Organic Syntheses via Transition Metal Complexes. 104.[1] Cyclopentadienyl Thiolacylates from (1-Alkynyl)carbene Complexes (M = Cr, W): Sulfur-Centered Fragmentation of Ligand Side Chains

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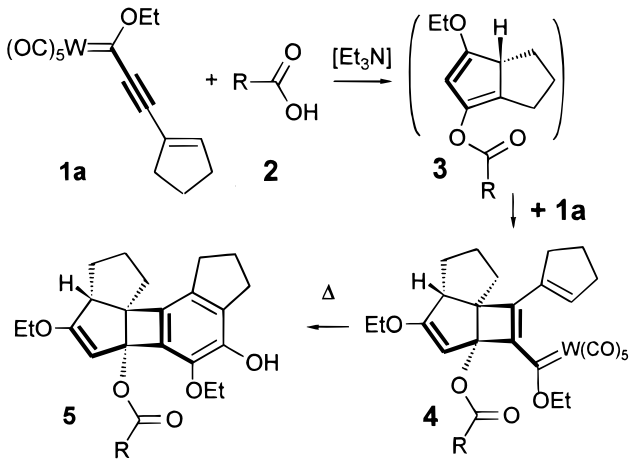
Cyclopentadienes containing sulfur substituents were generated by addition of sulfur nucleophiles to [1-alkynyl-2-(cycloalk-1-enyl)]carbene complexes **1a**−**f** (M = W, Cr). Cyclopentadienyl thiol(*NH*-imino)acylate-*N* complexes **12b**−**d**,**f**,**g** were obtained in 82−95% yields by addition of thioamides RC(=S)NH_2 (**10**; R = Ph, Me) to (1-alkynyl)carbene complexes **1** at 20 °C (20 min). Compounds **12** on thermolysis at 50 °C gave cyclopentene-1-thione complexes **9** and nitriles **13** by a sulfur-centered fragmentation of the ligand side chain. Addition of thioamide MeC(=S)NHPh (**16**) to (1-alkynyl)carbene complexes **1** afforded thermally stable cyclopentadienyl thiol(*NPh*-imino)acylate-*N* complexes **17b**,**c** in 94−96% yield. Valence isomers **18a**−**c** of the latter compounds were generated in 83−89% yields, if the reaction was performed in the presence of a base, e.g. triethylamine. Addition of thiocarboxylic acids **6a**,**b** to tungsten (1-alkynyl)carbene complexes **1a**,**b** at 20 °C produced cyclopentene-1-thione complexes **9a**,**b**. Addition of thiocarboxylic acids **6a**,**b** to the tungsten (1-alkynyl)carbene complex **19** at 20 °C afforded 4-(*S*-thioacyl)-1-tungsta-1,3-butadienes **20**.

Introduction

(1-Alkynyl)carbene complexes $(CO)_5M{=}C(OEt)C{\equiv}CR$ (M = Cr, W) have been applied as stoichiometric reagents in a number of high-yield transformations, which could be potentially useful to organic synthesis.[2] We recently reported on the formation of cyclopentadiene rings by π-cyclization of 1-metalla-1,3,5-hexatrienes,[3] which were readily derived from (1-alkynyl)carbene complexes **1** by addition of protic nucleophiles NuH.[4,5] To date, formation of cyclopentadienes has been found to be triggered by addition of secondary amines R_2NH, secondary phosphines R_2PH (R = *t*-Bu, *c*-C_6H_{11}),[6] and oxygen nucleophiles[7] ROH (R = Ph, 1-Napht, MeCO, $PhCH_2CO$, PhCO, 4-*t*-BuC_6H_4CO), respectively, to (1-alkynyl)carbene complexes **1**. While nitrogen or phosphorus nucleophiles led to production of cyclopentadiene complexes, oxygen nucleophiles gave highly reactive metal-free cyclopentadienes, e.g. 1-acyl-3-alkoxy cyclopentadienes **3**. The latter compounds underwent a cascade of reactions initiated by spontaneous formation of tricyclic [2 + 2] cycloadducts **4** with (1-alkynyl)-carbene complex **1a**, which could be subsequently transformed into pentacyclic compounds **5** by thermally induced fragmentation (Scheme 1).[7]

Scheme 1. Cyclopentadiene Rings by Addition of Oxygen Nucleophiles to (1-Alkynyl)carbene Complex 1a



We now wish to report on the generation of cyclopentadienes containing sulfur substituents, such as thiol-

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† Crystal structure analyses.

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(2) For a recent review on (1-alkynyl)carbene complexes see: Aumann, R.; Nienaber, H. *Adv. Organomet. Chem.* **1997**, *41*, 163−242.

(3) For a recent review on 1-metalla-1,3,5-hexatrienes and related compounds see: Aumann, R. *Eur. J. Org. Chem.* **2000**, 17−31.

(4) For a recent review on the preparation of five-membered carbocyclic rings from Fischer carbene complexes see: Herndon, J. W. *Tetrahedron* **2000**, *56*, 1257−1280.

(5) For related studies, in which 1-metalla-1,3,5-trienes were generated by addition of dienes to (1-alkynyl)carbene complexes, see: Barluenga, J.; Aznar, F.; Barluenga, S.; Fernández, M.; Martín, A.; García-Granda, S.; Pinera-Nicolás A. *Chem. Eur. J.* **1998**, *4*, 2280−2298.

