Organic Syntheses via Transition Metal Complexes, CV[‡]

Regiocontrol of Annelation of Cyclopentene-1-thiones and Cyclopenten-1-ones to Alkenes with the Aid of (1-Alkynyl)carbene Complexes (M = Cr, W)

He-Ping Wu,[a] Rudolf Aumann,*[a] Sabine Venne-Dunker,[a][‡‡] and Pauli Saarenketo[a][‡‡]

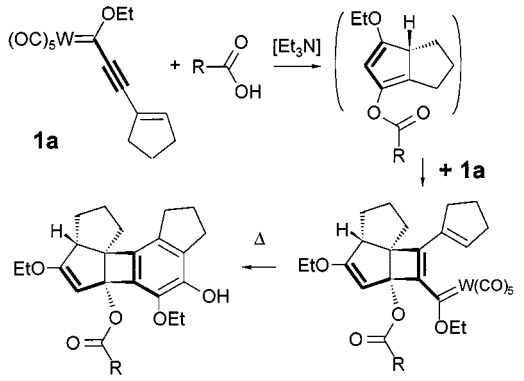
Dedicated to Professor Heinrich Vahrenkamp on the occasion of his 60th birthday

Keywords: Carbene complexes / Chromium / Claisen rearrangement / Cyclopentadienes / Cyclopentene-1-thiones / 1-Metallahexatrienes / Sulfur heterocycles / Tungsten

Bicyclic olefins containing a 1-oxy-3-thiocyclopentadiene unit were obtained with high regioselectivity from [2-(cycloalk-1-enyl)-1-alkynyl]carbene complexes **1a–d** and thiols **2a–c** under mild conditions. If the reaction was performed in a protic solvent like ethanol, the produced allylthiocyclopentadienes **5** spontaneously underwent a thio Claisen rearrangement to give cyclopentene-1-thione complexes **3** in 62–72% yields. In nonprotic solvents, additional cyclopentene-1-thione complexes **6** and **7** were obtained as a result of the incorporation of two and three allylthiol units, respectively. Arylthiotetrahydroindene complexes **12b** and **c** could be isolated in 76–79% yields. The corresponding tetrahydropentalene derivative **12a** was unstable, but could be trapped by [2+2] cycloaddition of (1-alkynyl)carbene complex **1a** to give a stable (cyclobutenyl)carbene complex **15**. Hydrolysis of compounds **12a–c** afforded cyclopenten-1-ones **13a–c**.

Introduction

(1-Alkynyl)carbene complexes $(CO)_5M{=}C(OEt)C{\equiv}CR$ (M = Cr, W) have been utilized as stoichiometric reagents in a number of high-yield transformations, potentially useful in organic synthesis.[2] We recently reported on the formation of cyclopentadienes[3] by π-cyclization of 1-metalla-1,3,5-hexatrienes,[4,5] which were readily derived from [2-(cyclopent-1-enyl)-1-alkynyl]carbene complex **1a** by addition of protic nucleophiles NuH.[6] For example, formation of cyclopentadienes could be triggered by addition of secondary amines R_2NH, secondary phosphanes R_2PH (R = *t*Bu, *c*C_6H_{11}),[7] and oxygen nucleophiles[8] ROH (R = aryl, aroyl and acyl), respectively, to (1-alkynyl)carbene complex **1a**. Whilst nitrogen or phosphorus nucleophiles led to production of cyclopentadiene complexes, oxygen nucleophiles gave highly reactive, metal-free cyclopentadienes, such as 1-acyloxy-3-alkoxytetrahydropentalenes. The latter compounds underwent a cascade of reactions initiated by the formation of a tricyclic [2+2] cycloadduct with (1-alkynyl)carbene complex **1a**, which on thermolysis underwent a π-cyclization involving an insertion of carbon monoxide to give a pentacyclic compound (Scheme 1).[8,9]



Scheme 1. Cascade reaction initiated by addition of oxygen nucleophiles RCO_2H to [2-(cyclopent-1-enyl)-1-alkynyl]carbene tungsten complex **1a**

Reaction of sulfur nucleophiles, like thioacylates $RC(=O)S^-$ or thio(imino)acylates $RC(=NH)S^-$, with [2-(cycloalk-1-enyl)-1-alkynyl]carbene complexes **1a–c** were found to afford bicyclic cyclopentadienes containing sulfur substituents.[1] We now wish to report that the allylthiocyclopentadienes **5** thus generated spontaneously underwent a thio Claisen rearrangement to give cyclopentene-1-thione complexes **3** in 62–72% yields (Scheme 2, Table 1).

[‡] Part CIV: Ref.[1]
[‡‡] Crystal structure analyses
[a] Organisch-Chemisches Institut der Universität Münster, Corrensstraße 40, 48149 Münster, Germany
Fax: (internat.) + 49-(0)251/833-6502
Email: aumannr@uni-muenster.de

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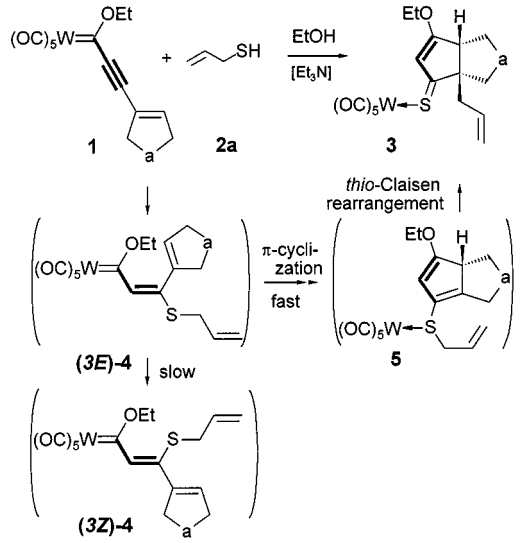


Scheme 2. Allylthiocyclopentadiene complexes **5** from {[2-(cycloalk-1-enyl)-1-alkynyl]carbene}tungsten complexes **1** and its spontaneous bridgehead allylation by thio Claisen rearrangement

Table 1. Assignments of structural groups in Scheme 2

3	a	[**3**]%
a	CH_2	62
b	CH_2CH_2	72
c	$CH_2CH_2CH_2$	65

Generation and Thio Claisen Rearrangement of Allylthiocyclopentadiene Complexes 5

Addition of allylthiol (**2a**) to {[2-(cycloalk-1-enyl)-1-alkynyl]carbene}tungsten complexes **1a−c** in ethanol in the presence of triethylamine at 20 °C (5 min) resulted in the formation of cyclopentene-1-thione complexes **3**, in which an allyl group was attached to the bridgehead carbon atom (Scheme 2). Compounds **3** are stable enough to be isolated by chromatography on silica gel, since the $W(CO)_5$ unit functions as a protection group for the thione moiety. Metal-free thiones of this type would not survive these conditions.[10,11]

Formation of compounds **3** is assumed to follow the reaction paths outlined in Scheme 2. Though 1-metalla-1,3,5-hexatrienes **4** and cyclopentadiene complexes **5** have not been characterized in this case, the reaction course can be presumed on the basis of earlier studies, in which such compounds have been isolated and fully characterized by crystal structure analyses.[1,7]

The structural assignment of compounds **3** is based on ^1H and ^{13}C NMR spectra, including $^3J(H,H)$- and $^{2,3}J(C,H)$ measurements and a crystal structure analysis of compound **3b** (Figure 1). The W−S1−C2−C3 backbone is planar [dihedral angle = 0.00°; angle C2−S1−W = 113.6(2)°] and the plane defined by this unit bisects the angle between two neighbouring carbonyl ligands [C21−W−S1−C2 = 45.0(1)°]. The C2−C3 distance of 1.392(5) Å is much shorter than expected for a C−C single bond, and is similar to C3−C4 [1.325(7) Å], implying a strong π-polarization with a negative charge at $W(CO)_5^-$ and a positive charge centred at the allyl unit C2−C3−C4, in line with the downfield shift of the signals of these carbon atoms in the NMR spectrum (e.g. compound **3b**: C4: δ = 194.7; C3: δ = 120.6; C2: δ = 239.9).

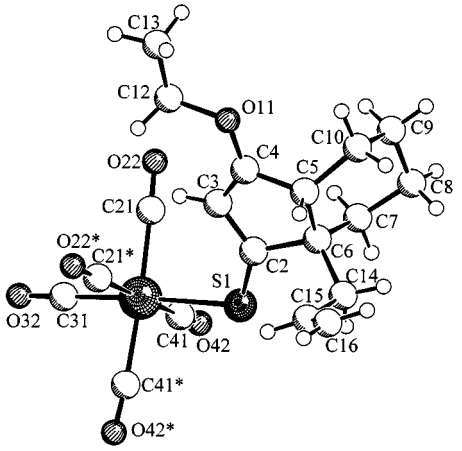
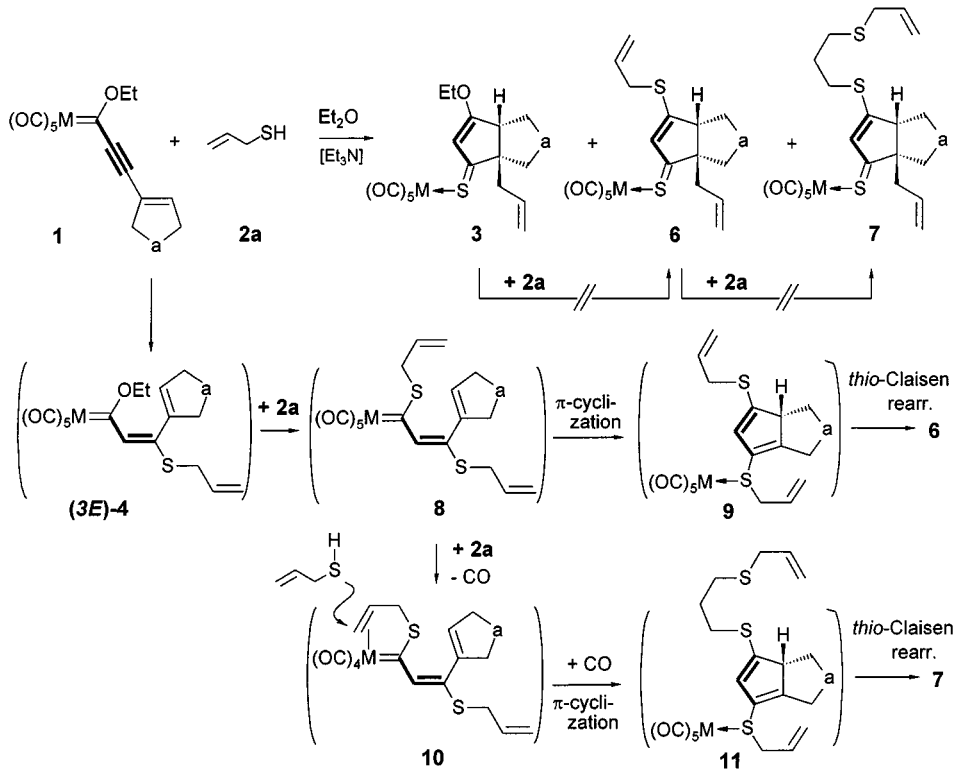


