* isomer: δ 5.58, 5.29 (s, Cps); 2.99 (br, 2H, anti-CH_2); 2.18 (s, 2H, CH_2), 1.60 (br, 2H, syn-CH_2); *exo* isomer: δ 5.61, 5.26 (s, Cps); 3.10 (br, 2H, anti-CH_2); 2.10 (s, 2H, CH_2), 1.15 (br, 2H, syn-CH_2). ^{13}C NMR, $CDCl_3$: δ 229.0, 218.6, 208.1 (CO); 106.6 (C); 92.4, 87.8 (2 Cps); 25.7 (CH_2); -11.0 (CH_2). MS, FAB m/e: 720 (M^+), 692 (M^+-CO), 636 (M^+-3CO), 608 (M^+-4CO), 580 (M^+-5CO). Anal. data for $C_{20}H_{16}O_6W_2$: Calcd. C, 33.36; H, 2.24; found: C, 33.51; H, 2.11.

X-ray analysis. Dark red crystals of **3** suitable for X-ray diffraction study were grown directly from CH_2Cl_2. A suitable single crystal of dimensions 0.11x0.24x0.30 mm^3 was glued to a glass fiber and mounted on an Enraf-Nonius CAD4 diffractometer. Initial lattice parameters were determined from a least-squares fit to 25 accurately centered reflections $16.88 < 2\theta < 27.12°$. An empirical correction for absorption ($\mu = 134.48\ cm^{-1}$), based on the azimuthal scan data, was applied to the intensities. Crystallgraphic computations were carried out using the NRCC structure determination package. Final refinement using full-matrix, least squares converged smoothly to values of R = 0.057 and R_w = 0.056.

For **5'**, the data were collected on a Siemens SMART CCD system using 3kW sealed-tube molybdenum K radiation (T=295K). Exposure time was 5 sec per frame. Sadabs (Siemens area detector absorption) absorption correction was applied, and decay was negligible. Data were processed and the structure was solved and refined by the SHELXTL program. The structure was solved using direct methods and confirmed by Patterson methods refining on intensities of all data (3925 reflections) to give R_F = 0.0633, Rw_{F2} = 0.1389. In the structure determination of **5'**, the composite scattering factors were used for S(2) and O(5) in the final least square refinement. The scattering factor for S(2) was set to be the sum of 67% of the scattering factor of S and 33% of that of O. And the scattering factor for O(5) was set to be the sum of 33% of the scattering factor of S and 67% of that of O. And the procedures for the structure determination of **7** were similar to that of **3**. The final residuals of the refinement R and R_w were 0.038 and 0.038, respectively, for **7**. Final values of all refined atomic positional parameters (with esd's), and tables of thermal parameters are given in the supporting information.

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References

1 W. A. Herrmann and J. Plank, *Angew. Chem., Int. Ed. Engl.* 1978, **17**, 525. T. W. Bodner and A. R. Cutler, *J. Am. Chem. Soc.* 1983, **105**, 5926. P. T. Barger, B. D. Santarsiero, J. Armantrout and J. E. Bercaw, *J. Am. Chem. Soc.* 1984, **106,** 5178. M.

D. Curtis, L. Messerle, J. J. D'Errico, H. E. Solis, I. D. Barcelo and W. M. Butler, *J. Am. Chem. Soc.* 1987, **109**, 3603. G. L. Geoffroy and S. L. Bassner, *Adv. Organomet. Chem.* 1988, **28**, 1.

2 M. C. Fermin, A. S. Hneihen, J. J. Maas and J. W. Bruno, *Organometallics* 1993, **12**, 1845. M. C. Fermin and J. W. Bruno, *J. Am. Chem. Soc.* 1993, **115**, 7511. E. Bleuel, M. Laubender, B. Weberndörfer and H. Werner, *Angew. Chem., Int. Ed. Engl.* 1999, **38**, 156.

3 D. A. Straus and R. H. Grubbs, *J. Am. Chem. Soc.* 1982, **104**, 5499. E. J. Moore, D. A. Straus, J. Armantrout, B. D. Santarsiero, R H. Grubbs and J. E. Bercaw, *J. Am. Chem. Soc.* 1983, **105**, 2068. C. A. Rusik, T. L. Tonker and J. L. Templeton, *J. Am. Chem. Soc.* 1986, **108**, 4652. C. A. Rusik, M. A. Collins, A. S. Gamble, T. L. Tonker and J. L. Templeton, *J. Am. Chem. Soc.* 1989, **111**, 2550.

4 W. T. Brady, in *The Chemistry of Ketenes, Allenes, and Related Compounds*; Patai, S.; Ed. Wiley: New York, 1980; Chapter 8.