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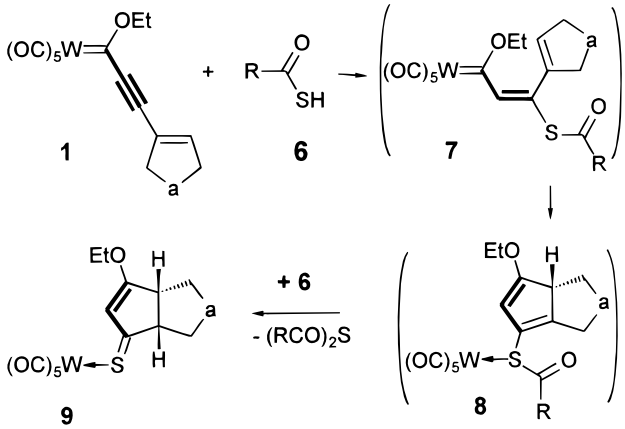
Scheme 2. (Cyclopentene-1-thione) Complexes by Fragmentation of Cyclopentadiene Thiolacylate Complexes



1,7-9	a	6	R
a	CH_2	**a**	Me
b	CH_2CH_2	**b**	Ph

9	a	Conditions[a]	[9]%[b]
a	CH_2	**1a**:**6a** = 1:2, 2 h	76
a	CH_2	**1a**:**6a** = 1:1, 4 h	48
a	CH_2	**1a**:**6b** = 1:2, 6 h	73
b	CH_2CH_2	**1b**:**6a** = 1:2, 2 h	71
b	CH_2CH_2	**1b**:**6a** = 1:1, 2 h	39
b	CH_2CH_2	**1b**:**6b** = 1:2, 6 h	69

[a] Reaction time at 20 °C and molar ratio of compounds **1** and **6**. [b] Isolated yields of compounds **9** after chromatography on silica gel.

acylates RC(═O)S$^-$, thiol(*NH*-imino)acylates RC(═NH)S$^-$, and thiol(*NPh*-imino)acylates MeC(═NPh)S$^-$, respectively, with high regioselectivity and under mild conditions.

Cyclopentadienyl Thiolacylate Complexes

Addition of thiocarboxylic acids **6a**,**b** to (1-alkynyl)-carbene tungsten complexes **1a**,**b** in the presence of a base, e.g. triethylamine, at 20 °C affords cyclopentene-1-thione complexes **9a**,**b** (Scheme 2). Optimal yields were obtained, if 2 equiv (instead of 1) of thiocarboxylic acid was applied.

Even though intermediates of this reaction have not been isolated, it can be reasonably assumed that 4-(thiocarboxy)-1-tungsta-1,3,5-hexatrienes **7** are formed and rapidly undergo π-cyclization to cyclopentadiene complexes **8**. Support of this hypothesis is provided by related studies with nitrogen and phosphorus nucleophiles,[6] as well as by a direct observation of compound **8b** in solution by ^{1}H and ^{13}C NMR spectra. Compound **8a**, which is expected to be even less stable than compound **8b** for reasons of ring strain, could not be detected by NMR spectra. While 1,3-dioxycyclopentadienes **3** are very reactive and were found to rapidly generate [2 + 2] cycloadducts with (1-alkynyl)carbene complex **1a** (Scheme 1),[7] a corresponding [2 + 2] cycloadduct has not been formed from sulfur compounds **8** (Scheme 2). On the basis of the fact that best yields of the cyclopentene-1-thione complexes **9** are obtained if 2 equiv of thiocarboxylic acids **6** is reacted with (1-alkynyl)carbene complex **1**, it is thought that the second equivalent of compound **6** would induce a transfer of the *S*-acyl group from compound **8** to give cyclopentene-1-thione complexes **9**. The latter compounds are quite stable, and all attempts to smoothly disengage the sulfur ligand from the tungsten compounds **9**, e.g. by reaction with pyridine in THF, resulted in formation of intractable product mixtures. The metal moiety of compounds **9** must therefore be considered as a kind of protecting group. While the chemistry of thioketones has been extensively investigated,[8] α,β-unsaturated thioketones have been scarcely studied.[9,10]

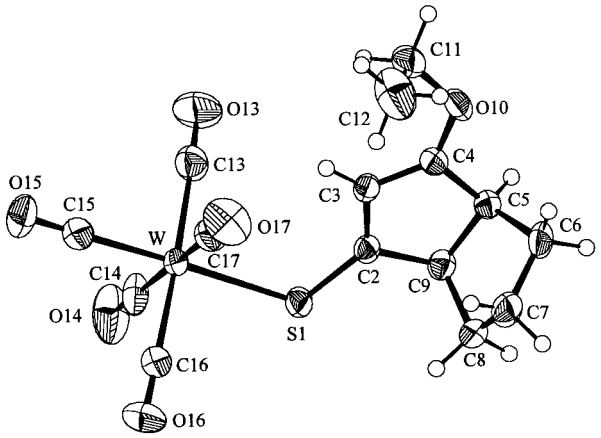


Figure 1. Molecular structure of hexahydropentalene-1-thione complex **9a**. Selected bond lengths (Å) and angles (deg): W−S1 = 2.543(2), S1−C2 = 1.669 (4), C2−C3 = 1.397 (5), C2−C9 = 1.513 (5), C3−C4 = 1.360(5), C4−O10 = 1.318(4), C4−C5 = 1.494(5), C5−C6 = 1.539(6), C5−C9 = 1.547(5), C6−C7 = 1.50(6), C7−C8 = 1.511(7), C8−C9 = 1.542(6); C2−S1−W = 115.7(1); C3−C2−C9 = 110.4(3), C3−C2−S1 = 128.9(3), C9−C2−S1 = 120.6(3), C4−C3−C2 = 108.9(3), O10−C4−C3 = 130.0(4), O10−C4−C5 = 116.1(3), C3−C4−C5 = 113.8(3), C4−C5−C6 = 112.0(4), C4−C5−C9 = 102.4(3), C6−C5−C9 = 105.8 (3), C7−C6−C5 = 104.4(3), C6−C7−C8 = 103.6(4), C7−C8−C9 = 103.8-(4), C2−C9−C8 = 113.9(3), C2−C9−C5 = 104.4(3), C8−C9−C5 = 105.2(3), C4−O10−C11 = 118.3(3).