Figure 1. Molecular structure of *C*-allylcyclopentene-1-thione complex **3b**; selected bond lengths [Å] and angles [°]: W1−S1 2.537(1), S1−C2 1.647(4), C2−C3 1.392(5), C2−C6 1.550(6), C3−C4 1.325(7), C4−C5 1.495(6), C5−C6 1.559(7), C5−C10 1.572(8), C6−C14 1.539(7), C6−C7 1.557(13), C10−C9 1.503(12), C7−C8 1.526(18), C8−C9 1.482(15), C14−C15 1.503(16); C2−S1−W11 113.6(2), C3−C2−C6 109.2(4), C3−C2−S1 128.5(3), C6−C2−S1 120.8(3), C4−C3−C2 109.6(4), O11−C4−C3 130.3(4), O11−C4−C5116.3(4), C3−C4−C5 113.5(4), C4−C5−C6 102.4(4), C4−C5−C10 120.0(4), C6−C5−C10 112.9(4), C14−C6−C2 110.1(4), C14−C6−C7 110.0(5), C2−C6−C7 110.6(5), C14−C6−C5 110.2(4), C2−C6−C5 100.4(4), C7−C6−C5 115.1(5), C9−C10−C5 116.5(6), C8−C7−C6 113.0(8), C9−C8−C7 109.0(8), C8−C9−C10 111.3(9), C15−C14−C6 113.9(6), C16−C15−C14 122.3(12)

A marked influence of the solvent on the reaction of [2-(cycloalk-1-enyl)-1-alkynyl]carbene complexes **1** and allylthiol (**2a**) has been observed. Whilst compounds **3** were produced in good yields if ethanol was used as solvent, additional products **6** and **7** were obtained in aprotic solvents, such as diethyl ether (Scheme 3).

Compounds **6** and **7** were isolated by chromatography and were characterized spectroscopically. It was shown on the basis of NMR measurements that the cyclopentenones **6** were not formed by thiolysis of compounds **3** under the reaction conditions, even if the reaction time was extended to 12 h (at 20 °C). Furthermore, similar studies ruled out possible derivation of compounds **7** from compounds **6**. Accordingly, it is assumed that 2,4-bis(allylthio)-1-metalla-1,3,5-hexatrienes **8** are formed as key intermediates by substitution of the 2-ethoxy group of compounds (3*E*)-**4** by an allylthio unit (Scheme 3, Table 2). π-Cyclization of compounds **8** and subsequent thio Claisen rearrangement are presumed to afford allyl derivatives **6**. Addition of a third allylthiol (**2a**) is assumed to require formation of chelate intermediates **10** as precursors to cyclopentadiene derivatives **11**, from which compounds **7** are finally obtained. It



Scheme 3. Bridgehead allylation products **6** and **7** by incorporation of two and three allylthio units, respectively

Table 2. Assigments of structural groups in Scheme 3

3−**6**	M	a	[**3**]%	[**6**]%	[**7**]%
a	W	CH_2	17	37	13
b	W	CH_2CH_2	15	41	11
c	W	$CH_2CH_2CH_2$	49	–	–
d	Cr	CH_2CH_2	46	9	–

should be noted that reactions involving a chain extension of allyl-type carbene complexes have not been reported to date.

In an attempt to provide experimental evidence that 1-oxy-3-thiotetrahydropentalenes, -indenes and -hexahydroazulenes were indeed generated from [2-(cycloalk-1-enyl)-1-alkynyl]carbene complexes (Schemes 2 and 3), we studied the formation of supposedly more stable arylthio derivatives of this type. Compounds of the latter type could indeed be obtained, but were found to readily undergo (base-induced) rearrangement reactions and also (acid-induced) hydrolysis, depending on the reaction conditions.

Reaction of (1-Alkynyl)carbene Complexes 1a−c with Arylthiols 2b and c

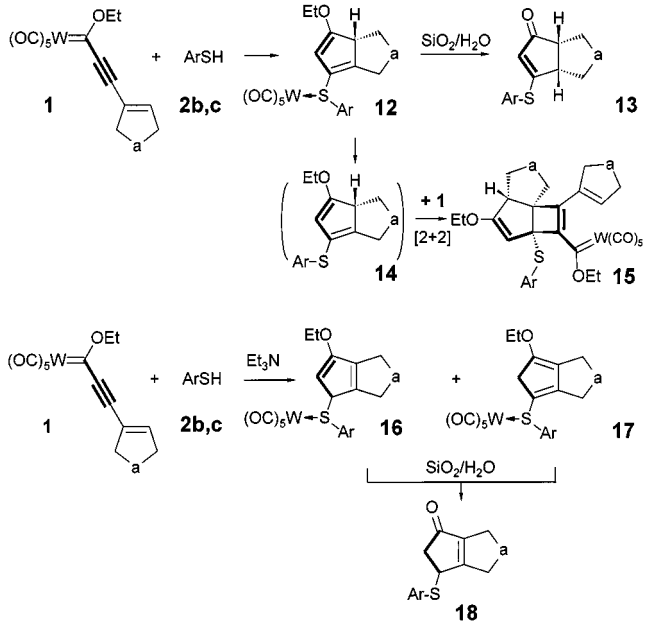
Addition of arylthiols **2b** and **c** to [2-(cyclohex-1-enyl)-1-alkynyl]carbene complex **1b** (20 °C, 2 h) yielded tetrahydroindene derivatives **12b** and **c**, which could be isolated from the reaction mixture by crystallization (Scheme 4, Table 3). Attempts to isolate compounds **12a**,**b** and **d** by chromatography on silica gel led to the production of (metal-free) tetrahydropentalenone **13a**, -tetrahydroindenone **13b** and -hexahydroazulenone **13d**, respectively.[12] Application of an excess of (1-alkynyl)carbene complex **1a** in its reaction with phenylthiol **2b** resulted in the formation of a [2+2] cycloadduct **15a** between the highly reactive tetrahydropentalene **14a** and compound **1a**.[8,13] [2+2] Cycloadducts (**15b** and **c**) to the SC=C units of tetrahydroindene- and hexahydroazulenes **14b** and **14d** were not obtained. If the reaction between (1-alkynyl)carbene complex **1a** and compound **2b** was performed in the presence of triethylamine at −20 °C, it resulted in the formation of an isomer (**17a**) of compound **12a** in 85% isolated yield. (1-Alkynyl)-carbene complex **1b** under similar conditions gave tetrahydroindene complexes **16b** and **c**, which could be isolated in 80−82% yield by crystallization, but which were transformed into tetrahydroindenones **18** if chromatography on silica gel was attempted.

The structural assignment of compounds **12**−**18** is based on ^{1}H- and ^{13}C-NMR spectra. The compounds are easily distinguished by the different chemical shifts of the olefinic proton signals, each in a narrow range, for cyclopentadienes (e.g. **12b**: 2-H: δ = 5.18; **16b**: 2-H: δ = 5.02; **16c**: 2-H: δ = 5.13) and cyclopentenones (e.g. **13b**: 2-H: δ = 5.59), a characteristic signal shift of the methine proton signals of isomers **12**, **16** and **17** (e.g. **12b**: 3a-H: δ = 2.86; **16b**: 1-H: δ = 3.93; **17a**: 2-H_2: δ = 3.56), and the characteristic pattern of CH_2 and =CH signals of isomers **13** and **18** (e.g. **13a**: 2-H: δ = 5.60; **18a**: 2-H_2: δ = 2.07). Hydrolysis of cyclopentadienes **12** to cyclopentenones results in drastic changes in chemical shifts (e.g. **12b/13b**: C-1: δ = 143.0/182.1; C-2: δ = 100.9/123.5; C-3: δ = 169.1/203.7). It should be noted that

systematic shift changes are imposed by ring strain effects within the bicyclic system (e.g. **13a**: 3a-H and 6a-H/C-3a and C-6a: δ = 2.94 and 2.59/52.5 and 48.7; **13b**: 3a-H and 7a-H/C-3a and C-7a: δ = 2.62 and 2.30/47.5 and 43.2; **13d**: 3a-H and 8a-H/C-3a and C-8a: δ = 2.90 and 2.44/52.6 and 49.2; **18a**: C-3a and C-6a: δ = 181.9 and 151.2; **18b**: C-3a and C-7a: δ = 168.6 and 141.4).[14]

Structural details for the (cyclobutenyl)carbene complex **15a** were derived from a crystal structure analysis (Figure 2). The W=C4−C5=C51 unit is twisted by 120.7(4) °, whilst the C5=C51−C52=C56 moiety adopts an almost planar *s-trans* configuration with an dihedral angle of −178.8(4)°. The cyclobutenyl ring exhibits a trapezoidal shape, with the typical pattern of bond lengths [C5=C51 = 1.360(4) Å, C5−C6 = 1.532(4) Å, C51−C61 = 1.513(4) Å, C6−C61 = 1.598(4) Å] and bond angles [C51−C5−C6 = 93.7(2)°, C5−C51−C61 = 95.1(2)°, C5−C6−C61 = 85.3(3)°, C51−C61−C6 = 85.5(2)°].

