

Reactions of a dinuclear tungsten complex containing an O-co-ordinated bridging ketene with various heterocumulenes

Luxti J. J. Wang, Sen-Jen You, Shou-Ling Huang, Yu-Lee Yang, Ying-Chih Lin,*
 Gene-Hsiang Lee and Shie-Ming Peng

Department of Chemistry, National Taiwan University, Taipei, Taiwan 10764,
 Republic of China

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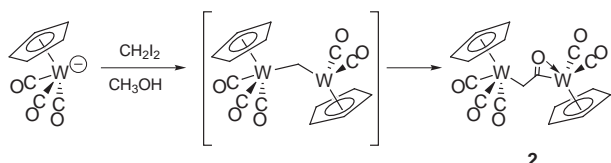
Treatment of the dinuclear O-co-ordinated ketene complex $W_2Cp_2(CO)_5(\mu-\eta^1:\eta^2-CH_2CO)$ ($Cp = \eta^5-C_5H_5$) with $PhCH_2NCS$ afforded the dark red bridging thioketene complex $W_2Cp_2(CO)_5(\mu-\eta^3-SC=CH_2)$. Reaction of the latter with HBF_4 gave the stable cationic product $[W_2Cp_2(CO)_5(\mu-SCMe_3)]BF_4$ by addition of a proton to the terminal carbon of the thioketene group. In the reaction of $W_2Cp_2(CO)_5(\mu-\eta^1:\eta^2-CH_2CO)$ with CS_2 cleavage of one CS bond is accompanied by insertion of the resulting sulfur atom into the tungsten-acyl bond to afford $W_2Cp_2(CO)_5(CS)-(\mu-CH_2COS)$. The Cp' analogue ($Cp' = \eta^5-C_5H_4Me$) was also prepared. The reaction of the trithiocarbonate $S=C(SCH_2)_2$ with $W_2Cp_2(CO)_5(\mu-\eta^1:\eta^2-CH_2CO)$ afforded the carbene complex $W_2Cp_2(CO)_5[C(SCH_2)_2](\mu-CH_2COS)$, and with allene gave the allylic complex $W_2Cp_2(CO)_5(\mu-\eta^1:\eta^3-CH_2COC_3H_4)$. Those of the complexes have been characterized by single crystal X-ray diffraction analysis.

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 systems² 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, **B**, containing a metal–metal bond are not readily carbonylated to μ -ketene complexes due to the stability of the dimetallacyclopropane skeleton.



Heterobimetallic ketene complexes have been prepared from the acylation of metal anions ML_n^- by $Fp-CH_2COCl$ [$Fp = FeCp(CO)_2$].⁷ We previously reported that reaction of CH_2I_2 with $W-Cp(CO)_3$ **1** in MeOH affords the dinuclear tungsten complex $W_2Cp_2(CO)_5(\mu-\eta^1:\eta^2-CH_2CO)$ **2**, which contains an O-co-ordinated ketene bridge.⁸ Formation of **2** is believed to proceed through carbonylation of the bimetallic methylene intermediate $W_2Cp_2(CO)_6(\mu-CH_2)$.

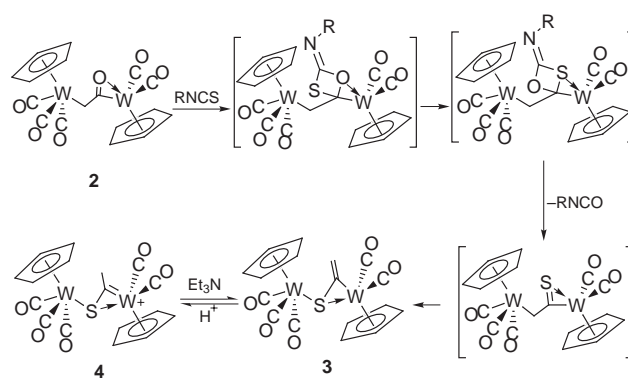


The ketene oxygen atom of complex **2** is weakly co-ordinated to the tungsten metal center and easily replaced by donor ligands **L** to give $W_2Cp_2(CO)_5L(\mu-\eta^1:\eta^2-CH_2CO)$.⁹ In the presence of CH_3CN , **2** is converted into the acetylide $W_2Cp_2(CO)_6(\mu-C\equiv C)$. Herein we report the reactions of **2** with various heterocumulenes.