Structural details of compound **9a** were derived from a crystal structure analysis (Figure 1). The W−S1−C2−C3 backbone is almost planar, with a dihedral angle of 4.3(4)° and C2−S1−W angle of 115.7(1)°, and bisects the angle between two neighboring carbonyl ligands, C17−W−S1−C2 = −44.1(2). On the basis of the sum of C−C bond angles of the bridgehead carbon atoms of 320.2° for C5 (C4−C5−C6 = 112.0(4)° + C4−C5−C9 = 102.4(3)° + C6−C5−C9 = 105.8(3)°) and 323.5° for C9 (C2−C9−C8 = 113.9(3)° + C2−C9−C5 = 104.4(3)° + C8−C9−C5 = 105.2(3)°), both of which are smaller than expected for an ideal tetrahedral configuration, the

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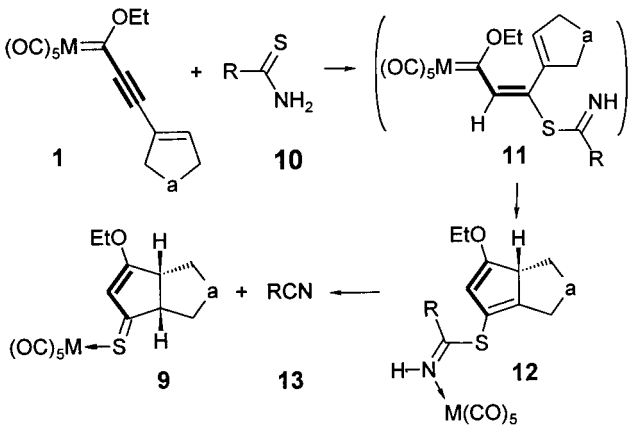
Scheme 3. Thiol(*NH*-imino)acylates of Tetrahydropentalenes, -indenes, and -azulenes 12, Respectively, from *NH*-Thioamides 10 and (1-Alkynyl)carbene Complexes 1



1,9	M	a	10	R
a	W	CH_2	**a**	Me
b	W	CH_2CH_2	**b**	Ph
c	W	$CH_2CH_2CH_2$		
d	Cr	CH_2		
e	Cr	CH_2CH_2		
f	Cr	$CH_2CH_2CH_2$		

12	M	R	a	[12]%[a]	fragmentation of 12[b]
a	W	Ph	CH_2	-	92 % **9a** at 20 °C, 0.3 h
b	W	Me	CH_2CH_2	91	92 % **9b** at 50 °C, 5 h
c	W	Ph	CH_2CH_2	94	94 % **9b** at 50 °C, 5 h
d	W	Me	$CH_2CH_2CH_2$	95	90 % **9c** at 50 °C, 5 h
e	Cr	Ph	CH_2	-	87 % **9d** at 20 °C, 0.3 h
f	Cr	Ph	CH_2CH_2	82	95 % **9e** at 50 °C, 5 h
g	Cr	Me	$CH_2CH_2CH_2$	90	95 % **9f** at 50 °C, 5 h

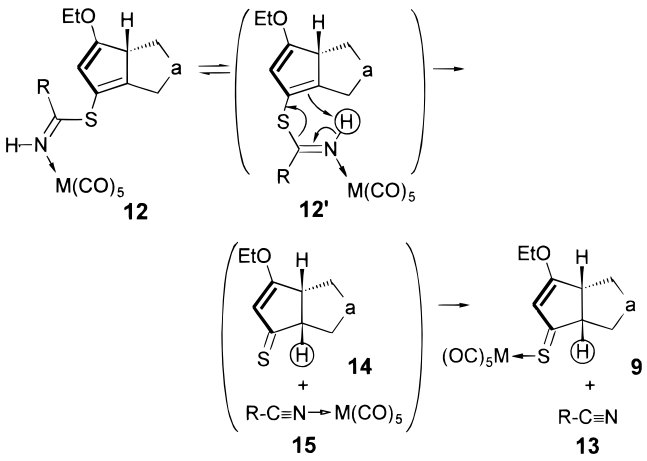
[a] Chemical yields of compounds **12** at 20 °C (20 min), molar ratio 1:1 of starting components **1** and **10**. [b] Chemical yields of compounds **9** on thermal fragmentation of compounds **12**.

hexahydropentalene skeleton is expected to be quite strained. The distance C2−C3 = 1.397(5) Å is much shorter than expected for a C−C single bond, and is similar to C3−C4 = 1.360(5) Å, implying a strong π-polarization with a positive charge centered at the allyl unit C2−C3−C4 and a negative charge at $W(CO)_5^-$. In line with this observation is the low-field shift of the carbon atoms, e.g. compound **9a**: C4, δ 195.0; C2 δ 121.5; C2, δ 237.5.

Cyclopentadienyl Thiol(*NH*-imino)acylate Complexes

Since cyclopentadiene derivatives **8** containing thiocarboxylate substituents could not be isolated but readily underwent solvolysis to cyclopentene-1-thione complexes **9a,b** (Scheme 2), we prepared cyclopentadienes **12** containing thiol(imino)acylate substituents, which were assumed to be more stable toward solvolysis than compounds **8**. Cyclopentadiene thiol(*NH*-imino)-acylate complexes **12b**−**d**,**f**,**g** were obtained in 82−95% yields by addition of thioamides $RC(=S)NH_2$ **10** to (1-alkynyl)carbene complexes **1** at 20 °C (20 min) (Scheme 3). Except for the tetrahydropentalene derivatives **12a**,**e**, which due to their inherent ring strain underwent a spontaneous fragmentation to complexes **9a**,**d** by elimination of benzonitrile (**13b**), the (more stable) thiol(*NH*-imino)acylates **12b**−**d**,**f**,**g**, containing six- and seven-membered-ring systems, could be isolated by crystallization and even survived purification by flash chromatography to an appreciable amount.

Scheme 4. Fragmentation of Thiol(*NH*-imino)acylates 12



Compounds **12** were stable in the solid state, but in solution at 50 °C (5 h) they underwent a smooth fragmentation into compounds **9** and nitriles **13**. This transformation could be followed by NMR spectra.

The pathway suggested for the fragmentation of thiol(*NH*-imino)acylates **12** is assumed to involve a *syn*/*anti* isomerization of the C=N bond to give the isomer **12′**, which exhibits the stereochemistry required for fragmentation presumably to give the metal-free cyclopentene-1-thione **14** and the nitrile complex $(RCN)M(CO)_5$ **15**, from which compounds **9** and **13** are finally derived by transmetalation (Scheme 4).