Structural details for compound **17a** were also obtained by a crystal structure analysis (Figure 3). The plane defined by the atoms W, S1 and C130 is strongly inclined against the almost planar adjacent ring [W−S1−C2−C3 =



Scheme 4. 1-Alkoxy-3-arylthiocyclopentadienes and related compounds generated from {[2-(cycloalk-1-enyl)-1-alkynyl]carbene}-tungsten complexes **1a−c** and arylthiols **2b**,**c**

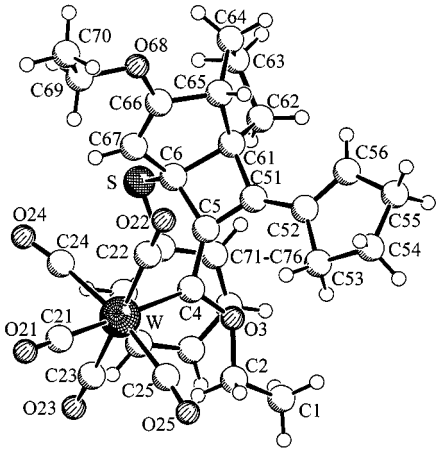


Figure 2. Molecular structure of cyclopentadiene complex **15a**; selected bond lengths [Å] and angles [°]: W−C4 2.187(3), O3−C4 1.318(4), C4−C5 1.472(4), C5−C51 1.360(4), C5−C6 1.532(4), C51−C52 1.444(4), C51−C61 1.513(4), C52−C56 1.332(4), C52−C53 1.505(4), C6−C67 1.490(5), C6−C61 1.598(4), C6−S 1.833(3), C61−C65 1.546(4), C65−C66 1.494(4), C66−C67 1.329(4), S−C71 1.776(4); O3−C4−C5 105.6(3), O3−C4−W 130.7(2), C5−C4−W 123.0(2), C51−C5−C4 132.3(3), C51−C5−C6 93.7(2), C4−C5−C6 134.0(2), C5−C51−C52 135.1(3), C5−C51−C61 95.1(2), C52−C51−C61 129.2(3), C56−C52−C51 124.6(3), C56−C52−C53 110.8(3), C51−C52−C53 124.6(3), C67−C6−C5 119.7(3), C67−C6−C61 103.3(2), C5−C6−C61 85.3(2), C67−C6−S 107.9(2), C5−C6−S 117.9(2), C61−C6−S 120.9(2), C51−C61−C62 119.3(3), C51−C61−C65 119.6(3), C62−C61−C65 105.9(2), C51−C61−C6 85.5(2), C62−C61−C6 118.6(2), C65−C61−C6 106.7(2), C66−C65−C61 102.6(2), C66−C65−C64 114.6(3), C61−C65−C64 105.8(3), C67−C66−O68 128.8(3), C67−C66−C65 115.4(3), O68−C66−C65 115.7(3), C66−C67−C6 111.7(3)

Table 3. Assignments of structural groups in Scheme 4

1	a	**2**	Ar
a	CH_2	**b**	C_6H_5
b	CH_2CH_2	**c**	*o*-$MeOC_6H_4$
c	$CH_2CH_2CH_2$		

12−18	a	Ar	[a]	Reaction cond.[b]	[**12**][c]	[**13**][d]	[**15**]	[**16**][c]	[**17**][c]	[**18**][d]
a	CH_2	C_6H_5	**1a**, **2b**	20 °C, 12 h	–	58	15	–	–	–
a	CH_2	C_6H_5	**1a**, **2b**	50 °C, 4 h, + B	–	12	–	–	–	30
a	CH_2	C_6H_5	**1a**, **2b**	−20 °C, 24 h, + B	–	–	–	–	85	–
b	CH_2CH_2	C_6H_5	**1b**, **2b**	20 °C, 12 h	79	62	–	–	–	–
b	CH_2CH_2	C_6H_5	**1b**, **2b**	50 °C, 4 h, + B	–	–	–	–	–	39
b	CH_2CH_2	C_6H_5	**1b**, **2b**	−20 °C, 24 h, + B	–	–	–	82	–	–
c	CH_2CH_2	*2*-$MeOC_6H_4$	**1b**, **2c**	20 °C, 12 h	76	–	–	–	–	–
c	CH_2CH_2	*2*-$MeOC_6H_4$	**1b**, **2c**	50 °C, 4 h, + B	–	–	–	–	–	45
c	CH_2CH_2	*2*-$MeOC_6H_4$	**1b**, **2c**	−20 °C, 24 h, + B	–	–	–	80	–	–
d	$CH_2CH_2CH_2$	C_6H_5	**1c**, **2b**	20 °C, 12 h	–	58	–	–	–	–

[a] Starting material, molar ratio of compounds **1:6** = 1:1. – [b] Reaction temperature, reaction time, + B = in the presence of Et_3N. – [c] Yields of corresponding products isolated by crystallization at −20 °C. – [d] Isolated yields of corresponding products after chromatography on silica gel.

59.7(11)°]. In line with expectation, a trigonal-pyramidal S1 atom geometry, which is indicated by the sum of bond angles (329.5°) between the atoms attached to it, leads to the production of an enantiomeric mixture. The enantiomers separated spontaneously on crystallization, and only one enantiomer was analysed by crystal structure analysis.

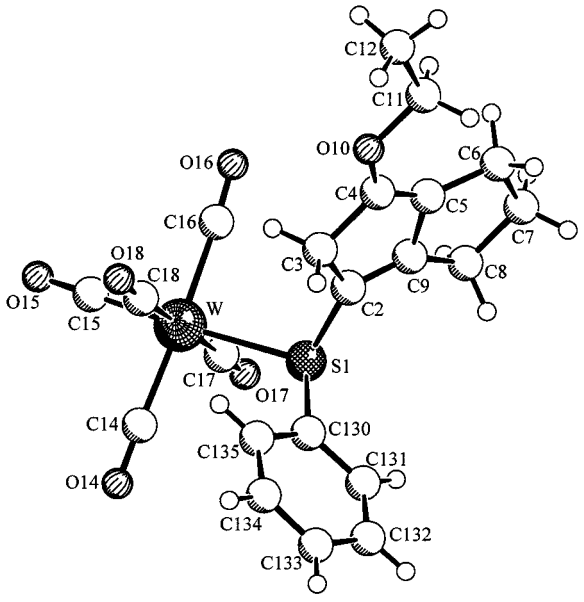
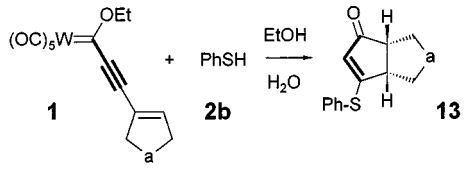


Figure 3. Molecular structure of tetrahydropentalene complex **17a**; selected bond lengths [Å] and angles [°]: W−S1 2.561(3), S1−C2 1.764(11), S1−C130 1.810(12), C2−C9 1.332(16), C2−C3 1.513(16), C3−C4 1.518(17), C4−C5 1.325(17), C4−O10 1.338(15), C5−C9 1.464(18), C5−C6 1.494(17), C6−C7 1.50(2), C7−C8 1.50(2), C8−C9 1.477(17), O10−C11 1.431(17), C11−C12 1.57(2); C2−S1−C130 103.4(5), C2−S1−W 110.8(4), C130−S1−W 115.3(4), C9−C2−C3 109.7(10), C9−C2−S1 124.7(9), C3−C2−S1 125.6(9), C2−C3−C4 101.2(10), C5−C4−O10 133.2(13), C5−C4−C3 110.4(12), O10−C4−C3 116.3(11), C4−C5−C9 108.8(12), C4−C5−C6 142.5(14), C9−C5−C6 108.5(11), C5−C6−C7 105.8(12), C8−C7−C6 109.6(11), C9−C8−C7 105.7(11), C2−C9−C5 109.8(11), C2−C9−C8 139.9(13), C5−C9−C8 110.3(10)



Scheme 5. Production of cyclopentenones **13** in a one-pot procedure

Table 4. Assignments of structural groups in Scheme 5

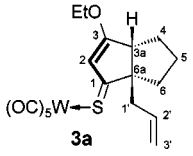
13	a	[**13**]%
a	CH_2	83
b	CH_2CH_2	75
d	$CH_2CH_2CH_2$	80

Cyclopentenones **13** could be readily obtained in a one-pot procedure by reaction of [2-(cycloalk-1-enyl)-1-alkynyl]-carbene complexes **1a−c** with phenylthiol (**2b**) in ethanol (instead of diethyl ether) (Scheme 5, Table 4).

Experimental Section

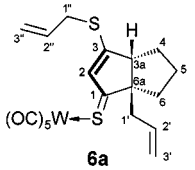
All operations were carried out under argon. All solvents were dried and distilled prior to use. − All ^{1}H- and ^{13}C-NMR spectra were routinely recorded with Bruker ARX 300 and AM 360 instruments. − IR spectra were recorded with a Biorad Digilab Division FTS-45 FT-IR spectrophotometer. − Elemental analysis were determined with a Perkin−Elmer 240 elemental analyser. − Analytical TLC plates, Merck DC-Alufolien Kieselgel 60$_{F240}$, were viewed by UV light (254 nm) and stained by iodine. R_f values refer to TLC tests. Chromatographic purifications were performed on Merck Kieselgel 100. Pentacarbonyl[3-(cyclopent-1-enyl)-1-ethoxy-2-propyn-1-ylidene]tungsten (**1a**), pentacarbonyl[3-(cyclohex-1-enyl)-1-ethoxy-2-propyn-1-ylidene]tungsten (**1b**), pentacarbonyl[3-(cyclohept-1-enyl)-1-ethoxy-2-propyn-1-ylidene]tungsten (**1c**) and pentacarbonyl[3-(cyclohex-1-enyl)-1-ethoxy-2-propyn-1-ylidene]-chromium (**1d**) were prepared according to ref.[7]

(6a-Allyl-3-ethoxy-4,5,6,6a-tetrahydro-3a*H*-pentalene-3-thione-*S*)-pentacarbonyltungsten (3a), (6a-Allyl-3-allylthio-4,5,6,6a-tetrahydro-3a*H*-pentalene-3-thione-*S*)pentacarbonyltungsten (6a) and (6a-Allyl-3-allylthiopropylthio-4,5,6,6a-tetrahydro-3a*H*-pentalene-3-thione-*S*)pentacarbonyltungsten (7a): Pentacarbonyl(3-cyclopentenyl-1-ethoxy-2-propyn-1-ylidene)tungsten (**1a**) (236 mg, 0.50 mmol) was added with stirring at 20 °C to allylthiol (**2a**) (37 mg, 0.50 mmol) and triethylamine (25 mg, 0.25 mmol) in 2 mL of ethanol in a 2 mL screw-top vessel. Compound **1a** was completely consumed within 5 min, to give a orange solution. The solvent was removed after 0.5 h at 20 °C and the residue was separated by rapid chromatography on silica gel (column 20 × 2 cm) with *n*-pentane/dichloromethane (10:1) to afford an orange fraction containing compound **3a** (169 mg, 62%, R_f = 0.4 in *n*-pentane/dichloromethane, 5:1; m.p. 67 °C). If the reaction was performed in diethyl ether (instead of ethanol) for 6 h at 20 °C, it afforded two violet compounds **6a** and **7a** in addition to compound **3a**. Rapid chromatography on silica gel (column 20 × 2 cm) with *n*-pentane/dichloromethane (10:1) gave compound **6a** (101 mg, 37%, R_f = 0.5 in *n*-pentane/dichloromethane, 5:1, violet crystals from *n*-pentane at −15 °C, m.p. 49 °C), an orange fraction containing compound **3a** (46 mg, 17%) and a red fraction of compound of **7a** (41 mg, 13%, R_f = 0.3 in *n*-pentane/ dichloromethane, 5:1, red oil). Compounds **3a, 6a** and **7a** are unstable in solution.