5 Y. C. Lin, J. C. Calabrese and S. S. Wreford, *J. Am. Chem. Soc.* 1983, **105**, 1679. Y. C. Lin, *J. Chin. Chem. Soc.* 1985. **32**, 295. M. C. Chen, Y. J. Tsai, C. T. Chen, Y. C. Lin, T. W. Tseng, G. H. Lee and Y. Wang, *Organometallics* 1991, **10**, 378. E. D. Morrison, G. R. Steinmetz, G. L. Geoffroy, W. C. Fultz and A. L. Rheingold, *J. Am. Chem. Soc.* 1984, **106**, 4783. S. C. H. Ho, D. A. Straus, J. Armantrout, W. P. Schaefer and R. H. Grubbs, *J. Am. Chem. Soc.* 1984, **106**, 2210. E. D. Morrison and G. L. Geoffroy, *J. Am. Chem. Soc.* 1985, **107**, 3541. J. S. Holmgren, J. R. Shapley, S. R. Wilson and W. T. Pennington, *J. Am. Chem. Soc.* 1986, **108**, 508.

6 W. A. Herrmann, *Adv. Organomet. Chem.*, 1982, **20**, 159. W. A. Herrmann, *Angew. Chem., Int. Ed. Engl.*, 1982, **21**, 117. R. J. Puddephatt, *Comments Inorg. Chem.* 1982, **2**, 69a. R. J. Puddephatt, *Polyhedron* 1988, **7**, 767.

7 M. Akita, A. Kondoh and Y. Moro-oka, *J. Chem. Soc. Chem. Commun.* 1986, 1296.

8 Y. L. Yang, L. J. Wang, Y. C. Lin, S. L. Huang, M. C. Chen, G. H. Lee and Y. Wang, *Organometallics* 1997, **16**, 1573.

9 Mononuclear thioketene complexes are known: F. Drews, F. Edelmann, and U. Behrens, *J. Organomet. Chem.* 1986, **315**, 369. J. Wolf, R. Zolk, U. Schubert and H. Werner, *J. Organomet. Chem.* 1988, **340**, 161. H. Werner and U. Brekau, *Z. Naturforsch., Teil B.* 1989, **44**, 1438. H. Werner, T. Rappert, T. and J. Wolf, *Isr. J. Chem.* 1990, **30**, 377.

10 A. Bax, M. Ikura, L. E. Kay, D. A. Torchia and R. Tschudin, *J. Magn. Res.* 1990, **86**, 304. S. Roy, M. Z. Papastarros, V. Sanches and A. G. Redfield, *Biochem.* 1984, **23**, 4395 A. Bax and M. F. Summers, *J. Am. Chem. Soc.* 1986, **108**, 2093. T. J. Norwood, J. Boyd, J. E. Heritage, N. Soffe and I. D. Campbell, *J. Magn. Res.* 1990, **87**, 488. A. Bax and S. Subramanian, *J. Magn. Reson.*, 1986, **67**, 565.

11 M. Bamber, S. F. T. Froom, M. Green, M. Schulz and H. Werner, *J. Organomet. Chem.* 1992, **434**, C19.

12 M. Herberhold, W. Jellen and H. H. Murray, *J. Organomet. Chem.* 1984, **270**, 65.

13 R. Drews, F. Edelmann and U. Behrens, *J. Organomet. Chem.* 1986, **315**, 369.

14 A. M. English, K. R. Plowman, I. M. Baibich, J. P. Hickey, I. S. Butler, G. Jaouen and P. Lemaux, *J. Organomet. Chem.* 1981, **205**, 177.

15 F. J. Brown, *Prog. Inorg. Chem.* 1980, **27**, 1. R. J. Angelici, F. B. McCormick and R. A. Pickering, in "*Fundamental Research in Organometallic Chemistry*" (M. Tsutsui, Y. Ishii, H. Yaozeng, eds.) Van Nostrand, New York, 1982, p.347. B. E. Boland-Lussier and R. P. Hughes, *Organometallics* 1982, **1**, 635. S. Myrvold, O. A. Nassif, G. Semelhago, A. Walker and D. H. Farrar, *Inorg. Chim. Acta* 1986, **117**, 17. G. Beck and W. P. Fehlhammer, *Angew. Chem., Int. Ed. Engl.* 1988, **27**, 1344.

16 H. Werner, K. Leonhard, O. Kolb, E. Rottinger and H. Vahrenkamp, *Chem. Ber.* 1980, **113**, 1654.

17 H. Werner, M. Ebner and H. Otto, *J. Organomet. Chem.* 1988, **350**, 257.

18 J. Qi, P. W. Schrier, P. E. Fanwick and R. A. Walton, *J. Chem. Soc. Chem. Commun.* 1991, 1737.

19 P. V. Broadhurst, B. F. G. Johnson, J. Lewis and P. R. Raithby, *J. Chem. Soc., Dalton Trans.* 1982, 1641.

20 J. Fortune and A. R. Manning, *Organometallics* 1983, **2**, 1719.

21 Sulfur insertion into Mo-acyl bond from coordinated xanthate has been reported; L. Contreras, A. Pizzano, L. Schez, E. Carmona, A. Monge and C. Ruiz, *Organometallics* 1995, **14**, 589.