Spectroscopic features characteristic of cyclopentene-1-thione complexes **9** include the chemical shifts of the bridgehead protons (e.g., **9a** at δ 2.54 and 2.84 and **9b** at δ 2.47 and 2.51) as well as the corresponding carbon atoms (e.g., **9a** at δ 52.5 and 58.1 and **9b** at δ 46.6 and 52.4) at relatively low field, which appears to be associated not only with the influence of the neighboring π-systems but also with the angle strain induced by the ring size (vide supra). A marked downfield shift is observed also for the signals 2-H and C2 of cyclopentene-1-thiones **9** (2-H at δ 6.35−6.49 and C2 at δ ca. 120) compared to the cyclopentadienes **12** derived thereof (2-H at δ 4.44−4.68 and C2 at δ ca. 100). In line with expectation is the low-field shift of the carbon signals of the C=S unit (e.g., **9a** at δ 237.5 and **9b** at 236.8) as well as of the C=N moiety (e.g., **12b** at δ 190.7 and **12c** at 191.8), which in each case is influenced by coordination to the $M(CO)_5$ moiety.

The tetrahydroindene compound **12b** was characterized by a crystal structure analysis (Figure 2). The unsaturated five-membered ring exhibits the expected pattern of alternating bond distances: C2−C6 = 1.333(4) Å, C2−C3 = 1.469(4) Å, C3−C4 = 1.341(4) Å, C4−C5 = 1.499(4) Å. The saturated six-membered ring adopts a chair conformation. The $W(CO)_5$ unit is attached to the *NH*-iminium (not to the sulfur) atom of the thiol(*NH*-iminium)acylate unit in an essentially planar sickle-shape arrangement of the W1,N15,C14,-S1,C2 backbone: W1−N15−C14−S1 = −3.0(4)°, N15−

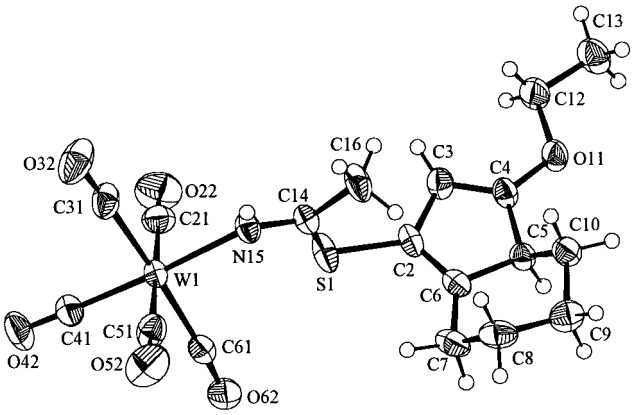


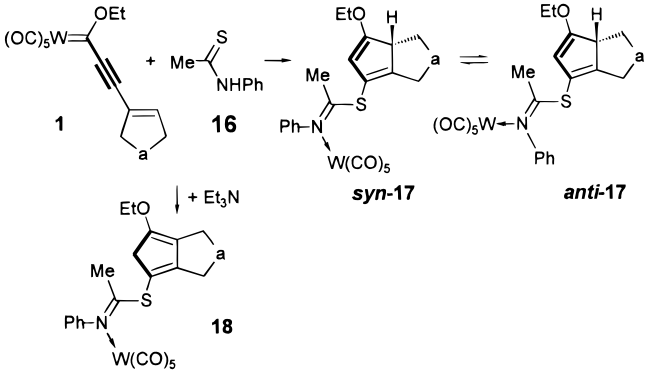
Figure 2. Molecular structure of tetrahydroindene complex **12b**. Selected bond lengths (Å) and angles (deg): W1−N15 = 2.227 (3), S−C14 = 1.736(3), S1−C2 = 1.765(3), C2−C6 = 1.333(4), C2−C3 = 1.469(4), C3−C4 = 1.341(4), C4−O11 = 1.353(3), C4−C5 = 1.497(4), C5−C6 = 1.499(4), C5−C10 = 1.528(4), C6−C7 = 1.495(4), C7−C8 = 1.523(5), C8−C9 = 1.519(5), C9−C10 = 1.518(5), O10−C12 = 1.433(4), C12−C13 = 1.491(4), C14−N15 = 1.277(4), C14−C16 = 1.499(4); C14−S1−C2 = 103.7(1), C6−C2−C3 = 1.5(3), C6−C2−S1 = 125.2(2), C3−C2−S1 = 123.3(2), C4−C3−C2 = 106.3(3), C3−C4−O11 = 130.7(3), C3−C4−C5 = 111.5(3), O11−C4−C5 = 117.8(3), C4−C5−C6 = 102.3(2), C4−C5−C10 = 115.6(3), C6−C5−C10 = 110.6(2), C2−C6−C7 = 131.5(3), C2−C6−C5 = 108.5(3), C7−C6−C5 = 119.4-(3), C6−C7−C8 = 108.6 (3), C9−C8−C7 = 110.7(3), C10−C9−C8 = 111.3(3), C9−C10−C5 = 109.4(3), C4−O11−C12 = 114.4(2), O11−C12−C13 = 108.6(3), N15−C14−C16 = 122.5(3), N15−C14−S1 = 117.4(2), C16−C14−S1 = 120.2-(2), C14−N15−W1 = 135.0(2).

C14−S1−C2 = −172.6(3)°, perpendicular to the cyclopentadiene ring, C14−S1−C2−C3 = −93.4(3)°.