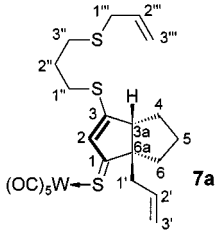
Compound 3a: ^{1}H NMR (C_6D_6): δ = 6.52 (s, 1 H, 2-H), 5.40 (m, 1 H, 2′-H), 4.90 (m, 2 H, 3′-H_2), 3.49 (2 H, OCH_2), 2.65 (dd, 1 H, 3a-H), 2.48 and 2.06 (each dd, each 1 H, diastereotopic 1′-H_2), 1.84 (m, 1 H), 1.42 (m, 1 H), 1.25−1.02 (m, 4 H), 0.81 (t, 3 H, OCH_2CH_3). − ^{13}C NMR (C_6D_6): δ = 239.8 (C_q, C=S), 201.8 and 198.4 [*trans*- and *cis*-CO of W(CO)$_5$], 193.7 (C_q, C-3), 133.2 (CH,

C-2′), 121.6 (CH, C-2), 119.0 (CH_2, C-3′), 69.5 (OCH_2), 66.7 (C_q, C-6a), 55.6 (CH, C-3a), 43.9 (CH_2, C-1′), 38.4, 28.2 and 24.6 (each CH_2, C-4−C-7), 13.6 (OCH_2CH_3). − IR (hexane): ṽ (%) = 2066.8 (5), 1940.9 (100), 1911.8 cm $^{-1}$ (30) [ν(C≡O)]. − MS (70 eV); *m/z* ^{184}W (%): 546 (21) [M^+], 462 (35) [M^+ − 3 CO], 434 (42) [M^+ − 4 CO], 406 (67) [M^+ − 5 CO]. − $C_{18}H_{18}O_6SW$ (546.3): calcd. C 39.54, H 3.29; found C 39.55, H 3.39.



6a

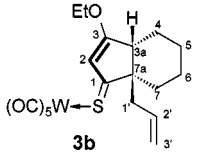
Compound 6a: ^{1}H NMR (C_6D_6): δ = 7.01 (s, 1 H, 2-H), 5.44 (m, 1 H, 2′′-H), 5.33 (m, 1 H, 2′-H), 5.06 (dd, 2 H, 3′′-H), 4.88 (m, 2 H, 3′-H), 3.05 (m, 2 H, 1′′-H), 2.38 and 2.03 (each dd, each 1 H, diastereotopic 1′-H_2), 2.78 (dd, 1 H, 3a-H), 1.71 (m, 1 H), 1.39 (m, 2 H), 1.18 (m, 3 H). − ^{13}C NMR (C_6D_6): δ = 236.3 (C_q, C=S), 201.7 and 198.1 [*trans*- and *cis*-CO of $W(CO)_5$], 137.2 (CH, C-2), 133.1 (CH, C-2′), 130.2 (CH, C-2′′), 120.2 (CH_2, C-3′′), 118.9 (CH_2, C-3′), 70.4 (C_q, C-6a), 60.3 (CH, C-3a), 44.4 (CH_2, C-1′), 36.0 (CH_2, C-1′′); 38.2, 30.9, 24.6 (each CH_2, C-4 − C-6). − IR (hexane): ṽ (%) = 2067.5 (5), 1941.5 (100), 1912.2 cm $^{-1}$ (30) [ν(C≡O)]. − MS (70 eV), *m/z* ^{184}W (%): 574 (35) [M^+], 462 (75) [M^+ − 4 CO], 434 (68) [M^+ − 5 CO]. − $C_{19}H_{18}O_5S_2W$ (574.3): calcd. C 39.70, H 3.13; found C 39.68, H 3.34.



7a

Compound 7a: ^{1}H NMR (C_6D_6): δ = 7.07 (1 H, s, 2-H), 5.62 (1 H, m, 2′′′-H), 5.37 (1 H, m, 2′-H), 4.91 (4 H, m, 3′-H and 3′′′-H), 2.80 (2 H, m, 1′′′-H_2), 2.67 and 2.24 (each 2 H, each t, 1′′- and 3′′-H_2), 2.38 (1 H, dd, 3a-H), 2.42 and 2.06 (each 1 H, each dd, diastereotopic 1′-H_2), 1.64 (2 H, m, 2′′-H_2), 1.74 (1 H, m), 1.40 (2 H, m) and 1.20 (3 H, m) (4-H_2−6-H_2). − ^{13}C NMR (C_6D_6): δ = 236.0 (C_q, C=S), 201.7 and 198.2 [*trans*- and *cis*-CO of $W(CO)_5$], 136.9 (CH, C-2), 134.6 (CH, C-2′), 133.1 (CH, C-2′′′), 119.0 (CH_2, C-3′), 116.9 (CH_2, C-3′′′), 70.5 (C_q, C-6a), 60.3 (CH, C-3a), 44.4 (CH_2, C-1′), 34.9 (CH_2, C-1′′′); 32.4, 29.3 and 27.8 (each 2 H, t, t, "quint", each CH_2, C-1′′−C-3′′); 34.8, 31.0 and 24.6 (each CH_2, C-4−C-7). − IR (hexane): ṽ (%) = 2067.5 (5), 1939.6 (100), 1922.0 (40) [ν(C≡O)] cm $^{-1}$. − MS (70 eV), *m/z* ^{184}W (%): 648 (6) [M^+], 324 (40) [M^+ − $W(CO)_5$], 283 (50) [324 − C_3H_5], 209 (30) [283 − C_3H_6S], 91 (100).

(7a-Allyl-3-ethoxy-3a,4,5,6,7,7a-hexahydroindene-1-thione-*S*)-pentacarbonyltungsten (3b), (7a-Allyl-3-allylthio-3a,4,5,6,7,7a-hexahydroindene-1-thione-*S*)pentacarbonyltungsten (6b) and (6a-Allyl-3-allylsulfidopropylthio-4,5,6,6a-tetrahydro-3a*H*-indene-3-thione-*S*)-pentacarbonyltungsten (7b): Pentacarbonyl(3-cyclopentenyl-1-ethoxy-2-propyn-1-ylidene)tungsten (**1*b**) (243 mg, 0.50 mmol) was added to allylthiol (**2a**) (37 mg, 1.00 mmol) and triethylamine (25 mg, 0.25 mmol) in 2 mL of ethanol as described above to give an orange compound **3b** (201 mg, 72%, R_f = 0.6 in *n*-pentane/dichloromethane, 5:1, m.p. 65 °C). − If the reaction was performed in diethyl ether (instead of ethanol) for 6 h at 20 °C, it afforded two violet compounds **6b** and **7b** in addition to compound **3b**. Rapid chromatography on silica gel (column 20 × 2 cm) with *n*-pentane/dichloromethane (10:1) gave compound **6b** (113 mg, 41%, R_f = 0.5 in *n*-pentane/dichloromethane, 5:1, violet crystals from *n*-pentane at −15 °C, m.p. 46 °C), an orange fraction containing compound **3b** (42 mg, 15%) and a fraction with compound **7b** (36 mg, 11%, R_f = 0.5 in *n*-pentane/dichloromethane, 5:1, red oil). Compounds **3b, 6b** and **7b** are unstable in solution.



3b

Compound 3b: ^{1}H NMR (C_6D_6): δ = 6.54 (s, 1 H, 2-H), 5.41 (m, 1 H, 2′-H), 4.89 (m, 2 H, 3′-H_2), 3.54 (2 H, OCH_2), 2.50 (dd, 1 H, 3a-H), 2.34 and 2.04 (each dd, each 1 H, diastereotopic 1′-H_2), 1.58, 1.35 and 1.10 (each m, 1:4:3 H, 4-H_2−7-H_2), 0.83 (t, 3 H, OCH_2CH_3). − ^{13}C NMR (C_6D_6): δ = 239.9 (C_q, C=S), 201.9 and 198.5 [*trans*- and *cis*-CO of $W(CO)_5$], 194.7 (C_q, C-3), 133.0 (CH, C-2′), 120.6 (CH, C-2), 119.2 (CH_2, C-3′), 69.3 (OCH_2), 58.1 (C_q, C-7a), 50.3 (CH, C-3a), 44.5 (CH_2, C-1′); 34.3, 22.8, 18.6 and 18.4 (each CH_2, C-4−C-7), 13.6 (OCH_2CH_3). − IR (hexane): ṽ (%) = 2067.0 (5), 1940.8 (100), 1912.0 cm $^{-1}$ (30) [ν(C≡O)]. − MS (70 eV), *m/z* ^{184}W (%): 560 (17) [M^+], 476 (33) [M^+ − 3 CO], 448 (30) [M^+ − 4 CO], 420 (100) [M^+ − 5 CO]. − $C_{19}H_{20}O_6SW$ (560.3): calcd. C 40.69, H 3.57; found C 40.68, H 3.65.

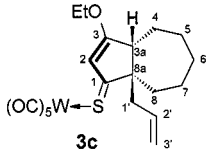
X-ray Crystal Structure Analysis of Compound 3b: Formula $C_{19}H_{20}O_6SW$, M = 560.26 gmol^{-1}, 0.30 × 0.20 × 0.10 mm, a = 11.532(1), b = 11.572(1), c = 15.896(1) Å, V = 2121.3(3) Å^3, $D_{calcd.}$ = 1.754 gcm^{-3}, μ = 55.74 cm^{-1}, empirical absorption correction via SORTAV (0.286 ≤ T ≤ 0.606), Z = 4, orthorhombic, space group *Pnma* (No. 62), λ = 0.71073 Å, T = 198(2) K, ω and scans, 4611 reflections collected (±h, ±k, ±l), $[(\sin\Theta)/\lambda]_{max}$ = 0.65 Å^{-1}, 2552 independent reflections and 2248 observed reflections [$I \geq 2\sigma(I)$], 176 refined parameters, R = 0.024, R_w^2 = 0.056, max./min. residual electron density ρ = 1.89/−1.32 eÅ^{-3}, hydrogen atoms calculated and riding, molecule is located on a mirror plane; therefore the cyclohexane ring and the propylene unit are disordered.[15]

Compound 6b: ^{1}H NMR (C_6D_6): δ = 7.07 (s, 1 H, 2-H), 5.45 (m, 1 H, 2′′-H), 5.38 (m, 1 H, 2′-H), 5.06 (dd, 2 H, 3′′-H), 4.88 (m, 2 H, 3′-H_2), 3.11 (m, 2 H, 1′′-H), 2.62 (dd, 1 H, 3a-H), 2.25 and 2.03 (each dd, each 1 H, diastereotopic 1′-H_2), 1.53 (m, 1 H), 1.36 (m, 3 H), 1.05 (m, 4 H). − ^{13}C NMR (C_6D_6): δ = 236.2 (C_q, C=S), 201.8 and 198.2 [*trans*- and *cis*-CO of $W(CO)_5$], 188.2 (C_q, C-3), 136.5 (CH, C-2), 133.0 (CH, C-2′), 130.0 (CH, C-2′′), 120.2 (CH_2, C-3′′), 119.0 (CH_2, C-3′), 62.0 (C_q, C-7a), 55.1 (CH, C-3a), 45.1 (CH_2, C-1′), 34.8 (CH_2, C-1′′); 34.6, 26.4, 19.1 and 18.9 (each CH_2, C-4−C-7). − IR (hexane): ṽ (%) = 2067.0 (5), 1940.9 (100), 1912.5 cm $^{-1}$ (30) [ν(C≡O)]. − MS (70 eV), *m/z* ^{184}W (%): 588 (30) [M^+], 476 (54) [M^+ − 4 CO], 448 (29) [M^+ − 5 CO]. − $C_{20}H_{20}O_5S_2W$ (588.4): calcd. C 40.79, H 3.40; found C 41.03, H 3.79.