Results and discussion

Reactions of complex **2** with isothiocyanate

Treatment of the O-co-ordinated ketene bridged complex **2** with $PhCH_2NCS$ in CH_2Cl_2 at room temperature for 30 min affords a dark red C,S-co-ordinated thioketene complex $W_2Cp_2(CO)_5(\mu-SC=CH_2)$ **3** in moderate yield (Scheme 1).⁹ The thioketene bridges the two metal centers in a $\mu-\eta^1:\eta^2$ -bonding mode with the CS portion behaving as a four-electron-donor ligand. Use of other organic isothiocyanates in this reac-

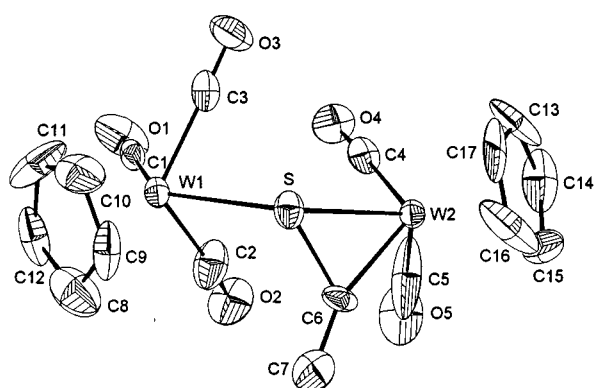


Scheme 1

tion 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 $J_{H-H} = 0.88$ Hz are assigned to the terminal protons of the thioketene ligand. These resonances are downfield relative to those of 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 $^1J_{C-H}$ and $^2J_{C-H}$ coupling with the olefinic protons; assignments were made *via* two dimensional heteronuclear multiple quantum and multiple bond correlation (HMQC and HMBC) NMR techniques.¹⁰

Table 1 Bond distances (Å) and bond angles (°) of complex **3**

W(1)–S	2.530(6)	S–C(6)	1.793(24)
W(1)–C(1)	1.97(3)	C(1)–O(1)	1.15(3)
W(1)–C(2)	2.061(25)	C(2)–O(2)	1.10(3)
W(1)–C(3)	1.995(23)	C(3)–O(3)	1.12(3)
W(2)–S	2.466(6)	C(4)–O(4)	1.17(3)
W(2)–C(4)	1.915(24)	C(5)–O(5)	1.10(3)
W(2)–C(5)	2.01(3)	C(6)–C(7)	1.31(4)
W(2)–C(6)	2.072(23)		
S–W(1)–C(1)	132.9(6)	W(1)–S–W(2)	126.82(25)
S–W(1)–C(2)	77.6(7)	W(1)–S–C(6)	115.5(7)
S–W(1)–C(3)	75.1(6)	W(2)–S–C(6)	55.6(8)
C(1)–W(1)–C(2)	80.0(11)	W(1)–C(1)–O(1)	177.7(20)
C(1)–W(1)–C(3)	75.5(9)	W(1)–C(2)–O(2)	172.8(23)
C(2)–W(1)–C(3)	111.4(11)	W(1)–C(3)–O(3)	178.6(20)
S–W(2)–C(4)	90.3(7)	W(2)–C(4)–O(4)	176.7(20)
S–W(2)–C(5)	116.0(9)	W(2)–C(5)–O(5)	172(4)
S–W(2)–C(6)	45.5(7)	W(2)–C(6)–S	78.9(8)
C(4)–W(2)–C(5)	76.5(14)	W(2)–C(6)–C(7)	158.4(21)
C(4)–W(2)–C(6)	114.5(9)	S–C(6)–C(7)	122.6(21)
C(5)–W(2)–C(6)	84.0(14)		

**Fig. 1** An ORTEP¹¹ drawing of $W_2Cp_2(CO)_5(\mu-CH_2CS)$ **3**.

In order to establish the structure, complex **3** was characterized by an X-ray diffraction analysis. An ORTEP drawing is shown in Fig. 1 and selected bond distances and angles are listed in Table 1. The thioketene ligand bridges the two metal centers with the sulfur atom in a bonding mode that differs from that seen in the O-co-ordinated 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 co-ordination differs from that of the bimetallic S-bridging thioketene complex $Mo_2Cp_2(CO)_4(\mu-SC=CR_2)$ which contains a metal–metal bond. This complex was prepared from reaction of cyclohexene sulfide with the bridging vinylidene complex $Mo_2Cp_2(CO)_4(\mu-C=CR_2)$.¹² No structure data were provided for it. Unlike the weakly co-ordinated oxygen in **2**, the bridging thio ligand in **3** is much more strongly co-ordinated to the tungsten metal centers. No reaction was observed between **3** and PPh_3 . It has been reported that the reaction of $WCp(CO)_3H$ with $S(NMe_2)_2$ affords the dinuclear S-bridging tungsten complex $[WCp(CO)_3]_2(\mu-S)$ which, upon reacting with CH_2N_2 , gives the thioformaldehyde complex $[WCp(CO)_2]_2(\mu-CH_2S)$.¹³

Conversion of complex **2** into **3** involves substitution of the ketene oxygen with sulfur and a change of co-ordination 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 co-ordinates to the metal center followed by migration of S to ketene because the reac-

tion of CS_2 with **2** (described below) does not involve loss of the oxygen atom.