Cyclopentadienyl Thiol(*NPh*-imino)acylate Complexes

Since cyclopentadiene derivates **12** are thermolabile due to the presence of an NH functionality and undergo fragmentation to cyclopentene-1-thione complexes **9** (Scheme 4), we generated thiol(*NPh*-imino)acylates **17**, which were anticipated to be more stable thermally. Reaction of tungsten (1-alkynyl)carbene complexes with (*N*-phenyl)thioacetamide (**16**) in diethyl ether at 20 °C affords a yellow precipitate of the compounds *syn*-**17** (Scheme 5). While the synthesis gave the compounds *syn*-**17** as a single stereoisomer, mixtures of *syn*- and *anti*-**17** were obtained from compounds *syn*-**17** in benzene at 50 °C. The mixture could not be separated by chromatography on silica gel, probably due to an interconversion of isomers under these conditions. Thus, the mixture was analyzed by NMR spectra. The most striking differences of chemical shifts of the corresponding isomers include the signals of N=CCH_3 (*syn*-**17** at δ 1.66 and *anti*-**17b** at δ 2.44) and *ortho*-H of C_6H_5 (*syn*-**17** at δ 6.44 and *anti*-**17b** at δ 6.84), as well as an NOE enhancement between N=CCH_3 and *ortho*-H of C_6H_5 for compound *syn*-**17b**, but not for *anti*-**17b**. It should be noted that migration of the methine proton within the cyclopentadiene ring was not observed at 50 °C.[11]

Scheme 5. Thiol(*NPh*-imino)acylates of Tetrahydropentalenes, -indenes, and -azulenes, from *NPh*-Thioamides 16 and (1-Alkynyl)carbene Complexes 1



17,18	a	[*syn*-**17**]%[a]	[b]	[**18**][c]
a	CH_2	-	-	89
b	CH_2CH_2	96	2:1	83
c	$CH_2CH_2CH_2$	94	4:5	86

[a] Chemical yields of compounds *syn*-**17** at 20 °C (25 min), molar ratio of starting components **1**:**10** = 1:1. [b] Molar ratio of *syn*- and *anti*-**17** after heating of *syn*-**17** to 50 °C (20 min). [c] Chemical yields of compounds **18**, if reaction between compounds **1** and **16** is performed in the presence of Et_3N at 20 °C (20 min).

Interestingly, it was possible to generate compounds **18**, which are isomers of compounds **17**, if the reaction between (1-alkynyl)carbene complex **1** with the (*N*-phenyl)thioacetamide **16** was performed in the presence of triethylamine at 20 °C (20 min) (Scheme 5).

The hexahydroazulene complex *syn*-**18c** was characterized by a crystal structure analysis (Figure 3). The unsaturated ring of the ligand exhibits the expected pattern of alternating bond distances, C4−C5 = 1.512-(3) Å, C5−C6 = 1.497(4) Å, C6−C7 = 1.353(8) Å, C7−C13 = 1.471(3) Å, C4−C13 = 1.350(4) Å. The seven-membered ring adopts a chair conformation. The $W(CO)_5$ unit is attached to the *NH*-iminium atom *syn* to the sulfur atom in an essentially planar sickle-shaped arrangement of the W1,N1,C2,S3,C4 backbone: W1−N1−C2−S3 = 8.6(3)°, N1−C2−S3−C4 = −170.0(2), almost perpendicular to the cyclopentadiene ring, C2−S3−C4−C5 = −85.3(2)°.

Experimental support of the assumption that 1-metalla-1,3,5-hexatrienes of type **7** (Scheme 2) would be intermediates in these reactions is provided by the isolation of thioenol esters **20** on addition of thiocarboxylic acids **6** to (1-alkynyl)carbene complex **19** (Scheme 6). The latter reaction follows a pattern similar to that previously found for the addition of carboxylic acid to compound **19**.[12] Other than 1-metalla-1,3,5-hexatrienes **7**, compounds **20** do not undergo π-cyclization at 20 °C and therefore could be isolated. They exhibit spectroscopic features, which are related to those of the corresponding acyloxy derivatives, including the expected ^{13}C and ^{1}H NMR shift of crucial NMR signals; e.g. **20a**: W=C δ 312.2, SC=O δ 196.5, C2 δ 140.0, OCH_2 δ 72.9; 2-H δ 7.33, OCH_2 δ 4.45; [(OC)$_5$W=

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(12) Aumann, R.; Jasper, B.; Läge, M.; Krebs, B. *Organometallics* **1994**, *13*, 3502−3509.

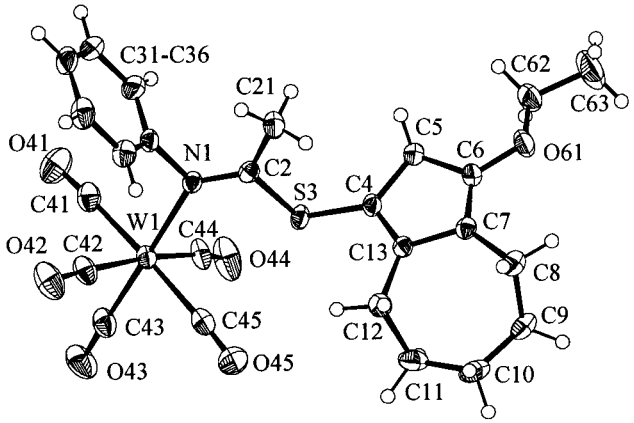
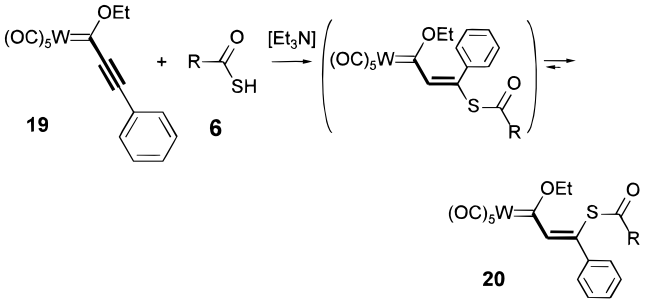