Compound 7b: ^{1}H NMR (C_6D_6): δ = 7.09 (1 H, s, 2-H), 5.62 (1 H, m, 2′′′-H), 5.39 (1 H, m, 2′-H), 4.90 (4 H, m, 3′- and 3′′′-H), 2.79 (2 H, m, 1′′′-H_2), 2.70 and 2.25 (each 2 H, each t, 1′′- and 3′′-H_2), 2.63 (1 H, dd, 3a-H), 2.26 and 2.03 (each 1 H, each dd, diastereotopic 1′-H_2), 1.66 (2 H, m, 2′′-H_2), 1.56 (1 H, m), 1.36 (4 H, m)

and 1.10 (3 H, m) (4-H_2−7-H_2). − ^{13}C NMR (C_6D_6): δ = 235.9 (C_q, C=S), 201.7 and 198.2 [*trans*- and *cis*-CO of $W(CO)_5$], 136.0 (CH, C-2), 134.6 (CH, C-2′), 132.9 (CH, C-2′′′),119.0 (CH_2, C-3′), 116.9 (CH_2, C-3′′′), 62.0 (C_q, C-7a), 55.0 (CH, C-3a), 44.9 (CH_2, C-1′), 34.9 (CH_2, C-1′′′); 32.9, 29.3 and 27.7 (each CH_2, C-1′′−C-3′′); 34.7, 26.3, 19.0 and 18.9 (each CH_2, C-4−C-7). − IR (hexane): $\tilde{\nu}$ (%) = 2067.5 (5), 1939.0 (100), 1922.2 (40) [ν(C≡O)] cm $^{-1}$. − MS (70 eV), *m/z* ^{184}W (%): 662 (4) [M^+], 338 (40) [$M^+ - W(CO)_5$], 297 (45) [338 − C_3H_5], 223 (35) [297 − SC_3H_6], 115 (100).

(8a-Allyl-3-ethoxy-4,5,6,7,8,8a-hexahydro-3a*H*-azulene-1-thione-*S*)-pentacarbonyltungsten (3c): Pentacarbonyl(3-cycloheptenyl-1-ethoxy-2-propyn-1-ylidene)tungsten (**1d**) (250 mg, 0.50 mmol) was treated with allylthiol (**2a**) (37 mg, 0.50 mmol) in the presence of triethylamine (25 mg, 0.25 mmol) in 2 mL of ethanol as described above. Chromatography after 3 h at 20 °C afforded compound **3c** (185 mg, 65%, R_f = 0.7 in *n*-pentane/dichloromethane, 5:1, orange oil). If the reaction was performed in toluene (instead of ethanol) it gave compound **3c** in 49% yield (140 mg).



3c

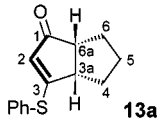
Compound 3c: ^{1}H NMR (C_6D_6): δ = 6.66 (s, 1 H, 2-H), 5.38 (m, 1 H, 2′-H), 4.90 (m, 2 H, 3′-H_2), 3.58 (2 H, OCH_2), 2.62 (dd, 1 H, 3a-H), 2.18 and 2.08 (each dd, each 1 H, diastereotopic 1′-H_2); 1.89, 1.65, 1.51, 1.32 and 0.96 (each m, 1:2:1:4:3 H, 4-H_2–8-H_2), 0.85 (t, 3 H, OCH_2CH_3). − ^{13}C NMR (C_6D_6): δ = 240.0 (C_q, C=S), 201.8 and 198.4 [*trans*- and *cis*-CO of $W(CO)_5$], 194.4 (C_q, C-3), 132.7 (CH, C-2′), 119.5 (CH, C-2), 118.1 (CH_2, C-3′), 69.1 (OCH_2), 58.9 (C_q, C-8a), 49.8 (CH, C-3a), 44.6 (CH_2, C-1′); 34.4, 22.7, 18.5 and 18.3 (each CH_2, C-4−C-7), 13.6 (OCH_2CH_3). − IR (hexane): $\tilde{\nu}$ (%) = 2067.9 (5), 1941.4 (100), 1912.2 cm $^{-1}$ (30) [ν(C≡O)]. − MS (70 eV), *m/z* ^{184}W (%): 574 (13) [M^+], 490 (19) [M^+ − 3 CO], 434 (39) [M^+ − 5 CO]. − $C_{20}H_{22}O_6SW$ (574.3): calcd. C 41.83, H 3.86; found C 42.57, H 3.98.

(7a-Allyl-3-ethoxy-3a,4,5,6,7,7a-hexahydroindene-1-thione-*S*)-pentacarbonylchromium (3d) and (7a-Allyl-3-allylthio-3a,4,5,6,7,7a-hexahydroindene-1-thione-*S*)pentacarbonylchromium (6d): Pentacarbonyl(3-cyclohexenyl-1-ethoxy-2-propyn-1-ylidene)chromium (**1d**) (178 mg, 0.50 mmol) was treated with allylthiol (**2a**) (37 mg, 0.50 mmol) in the presence of triethylamine (25 mg, 0.25 mmol) in 2 mL of toluene as described above to give compound **6d** (20 mg, 9%, R_f = 0.8 in *n*-pentane/dichloromethane, 5:1, violet crystals, m.p. 42 °C) and compound **3d** (98 mg, 46%, R_f = 0.7 in *n*-pentane/dichloromethane, 5:1, orange crystals from *n*-pentane at −15 °C, m.p. 58 °C).

Compound 3d: ^{1}H NMR (C_6D_6): δ = 6.50 (s, 1 H, 2-H), 5.39 (m, 1 H, 2′-H), 4.86 (m, 2 H, 3′-H), 3.51 (2 H, OCH_2), 2.51 (dd, 1 H, 3a-H), 2.34 and 2.03 (each dd, each 1 H, diastereotopic 1′-H_2); 1.58, 1.36 and 1.10 (each m, 1:4:3 H, 4-H_2−7-H_2), 0.85 (t, 3 H, OCH_2CH_3). − ^{13}C NMR (C_6D_6): δ = 241.9 (C_q, C=S), 223.6 and 216.8 [*trans*- and *cis*-CO of $W(CO)_5$], 194.9 (C_q, C-3), 133.0 (CH, C-2′), 119.1 (CH, C-2), 118.1 (CH_2, C-3′), 69.1 (OCH_2), 58.9 (C_q, C-7a), 49.8 (CH, C-3a), 44.6 (CH_2, C-1′); 34.4, 22.7, 18.5 and 18.3 (each CH_2, C-4−C-7), 13.6 (OCH_2CH_3). − IR (hexane): $\tilde{\nu}$ (%) = 1961.7 (5), 1932.1 (100), 1902.1 cm $^{-1}$ (30) [ν(C≡O)]. − MS (70 eV), *m/z* (%): 428 (13) [M^+], 344 (6) [M^+ − 3 CO], 316 (25) [M^+ − 4 CO], 288 (89) [M^+ − 5 CO]. − $C_{19}H_{20}O_6SCr$ (428.4): calcd. C 53.27, H 4.71; found C 53.05, H 4.69.

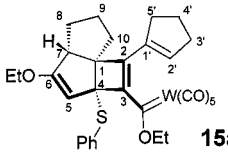
Compound 6d: ^{1}H NMR (C_6D_6): δ = 7.05 (s, 1 H, 2-H), 5.38 (m, 2 H, 2′- and 2′′-H), 4.94 (m, 4 H, 3′- and 3′′-H), 3.19 (m, 2 H, 1′′-H), 2.50 (dd, 1 H, 3a-H), 2.26 and 2.04 (each dd, each 1 H, diastereotopic 1′-H_2); 1.58, 1.35 and 1.06 (each m, 1:3:4 H, 4-H_2−7-H_2). − ^{13}C NMR (C_6D_6): δ = 238.7 (C_q, C=S), 221.6 and 216.5 [*trans*- and *cis*-CO of $W(CO)_5$], 188.0 (C_q, C-3), 133.9 (CH, C-2), 132.8 (CH, C-2′), 130.4 (CH, C-2′′), 120.1 (CH_2, C-3′′), 119.2 (CH_2, C-3′), 62.9 (C_q, C-7a), 54.6 (CH, C-3a), 45.2 (CH_2, C-1′), 35.7 (CH_2, C-1′′); 34.7, 26.3, 19.0 and 18.9 (each CH_2, C-4−C-7). − IR (hexane): $\tilde{\nu}$ (%) = 1962.8 (5), 1932.1 (100), 1903.2 cm $^{-1}$ (30) [ν(C≡O)]. − MS (70 eV), *m/z* (%): 456 (6) [M^+], 428 (10) [M^+ − 1 CO], 316 (57) [M^+ − 5 CO]. − $C_{20}H_{20}O_5S_2Cr$ (456.5): calcd. C 52.62, H 4.42; found C 52.43, H 4.40.