22 P. V. Yaneff, *Coord. Chem. Rev.* 1977, **23**, 183

23 T. W. Tseng, I. Y. Wu, J. H. Tsai, Y. C. Lin, D. J. Chen, G. H. Lee, M. C. Chen and Y. Wang, *Organometallics,* 1994, **13**, 3963. S. Doherty, M. R. J. Elsegood, W. Clegg and M. Waugh, *Organometallics,* 1996, **15**, 2688.

24 C. L. Hsing and Y. C. Lin, Manuscript in preparation.

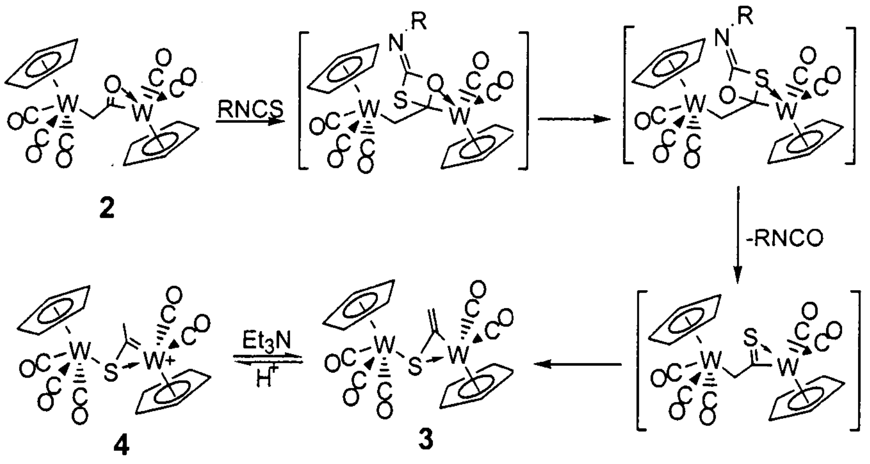
25 R. Aumann, H-D. Melchers and H-J. Weidenhaupt, *Chem. Ber.* 1987, **120**, 17.

26 R. K. Rulke, D. Kliphuid, C. J. Elsevier, J. Fraanje, K. Goubitz, P. W. N. M. van Leeuwen, K. Vrieze, *J. Chem. Soc., Chem. Commun.* 1994, 1817.

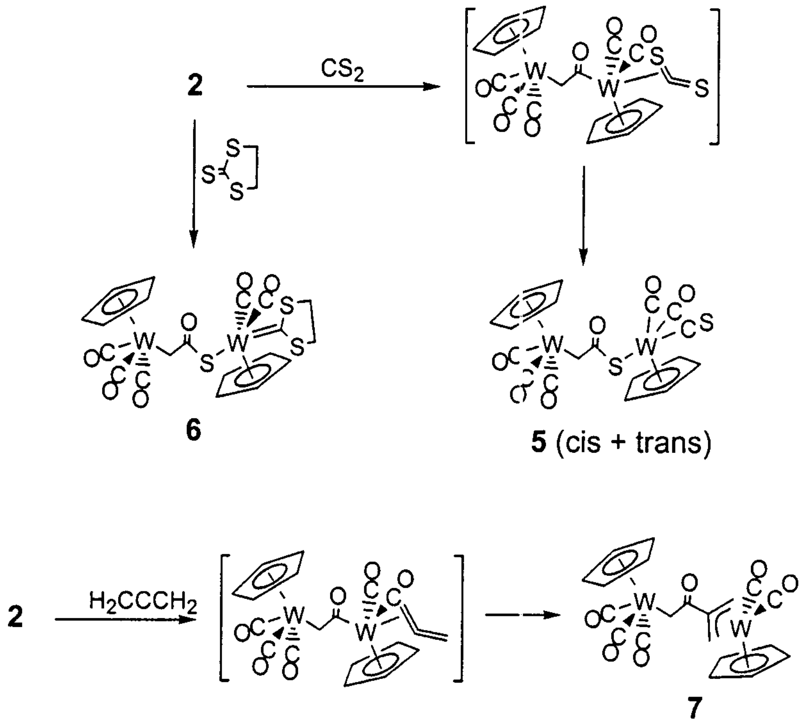
27 J. E. Thomasson, P. W. Robinson, D. A. Ross and A. Wojcicki, *Inorg. Chem.* 1971,

10, 2130.

28 I. Y. Wu, J. H. Tsai, B. C. Huang, S. C. Chen and Y. C. Lin, *Organometallics* 1993, **12**, 3971.



Scheme 1



Scheme 2