Figure 3. Molecular structure of hexahydroazulene complex *syn*-**18c** (code 1224.aum). Selected bond lengths (Å) and bond angles (deg): W1−N1 = 2.288(2), N1−C2 = 1.291(3), N1−C31 = 1.455(3), C2−C21 = 1.496(3), C2−S3 = 1.760(3), S3−C4 = 1.752(3), C4−C13 = 1.350(4), C4−C5 = 1.512(3), C5−C6 = 1.497(4), C6−C7 = 1.353(3), C7−C13 = 1.473(4), C7−C8 = 1.491(4), C8−C9 = 1.525(4), C9−C10 = 1.526(4), C10−C11 = 1.525(5), C11−C12 = 1.530(4), C12−C13 = 1.494(3); C2−N1−C31 = 116.6(2), C2−N1−W1 = 129.9(2), C31−N1−W1 = 113.5(2), N1−C2−C21 = 125.4(2), N1−C2−S3 = 115.7(2), C21−C2−S3 = 118.9(2), C2−S3−C4 = 107.2(1), C5−C4−C13 = 110.1(2), S3−C4−C13 = 123.5(2), S3−C4−C5 = 124.8(2), C4−C5−C6 = 101.2(2), C7−C6−O61 = 123.0(2), C5−C6−C7 = 111.9(2), C5−C6−O61 = 125.1(2), C6−C7−C13 = 107.2(2), C6−C7−C8 = 127.7(2), C8−C7−C13 = 125.1(2), C7−C8−C9 = 114.4(2), C8−C9−C10 = 114.2(2), C9−C10−C11 = 115.8-(3), C10−C11−C12 = 114.0(2), C11−C12−C13 = 113.8(2), C4−C13−C7 = 109.6(2), C4−C13−C12 = 127.9(2), C7−C13−C12 = 122.4(2).

Scheme 6. Generation of 4-(*S*-Thioacyl)-1-tungsta-1,3-butadienes 20



6,20	R	conditions[a]	[20] %[b]
a	Me	**19**:**6** = 1:1, 3 h	71
b	Ph	**19**:**6** = 1:1, 6 h	68

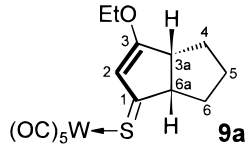
[a] Reaction time at 20 °C in a molar ratio of compounds **19** and **6**. [b] Isolated yields of compounds **20** after chromatography on silica gel.

C(OEt)CH=C(Ph)OCOMe:[12] W=C δ 306.2, OC=O δ 166.5, C2 δ 132.4, OCH_2 δ 80.2; 2-H δ 7.78, OCH_2 δ 4.50].

Experimental Section

All operations were carried out in an atmosphere of argon. All solvents were dried and distilled prior to use. All ^{1}H and ^{13}C NMR spectra were routinely recorded on Bruker ARX 300 and AM 360 instruments. IR spectra were recorded on a Biorad Digilab Division FTS-45 FT-IR spectrophotometer. Elemental analyses were determined on a Perkin-Elmer 240 elemental analyzer. Analytical TLC plates, Merck DC-Alufolien Kiesegel 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**) and -chromium (**1d**), pentacarbonyl[3-(cyclohex-1-enyl)-1-ethoxy-2-propyn-1-ylidene]tungsten (**1b**) and -chromium (**1e**), and pentacarbonyl[3-(cyclohept-1-enyl)-1-ethoxy-2-propyn-1-ylidene]tungsten (**1c**) and -chromium (**1f**) were prepared according to ref 6.

(a) Reaction of Thioacylic Acids with (1-Alkynyl)-carbene Complexes 1. (3a*R,6a*S**)-Pentacarbonyl(3-ethoxy-4,5,6,6a-tetrahydro-3a*H*-pentalene-1-thione-*S*)-tungsten (9a).** A solution of pentacarbonyl[3-(cyclopent-1-enyl)-1-ethoxy-2-propyn-1-ylidene)tungsten (**1a**; 236 mg, 0.50 mmol) in 1 mL of *n*-hexane was added dropwise to a solution of thioacetic acid (**6a**; 76 mg, 1.00 mmol) in 1 mL of diethyl ether/*n*-hexane (1:1) in the presence of triethylamine (40 mg, 0.40 mmol). The mixture was stirred for 2 h at 20 °C. Solvents were removed in vacuo, and the residue was rapidly separated by chromatography on silica gel (column 20 × 2 cm) with *n*-pentane/dichloromethane (3:1) to give a red fraction of compound **9a** (385 mg, 76%; R_f = 0.5 in *n*-pentane/diethyl ether 10:1, mp 76 °C). Reaction of compounds **1a** and **6a** in the molar ratio 1:1 resulted in lower yields of compound **9a** (ca. 48% after 4 h). Reaction of (1-alkynyl)carbene complex **1a** with thiobenzoic acid (**6b**) in the molar ratio 1:2 produced compound **9a** in 73% yield:



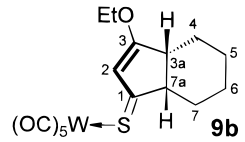
^{1}H NMR (C_6D_6): δ 6.29 (1 H, s, 2-H), 3.41 (OCH_2), 2.84 and 2.54 (1 H each, m each, 3a- and 6a-H); 1.72 and 1.37, 1.35, and 1.02 (1 H each, m each, diastereotopic 4-H_2 and 6-H_2), 1.11 and 0.90 (1 H each, m each, diastereotopic 5-H_2), 0.80 (3 H, t, OCH_2CH_3). ^{13}C NMR (C_6D_6): δ 237.5 (C_q, C=S), 202.3 and 198.8 (C_q each, *trans*- and *cis*-CO of $W(CO)_5$), 195.0 (C_q, C3), 121.5 (CH, C2), 69.9 (OCH_2), 58.1 and 52.5 (CH each, C3a and C6a), 33.0 and 28.3 (CH_2 each, C4 and C6), 24.2 (CH_2, C5), 14.0 (OCH_2CH_3). IR (diethyl ether; cm^{-1} (%)): 2067.3 (5), 1941.9 (100), 1912.2 (30) [ν(C≡O)]. MS (70 eV; *m*/*e* ^{184}W (%)): 506 (27) [M^+], 422 (100) [$M^+ - 3$ CO], 366 (40) [$M^+ - 5$ CO]. Anal. Calcd for $C_{15}H_{14}O_6SW$ (506.2): C, 35.56; H, 2.77. Found: C, 35.45; H, 2.76. X-ray crystal structure analysis of compound **9a** (code 1068.AUM): formula $C_{15}H_{14}O_6SW$, M = 506.17, red crystals 0.40 × 0.25 × 0.20 mm, a = 12.808(7) Å, b = 11.627(3) Å, c = 11.886(1) Å, β = 101.68(3)°, V = 1733.4-(11) Å^3, ρ_{calcd} = 1.940 g cm^{-3}, μ = 68.09 cm^{-1}, empirical absorption correction via ψ scan data (0.172 ≤ T ≤ 0.343), Z = 4, monoclinic, space group $P2_1/c$ (No. 14), λ = 0.710 73 Å, T = 223 K, $\omega/2\theta$ scans, 7161 reflections collected ($+h,\pm k,\pm l$), (sin $\theta)/\lambda$ = 0.62 Å^{-1}, 3526 independent (R_{int} = 0.055) and 2800 observed reflections ($I \geq 2\,\sigma(I)$), 209 refined parameters, R1 = 0.023, wR2 = 0.056, maximum residual electron density 0.89 (−1.67) e Å^{-3} close to tungsten, hydrogens calculated and refined as riding atoms.[13]