(6a*R,3a*S**)-3-Phenylthio-4,5,6,6a-tetrahydro-3a*H*-pentalen-1-one (13a) and (1*S**,4*R**,7*R**)-2-(Cyclopent-1-enyl)-6-ethoxy-3-(1,1,1,1,1-pentacarbonyl-2-ethoxy-1-tungsta-2-ethenyl)-4-phenylthiospirotricyclo[5.3.0^{1,4}.0^{1,7}]deca-2,5-diene (15a):** To pentacarbonyl(3-cyclopentenyl-1-ethoxy-2-propyn-1-ylidene)tungsten (**1a**) (236 mg, 0.50 mmol) in 1 mL of diethyl ether was added dropwise at 20 °C a solution of thiophenol (55 mg, 0.50 mmol) (**2b**) in 1 mL of diethyl ether. According to a TLC test, compound **1a** was consumed completely after 2 h at 20 °C. After stirring for 10 h at 20 °C, the mixture was centrifuged in order to remove $W(CO)_6$. Fast chromatography on silica gel (column 20 × 2 cm) with *n*-pentane/dichloromethane (6:1) afforded a red fraction containing compound **15a** (27 mg, 15%, R_f = 0.5 in *n*-pentane/dichloromethane 4:1, m.p. 74 °C). Subsequent elution with *n*-pentane/diethyl ether (3:1) gave a colourless polar fraction containing compound **13a** (67 mg, 58%, R_f = 0.4 in *n*-pentane/diethyl ether, 3:1). Compound **15a** was not formed if the (1-alkynyl)carbene complex **1a** was treated with an excess of 1.5 equivalents of thiophenol (**2b**), thus indicating that the reaction of the (1-alkynyl)carbene complex **1a** with thiophenol (**2b**) is faster than the [2+2] cycloaddition of **1a** to compound **14a**. If a solution of thiophenol (55 mg, 0.50 mmol) (**2b**) in 2 mL of ethanol was added to pentacarbonyl(3-cyclopentenyl-1-ethoxy-2-propyn-1-ylidene)tungsten (**1a**) (236 mg, 0.50 mmol) at 20 °C, the starting material was consumed after a few minutes (TLC test) to give cyclopenten-1-one **13a** in 83% yield.



13a

Compound 13a: ^{1}H NMR (C_6D_6): δ = 7.22 (d, 2 H, *o*-H Ph), 6.94 (m, 3 H, *p*-H and *m*-H Ph), 5.60 (s, 1 H, 2-H), 2.94 and 2.59 (each m, each 1 H, 3a-H and 6a-H), 1.97 (m, 1 H), 1.76 (m, 1 H), 1.39−1.21 (m, 4 H). − ^{13}C NMR (C_6D_6): δ = 205.0 (C_q, C=O), 181.5 (C_q, C-3); 134.7, 129.8 and 129.7 (each CH, 2:2:1, Ph), 130.0 (*i*-C, Ph), 126.3 (CH, C-2), 52.5 and 48.7 (each CH, C-3a and C-6a), 30.9, 29.4 and 24.2 (each CH_2, C-4−C-6). − IR (diethyl ether): $\tilde{\nu}$ (%) = 1701.9 cm $^{-1}$ (70) [ν(C=O)]. − MS (70 eV), *m/z* (%): 230 (100) [M^+]. − $C_{14}H_{14}OS$ (230.3): calcd. C 73.01, H 6.13; found C 72.97, H 6.04.

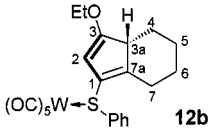


15a

Compound 15a: ^{1}H NMR (C_6D_6): δ = 7.57, 7.03 and 6.94 (each m, 2:1:2, Ph), 5.73 (m, 1 H, 2′-H), 5.37 (s, 1 H, 5-H), 4.56 and 4.31 (each m, each 1 H, diastereotopic W=COC*H*$_2$), 3.80 and 3.60 (each m, each 1 H, diastereotopic 6-OCH$_2$), 3.23 (dd, 1 H, 7-H), 2.62 (m, 1 H), 2.19 (m, 3 H), 1.92 (m, 2 H), 1.64 (m, 5 H), 1.03 (t, 6 H, 2 OCH$_2$C*H*$_3$). − ^{13}C NMR (C_6D_6): δ = 316.2 (W=C), 204.3 and 198.3 [each C_q, *trans*- and *cis*- CO of W(CO)$_5$], 164.1 (C_q, C-6), 159.8 (C_q, broad, C-3); 136.6, 136.0, 135.3 and 135.1 (each C_q, C-1′, C-2′, C-2 and *i*-C, Ph), 136.1, 128.8 and 128.2 (each CH, 2:2:1, Ph), 100.6 (CH, C-5), 78.2 (dynamically broadened W=CO*C*H$_2$), 75.2 (C_q, C-4), 65.3 (6-OCH$_2$), 64.0 (C_q, C-1), 49.9 (CH, C-7), 34.3, 33.5 and 23.6 (each CH$_2$, C-3′−C-5′); 33.4, 30.8 and 26.5 (each CH$_2$, C-8−C-10), 14.5 (2 OCH$_2$*C*H$_3$). − IR (diethyl ether): ṽ (%) = 2068.9 (5), 1947.1 (100), 1911.7 cm^{-1} (30) [ν(C≡O)]. − MS (70 eV), *m*/*z* ^{184}W (%): 730 (5) [M$^+$], 702 (20) [M$^+$ − CO], 618 (100) [M$^+$ − 4 CO], 590 (20) [M$^+$ − 5 CO]. − $C_{31}H_{30}O_7SW$ (730.5): calcd. C 50.83, H 4.11; found C 50.97, H 4.47.

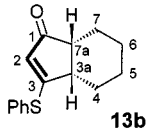
X-ray Crystal Structure Analysis of Compound 15a: Formula $C_{31}H_{30}O_7SW$, M = 730.46 gmol^{-1}, 0.25 × 0.25 × 0.20 mm, a = 15.558(1), b = 18.648(1), c = 10.051(1) Å, β = 94.49(1) °, V = 2907.1(4) Å^3, $D_{calcd.}$ = 1.669 gcm^{-3}, μ = 40.91 cm^{-1}, empirical absorption correction by SORTAV (0.428 ≤ T ≤ 0.495), Z = 4, monoclinic, space group $P2_1/c$ (No. 14), λ = 0.71073 Å, T = 198(2) K, ω and scans, 21588 reflections collected (±h, ±k, ±l), [(sinΘ)/λ]$_{max}$ = 0.71 Å^{-1}, 8808 independent reflections and 7197 observed reflections [I ≥ 2σ(I)], 363 refined parameters, R = 0.033, R_w^2 = 0.069, max./min. residual electron density ρ = 1.27/−0.82 eÅ^{-3}, hydrogen atoms calculated and riding.[15]

(3a*S)-Pentacarbonyl(3-ethoxy-1-phenylthio-4,5,6,7-tetrahydro-3a*H*-indene-*S*)tungsten (12b), 3-Phenylthio-3a,4,5,6,7,7a-hexahydroinden-1-one (13b) and 3-Ethoxy-1-phenylthio-4,5,6,7-tetrahydro-3a*H*-indene (14b):** Thiophenol (**2b**) (55 mg, 0.50 mmol) was treated with pentacarbonyl(3-cyclohexenyl-1-ethoxy-2-propyn-1-ylidene)-tungsten (**1b**) (243 mg, 0.50 mmol) in 2 mL of diethyl ether for 2 h as described above. Fast chromatography with *n*-pentane/dichloromethane (10:1) afforded a yellow fraction containing compound **12b** (235 mg, 79%, R_f = 0.8 in *n*-pentane/dichloromethane, 4:1, m.p. 67 °C). Compound **12b** in [D$_6$]benzene was transformed into the metal-free ligand **14b** and W(CO)$_6$ within 15 h at 20 °C according to NMR measurements. Chromatography of the reaction mixture resulting from compounds **1b** and **2b** after 12 h at 20 °C gave compound **13b** (76 mg, 62%, R_f = 0.5 in *n*-pentane/diethyl ether, 3:1, colourless oil). If a solution of thiophenol (55 mg, 0.50 mmol) (**2b**) in 2 mL of ethanol was added to pentacarbonyl(3-cyclohexenyl-1-ethoxy-2-propyn-1-ylidene)tungsten (**1b**) (243 mg, 0.50 mmol) at 20 °C, starting material was consumed after few min (TLC test) to give cyclopenten-1-one **13b** in 75% yield.



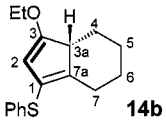
12b

Compound 12b: ^{1}H NMR (C_6D_6): δ = 7.52 (m, 2 H, *o*-H Ph), 6.97 (m, 3 H, *m*-H and *p*-H Ph), 5.18 (s, 1 H, 2-H), 3.39 (m, 2 H, OCH$_2$), 2.86 (dd, 1 H, 3a-H), 2.68 (m, 1 H), 2.23 (m, 1 H), 1.83 (m, 1 H), 1.64 (m, 1 H), 1.44−1.16 (m, 4 H), 0.99 (t, 3 H, OCH$_2$C*H*$_3$). − ^{13}C NMR (C_6D_6): δ = 201.2 and 197.9 [each C_q, *trans*- and *cis*-CO of W(CO)$_5$], 169.1 (C_q, C-3), 143.0 (C_q, C-1), 135.7 (C_q, *i*-C, Ph), 129.6, 129.5 and 128.9 (each CH, 2:2:1, Ph), 125.4 (C_q, C-7a), 100.9 (CH, C-2), 65.6 (OCH$_2$), 51.5 (CH, C-3a); 31.5, 28.8, 26.7 and 24.8 (each CH$_2$, C-4−C-7), 14.3 (OCH$_2$*C*H$_3$). − IR (diethyl ether): ṽ (%) = 2062.9 (5), 1933.8 (100), 1905.7 cm^{-1} (30) [ν(C≡O)]. − MS (70 eV), *m*/*z* ^{184}W (%): 596 (1) [M$^+$], 456 (5) [M$^+$ − 5 CO]. − $C_{22}H_{20}O_6SW$ (596.3): calcd. C 44.31, H 3.38; found C 44.21, H 3.35.



13b

Compound 13b: ^{1}H NMR (C_6D_6): δ = 7.27 (d, 2 H, *o*-H Ph), 6.97 (m, 3 H, *m*-H and *p*-H Ph), 5.59 (s, 1 H, 2-H), 2.62 and 2.30 (each m, each 1 H, 3a-H and 7a-H), 2.11 (m, 1 H), 1.81 (m, 1), 1.42−1.10 (m, 6 H). − ^{13}C NMR (C_6D_6): δ = 203.7 (C_q, C=O), 182.1 (C_q, C-3); 134.2, 129.8 and 129.7 (each CH, 2:2:1, Ph), 130.0 (C_q, *i*-C, Ph), 123.5 (CH, C-2), 47.5 and 43.2 (each CH, C-3a and C-7a), 30.0, 22.7 and 21.6 (each CH$_2$, 1:1:2, C-4−C-7). − IR (diethyl ether): ṽ (%) = 1699.8 cm^{-1} (70) [ν(C=O)]. − MS (70 eV), *m*/*z* (%): 244 (100) [M$^+$]. − $C_{15}H_{16}OS$ (244.4): calcd. C 73.73, H 6.60; found C 73.56, H 6.52.