Protonation of complex **3**

Protonation of complex **3** with HBF_4 takes place at the terminal carbon of the thioketene ligand affording $[W_2Cp_2(CO)_5(\mu-SCMe_3)]BF_4$ **4**. The IR spectrum of **4** displays absorption bands at 2048, 2029, 1968 and 1944 cm^{-1} , much higher than those (2036, 1947, 1916 and 1813 cm^{-1}) of the neutral complex **3**, indicating a cationic character. In the 1H NMR spectrum of **4** three singlet resonances at δ 5.95, 5.93 and 2.99 are assigned to the two cyclopentadienyl and the methyl groups, respectively. In the ^{13}C NMR spectrum, a downfield resonance at δ 256.6 is attributed to the carbene (or carbocation) carbon center of the CS group. The FAB mass spectrum shows parent peaks assignable to the cation at $m/z = 697$. Protonation of **3** with CF_3CO_2H gave the product $[W_2Cp_2(CO)_5(\mu-SC(O_2CCF_3)Me_3)]$ which displayed a parent peak at $m/z = 810$ in its FAB mass spectrum indicating that the trifluoroacetate moiety is bound. The protonation reaction is reversible; addition of triethylamine converts **4** into **3**. Protonation of the mononuclear cobalt complex $CoCp(PMe_3)(\eta^2-SC=CR_2)$ also occurs at the terminal carbon of the η^2 -co-ordinated thioketene ligand to give a thioacyl complex.^{9a}

Reaction of complex **2** with CS_2

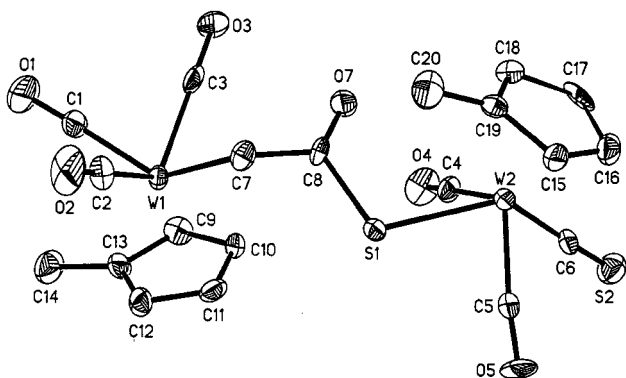
Treatment of a red dichloromethane solution of complex **2** with an excess of CS_2 for 30 min at room temperature afforded a scarlet red solution from which the dinuclear thiocarbonyl complex $W_2Cp_2(CO)_5(CS)(\mu-CH_2COS)$ **5** was isolated in 93% yield. The product is air stable and can be stored at room temperature. The 1H NMR analysis of the crude reaction mixture indicated that there were two products in a ratio of 4:1. In the spectrum of the crude product the two Cp resonances at δ 5.79, 5.54 and the singlet methylene resonance at δ 2.86 with a pair of tungsten satellites ($J_{W-H} = 5.2$ Hz) are assigned to the major product. Two singlet resonances at δ 5.71, 5.57 and resonances with an AB pattern centered at δ 2.91 are assigned to the minor product. Both sets display a relative intensity ratio of 5:5:2. The resonances at δ 2.91 assignable to the diastereotopic CH_2 group of the minor product imply asymmetry at the neighboring metal center. The singlet resonance at δ 2.86 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 those 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' ($\eta^5-C_5H_4Me$) analogue of **5** was also prepared as a mixture of isomers with the same ratio (4:1). In the ^{13}C NMR spectrum two downfield 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 complex **5'** were grown by careful addition of hexane to a CH_2Cl_2 solution. An X-ray diffraction study gave the structure shown in Fig. 2. Selected bond distances and angles are listed in Table 2. Co-crystallization of the *cis* and *trans* isomers causes disorder of the CS and CO ligands. The two W atoms are connected by a $\mu-CH_2COS$ 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