(3a*R,7a*S**)-Pentacarbonyl[thioacetic acid (3-ethoxy-4,5,6,7-tetrahydro-3a*H*-inden-1-yl) ester-*S*]tungsten (8b) and (3a*R**,7a*S**)-Pentacarbonyl(3-ethoxy-3a,4,5,6,7,7a-hexahydroindene-3-thione-*S*)tungsten (9b).** Pentacarbonyl[3-(cyclohex-1-enyl)-1-ethoxy-2-propyn-1-ylidene]tungsten (**1b**; 243 mg, 0.50 mmol) was reacted with thiobenzoic acid (**6b**; 138 mg, 1.00 mmol) in diethyl ether/*n*-pentane (1:1) as described above for 6 h at 20 °C. Chromatography on silica

gel (column 20 × 2 cm) afforded a red fraction of compound **9b** (179 mg, 69%, $R_f = 0.6$ in *n*-pentane/diethyl ether 10:1, mp 95 °C). Reaction of compound **1b** with thioacetic acid (**6a**) in a molar ratio of 1:2 gave compound **9b** in 71% yield, while the reaction in a 1:1 molar ratio afforded only a 39% yield. The NMR spectrum in [D_6]benzene of a solution of compound **1b** and thioacetic acid (**6a**) in a molar ratio of 1:2 in the presence of 0.5 equiv of Et_3N after 2 h at 20 °C shows signals of compound **8b** as the major product.

8b. ^{1}H NMR (C_6D_6): δ 4.98 (1 H, s, 2-H), 3.56 (OCH_2), 1.74 (3H, s, CH_3), 2.55−0.86 (9 H, m), 1.06 (3 H, t, OCH_2CH_3). ^{13}C NMR (C_6D_6): δ 202.0 and 198.5 [C_q each, *trans*- and *cis*-CO of $W(CO)_5$], 195.3 (C_q, C═O), 162.1 (C_q, C3), 141.4 (C_q, C1), 96.1 (CH, C2), 64.9 (OCH_2), 49.2 (CH, C3a), 30.1 (CH_3); 28.1, 24.6, and 20.5 (1:1:2, C4−C7), 13.7 (OCH_2CH_3).

9b.



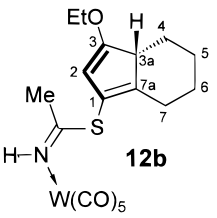
9b

^{1}H NMR (C_6D_6): δ 6.35 (1 H, s, 2-H), 3.52 (OCH_2), 2.47 and 2.51 (1 H each, 3a-H and 7a-H), 1.66 and 1.52, 1.36, and 1.20 (1 H each, m each, diastereotopic 4-H_2 and 7-H_2), 1.1−1.01 (4 H, m, 5-H_2 and 6-H_2), 0.89 (3 H, t, OCH_2CH_3). ^{13}C NMR (C_6D_6): δ 236.8 (C_q, C═S), 202.0 and 198.5 [C_q each, *trans*- and *cis*-CO of $W(CO)_5$], 195.8 (C_q, C3), 119.2 (CH, C2), 69.5 (OCH_2), 52.4 and 46.6 (CH each, C3a and C7a), 28.1 and 24.6 (CH_2 each, C4 and C7), 20.5 (2 CH_2, C5 and C6), 13.7 (OCH_2CH_3). IR (diethyl ether; cm^{-1} (%)): 2067.3 (5), 1941.1 (100), 1912.5 (30) [ν(C≡O)]. MS (70 eV; *m/e* ^{184}W (%)): 520 (33) [M^+], 464 (68) [$M^+ - 2$ CO], 436 (48) [$M^+ - 3$ CO], 408 (42) [$M^+ - 4$ CO], 380 (27) [$M^+ - 5$ CO].

(b) Reactions of Thioacylimino Acids 10 with (1-Alkynyl)carbene Complexes 1. Pentacarbonyl(3-ethoxy-4,5,6,6a-tetrahydro-3a*H*-pentalene-1-thione-*S*)tungsten (9a). A solution of pentacarbonyl[3-(cyclopent-1-enyl)-1-ethoxy-2-propyn-1-ylidene]tungsten (**1a**; 236 mg, 0.50 mmol) in 1 mL of *n*-hexane was added dropwise to a solution of thiobenzamide (**10a**; 69 mg, 0.50 mmol) in 1 mL of diethyl ether/*n*-hexane (1:1). A color change from brown to red was observed within 20 min at 20 °C, after which time the starting material was consumed completely according to TLC. Compound **9a** was obtained in 92% yield after chromatography on silica gel (vide supra).