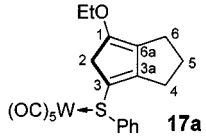
14b

Compound 14b: ^{1}H NMR (C_6D_6): δ = 7.41 (m, 2 H, *o*-H Ph), 6.86 (m, 3 H, *m*-H and *p*-H Ph), 5.08 (s, 1 H, 2-H), 3.34 (m, 2 H, OCH$_2$), 3.06 (dd, 1 H, 3a-H), 2.68 (m, 1 H), 2.37 (m, 1 H), 1.94 (m, 1 H), 1.64 (m, 1 H), 1.51−1.16 (m, 4 H), 1.01 (t, 3 H, OCH$_2$C*H*$_3$). − ^{13}C NMR (C_6D_6): δ = 169.1 (C_q, C-3), 142.6 (C_q, C-1), 134.7 (C_q, *i*-C, Ph); 129.8, 129.2 and 128.2 (each CH, 2:2:1, Ph), 123.5 (C_q, C-7a), 97.8 (CH, C-2), 65.2 (OCH$_2$), 51.4 (CH, C-3a), 31.6, 29.1, 26.4 and 25.3 (each CH$_2$, C-4−C-7), 14.4 (OCH$_2$*C*H$_3$).

(3a*S)-Pentacarbonyl[3-ethoxy-1-(2-methoxyphenylthio)-4,5,6,7-tetrahydro-3a*H*-indene-*S*]tungsten (12c):** Pentacarbonyl(3-cyclohexenyl-1-ethoxy-2-propyn-1-ylidene)tungsten (**1b**) (243 mg, 0.50 mmol) was treated with 2-methoxythiophenol (**2c**) (70 mg, 0.50 mmol) at 20 °C as described above to give compound **12c** (238 mg, 76%, R_f = 0.5 in *n*-pentane/dichloromethane, 1:3, m.p. 68 °C). − ^{1}H NMR (C_6D_6): δ = 7.40 and 6.39 (each d, each 1 H, 3-H and 6-H of C_6H_4), 6.91 and 6.62 (each t, each 1 H, 4-H and 5-H of C_6H_4), 5.18 (s, 1 H, 2-H), 3.37 (m, 2 H, 3-OCH$_2$), 3.35 (s, 3 H, OCH$_3$), 2.84 (dd, 1 H, 3a-H), 2.69 (m, 1 H), 2.22 (m, 1 H), 1.83 (m, 1 H), 1.63 (m, 1 H), 1.44−1.16 (m, 4 H), 0.98 (t, 3 H, OCH$_2$C*H*$_3$). − ^{13}C NMR (C_6D_6): δ = 201.2 and 197.9 [each C_q, *trans*- and *cis*-CO of W(CO)$_5$], 169.1 (C_q, C-3), 143.0 (C_q, C-1), 158.1 (C_q, C-2 of C_6H_4), 132.2 and 131.3 (each CH, C-4 and C-6 of C_6H_4), 123.7 (C_q, C-1 of C_6H_4), 121.1 and 111.7 (each CH, C-3 and C-5 of C_6H_4), 125.2 (C_q, C-7a), 100.9 (CH, C-2), 65.5 (OCH$_2$), 55.4 (OCH$_3$), 51.6 (CH, C-3a); 31.4, 28.7, 26.7 and 24.7 (each CH$_2$, C-4−C-7), 14.3 (OCH$_2$*C*H$_3$). − IR (diethyl ether): ṽ (%) = 2062.7 (5), 1933.8 (100), 1905.7 cm^{-1} (30) [ν(C≡O)]. − MS (70 eV), *m*/*z* ^{184}W (%): 626 (5) [M$^+$], 486 (10) [M$^+$ − 5 CO]. − $C_{23}H_{22}O_7SW$ (626.3): calcd. C 44.07, H 3.51; found C 43.87, H 3.62.

Pentacarbonyl(1-ethoxy-3-phenylthio-2,4,5,6-tetrahydro-pentalene-*S*)tungsten (17a): To pentacarbonyl(3-cyclopentenyl-1-ethoxy-2-propyn-1-ylidene)tungsten (**1a**) (236 mg, 0.50 mmol) in 1.5 mL of

hexane in a 2-mL screw-top vessel was added dropwise with stirring at −20 °C a solution of thiophenol (**2b**) (55 mg, 0.50 mmol) and triethylamine (20 mg, 0.20 mmol) in 0.5 mL of diethyl ether. A colour change from brown to yellow was observed immediately. Yellow crystals of compound **17a** were collected by centrifugation after 24 h at −20 °C and washed with precooled *n*-pentane at −20 °C (218 mg, 85%, R_f = 0.7 in *n*-pentane/diethyl ether, 3:1, m.p. 72 °C). Compound **17a** is very unstable at 20 °C and therefore should be stored below −30 °C. NMR spectra were recorded in $CDCl_3$ at −20 °C.

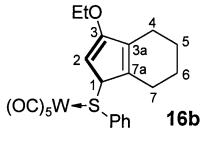


17a

Compound 17a: ^{1}H NMR (360 MHz, 253 K, $CDCl_3$): δ = 7.45, 7.41 and 7.33 (each m, 2:2:1, Ph), 4.09 (m, 2 H, OCH_2), 3.56 (s, 2 H, 2-H), 2.58 and 2.43 (each "t", each 2 H, 4-H_2 and 6-H_2), 2.16 (m, 2 H, 5-H_2), 1.33 (t, 3 H, OCH_2CH_3). − ^{13}C NMR (360 MHz, 253 K, $CDCl_3$): δ = 200.8 and 197.2 [each C_q, *trans*- and *cis*-CO of $W(CO)_5$], 165.4 (C_q, C-1), 155.8 (C_q, C-3), 138.3 (C_q, *i*-C, Ph), 129.2, 129.0 and 128.6 (each CH, 2:2:1, Ph), 119.7 and 106.2 (each C_q, C-3a and C-6a), 66.0 (OCH_2), 47.3 (CH_2, C-2); 29.9, 25.8 and 25.7 (each CH_2, C-4−C-6), 15.0 (OCH_2CH_3). − IR (diethyl ether): $\tilde{\nu}$ (%) = 2062.6 (5), 1934.6 (100), 1905.3 cm^{-1} (30) [ν(C≡O)]. − MS (70 eV), *m*/*z* ^{184}W (%): 582 (2) [M^+], 470 (8) [M^+ − 4 CO], 258 (59) [M^+ − $W(CO)_5$], 229 (100) [M^+ − $W(CO)_5$ − Et]. −$C_{21}H_{18}O_6SW$ (582.3): calcd. C 43.30, H 3.09; found C 43.58, H 3.17.

X-ray Crystal Structure Analysis of Compound 17a: Formula $C_{21}H_{18}O_6SW$, M = 582.26 gmol^{-1}, 0.30 × 0.30 × 0.20 mm, a = 7.297(1), b = 13.188(1), c = 22.343(2) Å, V = 2150.1(4) Å^3, $D_{calcd.}$ = 1.799 gcm^{-3}, μ = 55.03 cm^{-1}, empirical absorption correction by ψ scan data (0.289 ≤ T ≤ 0.406), Z = 4, orthorhombic, space group $P2_12_12_1$ (No. 19), λ = 0.71073 Å, T = 223(2) K, ω/2θ scans, 2505 reflections collected (+h, +k, −l), $[(\sin\Theta)/\lambda]_{max}$ = 0.62 Å^{-1}, 2505 independent reflections and 2263 observed reflections [$I \geq 2\sigma(I)$], 263 refined parameters, R = 0.031, R_w^2 = 0.101, max./min. residual electron density ρ = 0.94/−0.92 eÅ^{-3}, Flack parameter −0.02(3), hydrogen atoms calculated and riding.[15]

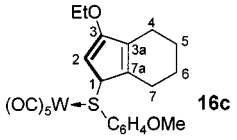
Pentacarbonyl(3-ethoxy-1-phenylthio-4,5,6,7-tetrahydro-1*H*-indene-*S*)tungsten (16b): Pentacarbonyl(3-cyclohexenyl-1-ethoxy-2-propyn-1-ylidene)tungsten (**1b**) (243 mg, 0.50 mmol) was treated with thiophenol (**2b**) (55 mg, 0.50 mmol) in the presence of triethylamine as described above to give compound **16b** (244 mg, 82%, R_f = 0.8 in *n*-pentane/dichloromethane, 1:3, m.p. 69 °C).



16b

Compound 16b: ^{1}H NMR (360 MHz, $CDCl_3$): δ = 7.44 ("d", 2 H, *o*-H Ph), 6.96 (m, 3 H, *m*-H and *p*-H Ph), 5.02 (d, 1 H, 2-H), 3.93 (d, 1 H, 1-H), 3.78 and 3.61 (each m, each 1 H, diastereotopic OCH_2), 2.17 (m, 1 H), 2.02 (m, 2 H), 1.79 (m, 1 H), 1.39 (m, 4 H), 1.10 (t, 3 H, OCH_2CH_3). − ^{13}C NMR (90 MHz, $CDCl_3$): δ = 200.1 and 197.6 [each C_q, *trans*- and *cis*-CO of $W(CO)_5$], 164.1 (C_q, C-3), 140.0 and 139.0 (each C_q, C-3a and C-7a), 134.5 (C_q, *i*-C, Ph); 132.2, 130.1 and 129.1 (each CH, 2:2:1, Ph), 94.4 (CH, C-2), 65.4 (OCH_2), 61.3 (CH, C-1); 23.9, 22.6, 21.9 and 21.5 (each CH_2, C-4−C-7), 14.4 (OCH_2CH_3). − IR (diethyl ether): $\tilde{\nu}$ (%) = 2067.6 (5), 1935.9 (100), 1898.2 cm^{-1} (50) [ν(C≡O)]. − MS (70 eV), *m*/*z* ^{184}W (%): 596 (5) [M^+], 484 (16) [M^+ − 4 CO], 272 (72) [M^+ − $W(CO)_5$]. − $C_{22}H_{20}O_6SW$ (596.3): calcd. C 44.27, H 3.35; found C 44.36, H 3.37.

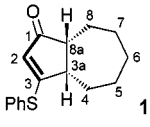
Pentacarbonyl[3-ethoxy-1-(2-methoxyphenylthio)-4,5,6,7-tetrahydro-1*H*-indene-*S*]tungsten (16c): Pentacarbonyl(3-cyclohexenyl-1-ethoxy-2-propyn-1-ylidene)tungsten (**1b**) (243 mg, 0.50 mmol) was treated with 2-methoxythiophenol (**2c**) (70 mg, 0.50 mmol) in the presence of triethylamine as described above. Workup as described above afforded compound **16c** (250 mg, 80%, R_f = 0.6 in *n*-pentane/dichloromethane, 1:3, m.p. 64 °C).