Table 2 Selected bond distances (Å) and angles (°) of complex **5'**

W(1)–C(1)	1.97(2)	S(2')–C(5) ^a	1.58(3)
W(1)–C(2)	1.98(2)	S(2)–C(6)	1.49(2)
W(1)–C(3)	2.00(2)	C(1)–O(1)	1.16(2)
W(1)–C(7)	2.32(2)	C(2)–O(2)	1.13(2)
W(2)–S(1)	2.489(4)	C(3)–O(3)	1.13(2)
W(2)–C(4)	2.03(2)	C(4)–O(4)	1.13(2)
W(2)–C(5)	1.97(2)	C(7)–C(8)	1.49(2)
W(2)–C(6)	2.00(2)	C(8)–O(7)	1.20(2)
S(1)–C(8)	1.820(14)		
C(1)–W(1)–C(2)	78.7(8)	W(2)–S(1)–C(8)	107.0(5)
C(1)–W(1)–C(3)	74.7(7)	W(1)–C(1)–O(1)	177(2)
C(1)–W(1)–C(7)	131.4(7)	W(1)–C(2)–O(2)	179(2)
C(2)–W(1)–C(3)	108.8(8)	W(1)–C(3)–O(3)	179.4(13)
C(2)–W(1)–C(7)	73.7(7)	W(2)–C(4)–O(4)	176(2)
C(3)–W(1)–C(7)	77.5(7)	W(2)–C(5)–S(2')	172(2)
S(1)–W(2)–C(4)	76.6(5)	W(2)–C(6)–S(2)	172.6(13)
S(1)–W(2)–C(5)	76.1(5)	W(1)–C(7)–C(8)	114.8(10)
S(1)–W(2)–C(6)	131.8(4)	S(1)–C(8)–C(7)	111.2(12)
C(4)–W(2)–C(5)	108.3(7)	S(1)–C(8)–O(7)	122.6(11)
C(4)–W(2)–C(6)	76.2(6)	C(7)–C(8)–O(7)	126.1(14)
C(5)–W(2)–C(6)	75.8(7)		

^a S(2) is 67% S and 33% O and S(2') is 33% S and 67% O.

**Fig. 2** An ORTEP drawing of $W_2Cp'_2(CO)_5(CS)(\mu-CH_2COS)$ **5'**.

$SC(O)CH_2$ 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.

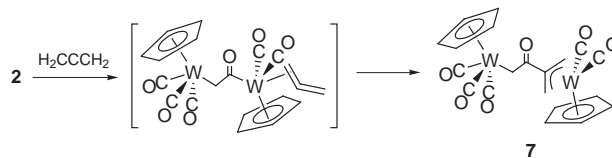
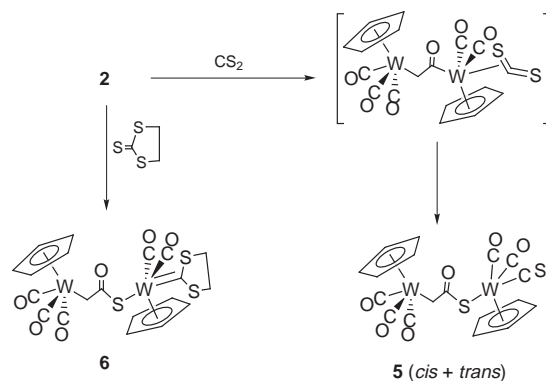
Complex **5** is stable in $CDCl_3$ and C_6D_6 , even at the refluxing temperatures. The CS ligand is not replaced under 1 atm of CO pressure. However, thermolysis of **5** in MeCN caused cleavage of the C–S bond of the bridging ligand to give the mononuclear complex $WCp(CO)_3(CH_2CO_2H)$ in high yield.⁹ Nucleophilic attack of water at the central carbon atom of the Me_2COS bridge took place in the presence of trace water in MeCN. The other half of **5**, namely $Cp(CO)_2(CS)WS$, decomposed at the refluxing temperature of MeCN to give an unidentified mixture. Reactivity of **5'** is similar to that of **5**.

Reaction of complex **2** with trithiocarbonate

Treatment of complex **2** with trithiocarbonate $S=C(SCH_2)_2$ afforded the dithiocarbene complex $W_2Cp'_2(CO)_5[C(SCH_2)_2](\mu-CH_2COS)$ **6** in 61% yield. In the ^{13}C NMR spectrum 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 2-D HMBC NMR experiment in which long range $^3J_{C-H}$ coupling was seen between the resonances at δ 266.3 (^{13}C) and 3.38 (1H NMR)

for the $M=C(SCH_2)_2$ ligand and between those at δ 229.6 (^{13}C) and 2.83 (1H) for the CH_2COS group. The FAB mass spectrum of **6** displays a parent peak at $m/z = 817$ as well as fragmentations attributed to successive losses of three CO ligands.

We believe that opening of the weakly co-ordinated ketene oxygen atom along with a π co-ordination of the $S=C$ bond of CS_2 or $S=C(SCH_2)_2$ to form an adduct (Scheme 2) may occur in

**Scheme 2**

the first stage, in analogy to the case of phosphine addition.⁹ Subsequent cleavage of the co-ordinated $C=S$ bond along with co-ordination of the CS moiety (as in the reaction of CS_2) or of the carbene unit (in the reaction of trithiocarbonate) and insertion of an S atom into the W–O bond accounts for the product. The η^2-CS_2 adduct has been reported for $CoCp(PMe_3)(\eta^2-CS_2)$ ¹⁶ and several platinum 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 $CoCp(CO)_2$ in the presence of CS_2 affords the thiocarbonyl sulfide cluster $Co_3Cp_3(\mu_3-CS)(\mu_3-S)$.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, it reacts with metal alkyls or hydrides by insertion, forming dithiocarboxylate or dithioformate complexes.

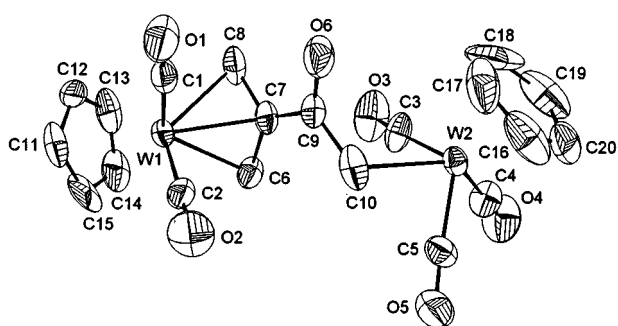
Reaction of complex **2** with allene

Reaction of gaseous allene with complex **2** readily occurred at room temperature to yield the dinuclear allylic complex $W_2Cp'_2(CO)_5[\mu-\eta^1:\eta^3-CH_2COC(CH_2)_2]$ **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 co-ordinated σ -allenyl group with another ligand co-ordinated 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 temperature, sharp reson-

Table 3 Selected bond distances (Å) and angles (°) of complex **7**

W(1)–C(1)	1.946(13)	C(2)–O(2)	1.161(16)
W(1)–C(2)	1.955(13)	C(3)–O(3)	1.145(16)
W(1)–C(6)	2.291(13)	C(4)–O(4)	1.145(17)
W(1)–C(7)	2.270(10)	C(5)–O(5)	1.182(17)
W(1)–C(8)	2.289(12)	C(6)–C(7)	1.401(18)
W(2)–C(3)	1.974(13)	C(7)–C(8)	1.417(20)
W(2)–C(4)	1.957(14)	C(7)–C(9)	1.536(17)
W(2)–C(5)	1.921(13)	C(9)–C(10)	1.446(20)
W(2)–C(10)	2.346(12)	C(9)–O(6)	1.220(16)
C(1)–O(1)	1.158(17)		
C(1)–W(1)–C(2)	75.9(6)	W(2)–C(4)–O(4)	178.5(14)
C(3)–W(2)–C(4)	75.1(6)	W(2)–C(5)–O(5)	177.3(11)
C(3)–W(2)–C(5)	109.7(6)	C(6)–C(7)–C(8)	116.2(11)
C(3)–W(2)–C(10)	82.1(5)	C(6)–C(7)–C(9)	124.4(12)
C(4)–W(2)–C(5)	76.9(6)	C(8)–C(7)–C(9)	119.0(12)
C(4)–W(2)–C(10)	134.1(5)	C(7)–C(9)–C(10)	117.8(11)
C(5)–W(2)–C(10)	74.1(6)	C(7)–C(9)–O(6)	118.2(12)
W(1)–C(1)–O(1)	176.5(10)	C(10)–C(9)–O(6)	123.9(11)
W(1)–C(2)–O(2)	177.8(10)	W(2)–C(10)–C(9)	111.6(8)
W(2)–C(3)–O(3)	175.0(10)		

**Fig. 3** An ORTEP drawing of $W_2Cp_2(CO)(\mu-CH_2COC(CH_2)_2)$ **7**.

ances at δ 92.4 (Cp) and -11.0 (CH_2) are assigned to the $Cp(CO)_3WCH_2$ part of **7**, and broad resonances at δ 87.8 and 25.7 are assigned to the $Cp(CO)_2W(allyl)$ part. In the 1H NMR spectrum the resonance of the methylene group of the ketene unit appears at δ 2.25 and those 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 HMBC and HMQC NMR 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. In the ^{13}C NMR spectrum the broad Cp resonance at δ 87.8 resolves into two sharp resonances also with a ratio 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 $W_2Cp_2(CO)_5[\mu-\eta^1:\eta^2-COC(CH_2)_2]$ prepared from the reaction of $W^+Cp(CO)_3$ with $WCp(CO)_2(C(CH_2)_2COCl)$.²⁴

Suitable crystals of complex **7** for X-ray diffraction analysis were obtained by recrystallization from hexane, and an ORTEP drawing of the molecule is shown in Fig. 3. Selected bond distances and angles are listed in Table 3. The two 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 $W-\eta^3-C_3H_5$ allyl derivatives and W–C single bonds, 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 substi-

tuted 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 a poorly co-ordinating ligand such as BF_4 to give the same insertion. The allene insertion proceeds considerably faster than the insertion of alkenes.