16c

Compound 16c: ^{1}H NMR (C_6D_6): δ = 7.42 and 6.39 (each d, each 1 H, 3-H and 6-H of C_6H_4), 6.94 and 6.65 (each t, each 1 H, 4-H and 5-H of C_6H_4), 5.13 (d, 1 H, 2-H), 4.56 (d, 1 H, 1-H), 3.84 and 3.67 (each m, each 1 H, diastereotopic OCH_2), 3.35 (s, 3 H, OCH_3), 2.13 (m, 1 H), 2.02 (m, 2 H), 1.67 (m,1 H), 1.37 (m, 4 H), 1.05 (t, 3 H, OCH_2CH_3). − ^{13}C NMR (C_6D_6): δ = 200.6 and 198.2 [each C_q, *trans*- and *cis*-CO of $W(CO)_5$], 163.8 (C_q, C-3), 158.1 (C_q, C-2 of C_6H_4), 139.7 and 139.2 (each C_q, C-3a and C-7a), 132.3 and 131.3 (each CH, C-4 and C-6 of C_6H_4), 123.9 (C_q, C-1 of C_6H_4), 121.1 and 111.6 (each CH, C-3 and C-5 of C_6H_4), 95.2 (CH, C-2), 65.4 (CH_2, OCH_2), 58.2 (CH, C-1), 55.4 (OCH_3); 24.4, 22.8, 22.0 and 21.7 (each CH_2, C-4−C-7), 14.4 (OCH_2CH_3). − IR (diethyl ether): $\tilde{\nu}$ (%) = 2062.8 (5), 1934.9 (100), 1905.8 (30) cm^{-1} [ν(C≡O)]. − MS (70 eV), *m*/*z* ^{184}W (%): 626 (5) [M^+], 514 (27) [M^+ − 4 CO], 302 (28) [M^+ − $W(CO)_5$]. − $C_{23}H_{22}O_7SW$ (626.3): calcd. C 44.07, H 3.51; found C 43.70, H 3.53.

3-Phenylthio-4,5,6,7,8,8a-hexahydro-3a*H*-azulen-1-one (13d): Pentacarbonyl(3-cycloheptenyl-1-ethoxy-2-propyn-1-ylidene)tungsten (**1c**) (250 mg, 0.50 mmol) was treated with thiophenol (**2b**) (55 mg, 0.50 mmol) in 2 mL of diethyl ether as described above. Chromatography of the mixture after 12 h at 20 °C with *n*-pentane/diethyl ether (5:1) afforded a colourless fraction containing compound **13d** (72 mg, 56%, R_f = 0.3 in *n*-pentane/diethyl ether, 5:1). If a solution of thiophenol (**2b**) (55 mg, 0.50 mmol) in 2 mL of ethanol was added to pentacarbonyl(3-cycloheptenyl-1-ethoxy-2-propyn-1-ylidene)tungsten (**1d**) (250 mg, 0.50 mmol) at 20 °C, starting material was consumed after a few minutes (TLC test) to give cyclopenten-1-one **13d** in 83% yield.



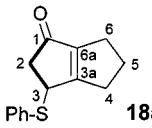
13d

Compound 13d: ^{1}H NMR (C_6D_6): δ = 7.28 ("d", 2 H, *o*-H Ph), 7.00 (m, 3 H, *m*-H and *p*-H Ph), 5.63 (s, 1 H, 2-H), 2.90 and 2.44 (each m, each 1 H, 3a-H and 8a-H), 1.89 (m, 2 H), 1.68−1.16 (m, 8 H). − ^{13}C NMR (C_6D_6): δ = 204.2 (C_q, C=O), 182.3 (C_q, C-3), 134.8, 129.9 and 129.3 (each CH, 2:2:1, Ph), 130.0 (C_q, *i*-C, Ph), 125.5 (CH, C-2), 52.6 and 49.2 (each CH, C-3a and C-8a); 31.3, 31.0, 28.2, 27.6 and 27.4 (each CH_2, C-4−C-7). − IR (diethyl ether): $\tilde{\nu}$ (%) = 1698.6 cm^{-1} (70) [ν(C=O)]. − MS (70 eV), *m*/*z*

(%): 258 (100) [M^+]. − $C_{16}H_{18}OS$ (258.4): calcd. C 74.38, H 7.02; found C 74.11, H 7.10.

3-Phenylthio-3,4,5,6-tetrahydro-2*H*-pentalen-1-one (18a): To pentacarbonyl(3-cyclopentenyl-1-ethoxy-2-propyn-1-ylidene)tungsten (**1a**) (236 mg, 0.50 mmol) in 1 mL of hexane was added dropwise with stirring at 20 °C a solution of thiophenol (**2b**) (55 mg, 0.50 mmol) and triethylamine (20 mg, 0.80 mmol) in 1 mL of *n*-pentane. After the mixture was stirred for 4 h at 50 °C, the solvent was removed and the residue was separated by chromatography on silica gel (column 20 × 2 cm) with *n*-pentane/diethyl ether, 4:1, to give a colourless oil containing compounds **13a** and **18a** (48 mg, 42%, **18a**:**13a** = 5:2, R_f = 0.4 in *n*-pentane/diethyl ether, 2:1).

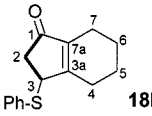
Compound 13a: See above.



18a

Compound 18a: ^{1}H NMR (C_6D_6): δ = 7.21 (m, 2 H, *o*-H Ph), 6.97 (m, 3 H, *m*-H and *p*-H Ph), 3.67 (d, 1 H, 3-H), 2.75 (m, 1 H), 2.28 (m, 1 H), 2.07 (d, 2 H, 2-H_2), 2.02−1.74 (m, 3 H), 1.28 (m, 1 H). − ^{13}C NMR (C_6D_6): δ = 197.7 (C_q, C=O), 181.9 (C_q, C-3a), 151.2 (C_q, C-6a), 134.7 (C_q, *i*-C, Ph); 131.9, 129.2 and 127.5 (each CH, 2:2:1, Ph), 49.6 (CH, C-3), 43.2 (CH_2, C-2), 30.2, 27.5 and 25.0 (each CH_2, C-4−C-6). − IR (hexane): $\tilde{\nu}$ (%) = 1708.5 cm^{-1} (70) [ν(C=O)]. − MS (70 eV), *m*/*z* (%): 230 (100) [M^+], 121 (80) [M^+ − SPh]. − $C_{14}H_{14}OS$ (230.3): calcd. C 73.02, H 6.13; found C 72.75, H 6.54.

3-Phenylthio-2,3,4,5,6,7-hexahydro-inden-1-one (18b): Pentacarbonyl(3-cyclohexenyl-1-ethoxy-2-propyn-1-ylidene)tungsten (**1b**) (243 mg, 0.50 mmol) was treated with thiophenol (**2b**) (55 mg, 0.50 mmol) in 2 mL of *n*-pentane in the presence of triethylamine. Workup as described above afforded a polar, colourless oil containing compound **18b** (47 mg, 39%, R_f = 0.6 in *n*-pentane/diethyl ether, 2:1).



18b

Compound 18b: ^{1}H NMR (C_6D_6): δ = 7.21 (m, 2 H, *o*-H Ph), 6.97 (m, 3 H, *p*- and *m*-H Ph), 3.63 (d, 1 H, 3-H), 2.50 (m, 3 H), 2.00 (d, 2 H, 2-H_2), 1.77 (m, 1 H), 1.30 (m, 4 H). − ^{13}C NMR (C_6D_6): δ = 203.0 (C_q, C=O), 168.6 (C_q, C-3a), 141.4 (C_q, C-7a), 134.2 (C_q, *i*-C, Ph); 132.5, 129.1 and 127.6 (each CH, 2:2:1, Ph), 48.2 (CH, C-3), 43.8 (CH_2, C-2); 26.4, 22.3, 21.6 and 20.5 (each CH_2, C-4−C-7). − IR (hexane): $\tilde{\nu}$ (%) = 1705.6 cm^{-1} (70) [ν(C=O)]. − MS (70 eV), *m*/*z* (%): 244 (90) [M^+]. − $C_{15}H_{16}OS$ (244.3): calcd. C 73.73, H 6.60; found C 73.64, H 6.53.

3-(2-Methoxyphenylthio)-2,3,4,5,6,7-hexahydroinden-1-one (18c): Pentacarbonyl(3-cyclohexenyl-1-ethoxy-2-propyn-1-ylidene)-tungsten (**1b**) (243 mg, 0.50 mmol) was treated with thiophenol (**2c**) (70 mg, 0.50 mmol) in 2 mL of *n*-pentane in the presence of triethylamine as described above to give the polar compound **18c** (62 mg, 45%, R_f = 0.7 in *n*-pentane/diethyl ether, 2:1, colourless oil]. − ^{1}H NMR (C_6D_6): δ = 7.27 and 6.47 (each "d", each 1 H, 3-H and 6-H of C_6H_4), 7.02 and 6.75 (each "t", each 1 H, 4-H and 5-H of C_6H_4), 3.85 (d, 1 H, 3-H), 3.32 (s, 3 H, OCH_3), 2.50 (m, 3 H), 2.04 (s, 2 H, 2-H_2), 1.81 (m, 1 H), 1.28 (m, 4 H). − ^{13}C NMR (C_6D_6): δ = 203.6 (C_q, C=O), 169.1 (C_q, C-3a), 159.2 (C_q, C-2 of C_6H_4), 141.4 (C_q, C-7a), 133.5 and 129.0 (each CH, C-6 and C-4 of C_6H_4), 123.3 (C_q, *i*-C of C_6H_4), 121.1 and 111.2 (each CH, C-3 and C-5 of C_6H_4), 55.2 (CH_3O), 47.0 (CH, C-3), 44.3 (CH_2, C-2); 26.6, 22.3, 21.6 and 20.6 (each CH_2, C-4−C-7). − IR (hexane): $\tilde{\nu}$ (%) = 1703.1 cm^{-1} (70) [ν(C=O)]. − MS (70 eV), *m*/*z* (%): 274 (70) [M^+]. − $C_{16}H_{18}O_2S$ (274.1): calcd. C 70.07, H 6.62; found C 70.33, H 6.74.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC-142494 (**15a**), -142495 (**17a**), and -142496 (**3b**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, CambridgeCB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033, E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. P. S. thanks the Finnish Academy for financial support.

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Received April 6, 2000
[O00175]