Concluding remarks

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

Experimental

General procedures

All manipulations were performed under nitrogen using vacuum line, dry-box and standard Schlenk techniques. The 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 on a Bruker Vector-22 instrument and frequencies (cm^{-1}) assigned relative to a polystyrene standard and FAB mass spectra 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 from $LiAlH_4$ and CaH_2 , respectively and THF from sodium–benzophenone. All other solvents and reagents were reagent grade used without further purification. The compound $W(CO)_6$ was purchased from Strem Chemical, dicyclopentadiene, CS_2 and CH_2I_2 from Merck. Complexes $[WCp(CO)_3]_2$,²⁷ $WCp(CO)_3^-$ **1**,²⁸ $W_2Cp_2(CO)_5(\mu-\eta^1:\eta^2-CH_2CO)$, **2** and the Cp' analogue **2'**⁸ were prepared according to the literature methods.

Reaction of complex **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 stirred for 30 min turning from red to dark red. Then the solvent was removed under vacuum, and the residual red oil redissolved in 5 mL of CH_2Cl_2 . Addition of 20 mL of hexane caused precipitation of a dark red product which was filtered off and washed with 2×10 mL of hexane to give $W_2Cp_2(CO)_5(\mu-SC=CH_2)$ **3**, (0.47 g) in 38% yield. IR, (cm^{-1} , $CHCl_3$): 2036vs, 1947vs, 1916 (sh) and 1813m [$\nu(CO)$]. 1H NMR, ($CDCl_3$): δ 6.32 (d, $J_{H-H} = 0.88$, $J_{W-H} = 6.90$, 1 H, =CH); 5.93 (d, $J_{H-H} = 0.88$ Hz, 1 H, =CH); 5.53, 5.42 (s, Cp). ^{13}C NMR, ($CDCl_3$): δ 242.1, 224.6, 214.2 (CO); 166.5 (CS); 117.9 (CH_2); 94.7, 92.5 (2 Cp). FAB MS: m/z 696 (M^+) and 668 ($M^+ - CO$). Calc. for $C_{17}H_{12}O_5SW_2$: C, 29.34; H, 1.74. Found: C, 29.48; H, 1.68%.

Complex $W_2Cp'_2(CO)_5(\mu-SC=CH_2)$ **3'**, was prepared from **2'** and $PhCH_2NCS$ in 33% yield using the same procedure. IR (cm^{-1} , $CHCl_3$): 2033vs, 1943vs, 1913 (sh) and 1816m [$\nu(CO)$]. 1H NMR, ($CDCl_3$): δ 6.25 (d, $J_{H-H} = 0.66$, 1 H, =CH); 5.86 ($J_{H-H} = 0.66$ Hz, 1 H, =CH); 5.53–5.14 (m, 8 H, C_5H_4); 2.18, 1.95 (s, Me). FAB MS: m/z 724 (M^+), 696 ($M^+ - CO$) and 668

($M^+ - 3CO$). Calc. for $C_{19}H_{16}O_5SW_2$: C, 31.52; H, 2.23. Found: C, 31.68; H, 2.33%.

Reaction of complex 3 with HBF_4

To a solution of complex 3 (0.20 g, 0.03 mmol) dissolved in 0.50 mL of $CDCl_3$ under nitrogen, HBF_4 (54% in diethyl ether, 0.30 mmol) was added. The solution changed from dark red to orange immediately. The solvent was removed under vacuum, and the red oil redissolved in 5 mL of CH_2Cl_2 . Addition of 20 mL of hexane caused precipitation of a dark red product which was filtered off and washed with 2×10 mL of hexane to give $[W_2Cp_2(CO)_5(\mu-SCMe)]BF_4$ 4 (0.21 g) in 95% total yield. IR (cm^{-1} , $CHCl_3$): 2048vs, 2029s, 1968s and 1944vs, $[\nu(CO)]$. 1H NMR, $CDCl_3$: δ 5.95 (s, 5 H, Cp); 5.93 (s, 5 H, Cp) and 2.99 (s, 3 H, 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 Cp); 35.5 (CH_3). FAB: MS m/z 697 (M^+), 669 ($M^+ - CO$) and 641 ($M^+ - 2CO$). Calc. for $C_{17}H_{13}BF_4O_5SW_2$: C, 26.04; H, 1.67. Found: C, 26.29; H, 1.82%.

Protonation using CF_3CO_2H and the same procedure afforded a similar product $[W_2Cp_2(CO)_5(\mu-SC(O_2CCF_3)Me)]$. The parent peak of this complex in the FAB mass spectrum appeared at $m/z = 810$. The 1H NMR spectrum is essentially the same as that of 4. IR (cm^{-1} , $CHCl_3$): 2051vs, 2031s, 1970s, 1945vs and 1787vs, $[\nu(CO)]$. 1H NMR, ($CDCl_3$): δ 5.88 (s, 5 H, Cp); 5.86 (s, 5 H, Cp); and 2.96 (s, 3 H, CH_3). FAB MS: m/z 810 (M^+), 782 ($M^+ - CO$), 754 ($M^+ - 2CO$) and 697 ($M^+ - CF_3COO$). Calc. for $C_{19}H_{13}F_3O_7SW_2$: C, 28.17; H, 1.62. Found: C, 28.44; H, 1.74%. When CF_3CO_2D is used, a 1H multiplet resonance at δ 2.94 ($J_{H-D} = 4.91$ 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 complex 2 with CS_2

To a solution of complex 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 min turning scarlet red. The solvent and excess of 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 caused precipitation of a red product which was filtered off and washed with 2×10 mL of hexane to give an isomeric mixture of *cis*- and *trans*- $W_2Cp_2(CO)_5(CS)(CH_2COS)$ 5 (1.24 g) in 93% total yield. IR (cm^{-1} , $CHCl_3$): 2024vs, 1927vs and 1594w $[\nu(CO)$ and $\nu(CS)]$. 1H NMR ($CDCl_3$): *trans* isomer, δ 5.79, 5.54 (s, Cp); 2.86 (s, $J_{W-H} = 5.2$ Hz, 2 H, CH_2), *cis* isomer, δ 5.71, 5.57 (s, Cp); 2.91 (AB pattern, $J_{H-H} = 3.3$ Hz, 2 H, CH_2). ^{13}C NMR ($CDCl_3$): δ 228.8, 224.8, 217.1, 216.8, 216.6, 215.1, 210.8, 210.3 and 209.1 (CO); *trans* isomer, 343.7 (CS); 228.9 (CH_2CO); 96.2, 91.8 (2 Cp); 1.5 (CH_2); *cis* isomer, 330.2 (CS); 228.4 (CH_2CO); 95.0, 91.8 (2 Cp); 0.9 (CH_2). FAB MS: m/z 756 (M^+), 728 ($M^+ - CO$), 700 ($M^+ - 2CO$), 628 ($M^+ - 3CO, CS$), 616 ($M^+ - 5CO$) and 600 ($M^+ - 4CO, CS$). Calc. for $C_9H_6O_3SW$: C, 28.59; H, 1.60. Found: C, 28.31; H, 1.41%.

A mixture of *cis* and *trans* isomers of complex $W_2Cp'_2(CO)_5(CS)(\mu-CH_2COS)$ 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'. IR (cm^{-1} , $CHCl_3$): 2021vs, 1923vs and 1593w $[\nu(CO)$ and $\nu(CS)]$. 1H NMR, ($CDCl_3$): *trans* isomer, δ 5.69–5.43 (m, 8 H, 2 C_5H_4); 2.84 (s, $J_{W-H} = 5.4$ Hz, 2 H, CH_2), 2.17 (s, 3 H, Me) 2.11 (s, 3 H, Me); *cis* isomer, δ 5.69–5.48 (m, 8 H, 2 C_5H_4); 2.88 (AB pattern, $J_{H-H} = 5.6$ Hz, 2 H, CH_2), 2.17 (s, 3 H, Me) 2.15 (s, 3 H, 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_2CO); 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_2CO); 114.1 (CMe), 108.2 (CMe); 96.2–91.2 (C_5H_4); 13.7, 13.3 (2Me);

1.7 (CH_2). FAB MS: m/z 784 (M^+), 756 ($M^+ - CO$), 728 ($M^+ - 2CO$), 656 ($M^+ - 3CO, CS$), 644 ($M^+ - 5CO$) and 628 ($M^+ - 4CO, CS$). Calc. for $C_{10}H_8O_3SW$: C, 30.63; H, 2.06. Found: C, 30.41; H, 1.84%.

Reaction of complex 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 min turning 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 recrystallized from CH_2Cl_2 -hexane (1:5) to give $W_2Cp_2(CO)_5[C(SCH_2)_2](\mu-CH_2COS)$ 6 (0.51 g) in 61% yield. IR (cm^{-1} , CH_2Cl_2): 2021vs, 1981m, 1925s and 1903s $[\nu(CO)]$. 1H NMR, ($CDCl_3$): δ 5.70, 5.57 (s, Cp); 3.38 (s, 4 H, SCH_2); 2.83 (s, 2 H, CH_2). ^{13}C NMR ($CDCl_3$): δ 266.3 (M=C); 229.6, 216.9, 216.8, 210.3 (CO and CS); 97.5, 91.9 (2 Cp); 44.9 (SCH_2); 2.1 (CH_2CO). FAB MS: m/z 817 ($M^+ + 1$), 788 ($M^+ - CO$), 759 ($M^+ - 2CO$) and 732 ($M^+ - 3CO$). Calc. for $C_{20}H_{16}O_6S_3W_2$: C, 29.43; H, 1.98. Found: C, 30.01; H, 1.81%.

Reaction of complex 2 with $H_2C=C=CH_2$

Gaseous allene was slowly bubbled through a deep red solution of complex 2 (2.30 g, 3.38 mmol) in 30.0 mL of CH_2Cl_2 at room temperature for 35 min until it turned light yellow. Then the solvent was removed under vacuum to yield a yellow oil which was further purified by recrystallization from CH_2Cl_2 -hexane (2:3) at -20 °C to give $W_2Cp_2(CO)_5[\mu-CH_2COC(CH_2)_2]$ 7, (2.24 g) in 92% yield. IR (cm^{-1} , CH_2Cl_2): 2022m, 1957w (sh), 1918vs and 1613m $[\nu(CO)]$. 1H NMR ($CDCl_3$, -10 °C): *endo* isomer; δ 5.58, 5.29 (s, Cp); 2.99 (br, 2 H, *anti*- CH_2); 2.18 (s, 2 H, CH_2); 1.60 (br, 2 H, *syn*- CH_2); *exo* isomer; δ 5.61, 5.26 (s, Cp); 3.10 (br, 2 H, *anti*- CH_2); 2.10 (s, 2 H, CH_2); 1.15 (br, 2 H, *syn*- CH_2). ^{13}C NMR ($CDCl_3$): δ 229.0, 218.6, 208.1 (CO); 106.6 (C); 92.4, 87.8 (2 Cp); 25.7 (CH_2); -11.0 (CH_2). FAB MS: m/z 720 (M^+), 692 ($M^+ - CO$), 636 ($M^+ - 3CO$), 608 ($M^+ - 4CO$) and 580 ($M^+ - 5CO$). Calc. for $C_{10}H_8O_3W$: C, 33.36; H, 2.24. Found: C, 33.51; H, 2.11%.

X-Ray analysis

Dark red crystals of complex 3 suitable for X-ray diffraction study were grown directly from CH_2Cl_2 . A suitable single crystal of dimensions $0.11 \times 0.24 \times 0.30$ mm 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 having $16.88 < 2\theta < 27.12^\circ$. Cell constants and other pertinent data are collected in Table 4. An empirical correction for absorption, based on the azimuthal scan data, was applied to the intensities. Crystallographic computations were carried out using the NRCC structure determination package.²⁹ Final refinement using full-matrix, least squares converged smoothly.

For complex 5' the data were collected on a Siemens SMART CCD system using 3 kW sealed-tube molybdenum K radiation. Exposure time was 5 s per frame. A SADABS (Siemens area detector absorption) absorption correction³⁰ was applied, and decay was negligible. Data were processed and the structure was solved and refined by the SHELXTL program.³¹ The structure was solved using direct methods and confirmed by Patterson methods refining on intensities of all data (3925 reflections) to give $R_F = 0.0633$, $R'_{F2} = 0.1389$. In the structure determination the composite scattering factors were used for S(2) and O(5) in the final least squares 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. 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. The procedures for the structure determination of 7 were similar to those for 3.

Table 4 Crystal and intensity collection data for $W_2Cp_2(CO)_5-(\mu-CH_2CS)$ **3**, $W_2Cp'_2(CO)_5(CS)(\mu-CH_2COS)$ **5'** and $W_2Cp_2(CO)_5-[\mu-CH_2COC(CH_2)_2]$ **7**

	3	5'	7
Chemical formula	$C_{17}H_{12}O_5SW_2$	$C_{20}H_{16}O_6S_2W_2$	$C_{20}H_{16}O_6W_2$
<i>M</i>	696.03	784.15	720.04
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$C2/c$
<i>a</i> /Å	9.755(2)	7.1019(8)	26.296(5)
<i>b</i> /Å	15.936(4)	46.339(4)	7.023(2)
<i>c</i> /Å	12.226(4)	7.511(10)	24.226(6)
β /°	111.81(2)	116.44(1)	118.30(2)
<i>V</i> /Å ³	1764.5(8)	2213(3)	3939.0(17)
<i>Z</i>	4	4	8
<i>T</i> /K	298	298	298
μ /cm ⁻¹	134.483	203.811	119.576
Total number of reflections	3100	4520	3483
Unique reflections	2105 ($I > 2\sigma(I)$)	3661 ($I > 3\sigma(I)$)	2549 ($I > 2\sigma(I)$)
<i>R</i>	0.057	0.056	0.038
<i>R'</i>	0.056	0.063	0.038

CCDC reference number 186/1466.

See <http://www.rsc.org/suppdata/dt/1999/2243/> for crystallographic files in .cif format.

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