(3a*R)-Pentacarbonyl[thioacetimidic acid (3-ethoxy-4,5,6,7-tetrahydro-3a*H*-inden-1-yl) ester-*N*]tungsten (12b) and Pentacarbonyl(3-ethoxy-3a,4,5,6,7,7a-hexahydroindene-1-thione-*S*)tungsten (9b).** Pentacarbonyl[3-(cyclohex-1-enyl)-1-ethoxy-2-propyn-1-ylidene]tungsten (**1b**; 243 mg, 0.50 mmol) was reacted with thioacetamide (**10**; 38 mg, 0.50 mmol) as described above to give compound **12b** (255 mg, 91%, $R_f =$ 0.5 in *n*-pentane/diethyl ether 10:1, mp 108 °C). Compound **12b** can be purified by fast chromatography on silica gel, but partial decomposition must be allowed in this case. Compound **12b** undergoes a smooth fragmentation into compound **9b** (vide supra) in 92% yield and acetonitrile (**13a**) (identified by MS and ^{13}C NMR) in dichloromethane at 50 °C, 5 h.

12b.



12b

^{1}H NMR (C_6D_6): δ 7.69 (1 H, s, NH), 4.65 (1 H, s, 2-H), 3.45 (2 H, m, OCH_2), 2.45 (1 H, dd, 3a-H), 2.22 and 0.77 (1 H each, m each, diastereotopic 7-H_2); 2.62 and 1.67, 1.58 and 0.81, 1.40, and 0.95 (1 H each, m each, diastereotopic 4-H_2−6-H_2), 1.39 (3 H, s, CH_3), 1.08 (3 H, t, OCH_2CH_3). ^{13}C NMR (C_6D_6): δ 202.6 and 198.6 [C_q each, *trans*- and *cis*-CO of $W(CO)_5$], 190.7 (C_q, C═N), 168.5 (C_q, C3), 147.8 (C_q, C1), 120.2 (C_q, C7a), 100.5 (CH, C2), 65.6 (OCH_2), 51.6 (CH, C3a), 28.7 (CH_3), 31.1 (CH_2, C7), 28.0 (CH_2, C4), 26.4 and 24.8 (CH_2 each, C5 and C6), 14.3 (OCH_2CH_3). IR (diethyl ether; cm^{-1} (%)): 2067.4 (5), 1931.1 (100), 1902.6 (30) [ν(C≡O)]. MS (70 eV; *m/e* ^{184}W (%)): 561 (8) [M^+], 520 (18) [$M^+ - CH_3CN$], 477 (11) [$M^+ - 3$ CO], 421 (10) [$M^+ - 5$ CO]. Anal. Calcd for $C_{18}H_{19}O_6NSW$ (561.3): C, 38.50; H, 3.38; N, 2.49. Found: C, 38.31; H, 3.37; N 2.09. X-ray crystal structure analysis of compound **12b** (code 1196.AUM): formula $C_{18}H_{19}NO_6SW$, $M = 561.25$, yellow-orange crystal 0.15 × 0.10 × 0.05 mm, $a = 7.355(1)$ Å, $b = 27.384(1)$ Å, $c = 10.663(1)$ Å, $\beta = 108.46(1)°$, $V = 2037.1(3)$ Å^3, $\rho_{calcd} = 1.830$ g cm^{-3}, $\mu =$ 58.05 cm^{-1}, empirical absorption correction via SORTAV (0.476 ≤ T ≤ 0.760), $Z = 4$, monoclinic, space group $P2_1/n$ (No. 14), λ = 0.710 73 Å, T = 198 K, ω and φ scans, 8286 reflections collected ($\pm h$, $\pm k$, $\pm l$), (sin θ)/$\lambda = 0.65$ Å^{-1}, 4672 independent ($R_{int} = 0.022$) and 4126 observed reflections ($I \geq 2\sigma(I)$), 250 refined parameters, R1 = 0.024, wR2 = 0.053, maximum residual electron density 0.78 (−1.65) e Å^{-3} close to tungsten, hydrogens calculated and refined as riding atoms.[13]

Pentacarbonyl[thiobenzimidic acid (3-ethoxy-4,5,6,7-tetrahydro-3a*H*-inden-1-yl) ester-*N*]tungsten (12c) and Pentacarbonyl(3-ethoxy-3a,4,5,6,7,7a-hexahydroindene-1-thione-*S*)tungsten (9b). A mixture of pentacarbonyl[3-(cyclohex-1-enyl)-1-ethoxy-2-propyn-1-ylidene]tungsten (**1b**; 243 mg, 0.50 mmol) and thiobenzamide (**10b**; 69 mg, 0.50 mmol) in a 2 mL screw-top vessel in 2 mL of diethyl ether was stirred for 20 min to give a yellow solution. The solvent was replaced by *n*-pentane, from which compound **12c** was obtained at −15 °C (293 mg, 94%, $R_f = 0.5$ in *n*-pentane/diethyl ether 10:1, yellow crystals, mp 114 °C). Compound **12c** undergoes a smooth fragmentation into compound **9b** (vide supra) in 94% yield and benzonitrile (**13b**) (identified by MS and ^{13}C NMR) in dichloromethane at 50 °C (5 h).

12c. ^{1}H NMR (C_6D_6): δ 8.29 (1 H, s, NH); 6.87, 6.76, and 6.60 (1:2:2 H, Ph), 4.44 (1 H, s, 2-H), 3.28 (2 H, m, OCH_2, 2.20 (1 H, dd, 3a-H), 2.01 and 0.70 (1 H each, m each, diastereotopic 7-H_2); 2.57 and 1.63, 1.54 and 0.83, 1.34 and 0.90 (1 H each, m each, diastereotopic 4-H_2−6-H_2), 0.93 (3 H, t, OCH_2CH_3). ^{13}C NMR (C_6D_6): δ 202.8 and 198.6 [C_q each, *trans*- and *cis*-CO of $W(CO)_5$], 191.8 (C_q, C═N), 167.6 (C_q, C3), 145.5 (C_q, C1), 137.5 (C_q, *i*-C Ph); 130.6, 128.1, and 127.2 (1:2:2, Ph), 120.1 (C_q, C7a), 100.5 (CH, C2), 65.3 (OCH_2), 51.3 (CH, C3a), 30.5 (CH_2, C7), 28.0 (CH_2, C4), 26.4 and 24.7 (CH_2 each, C5 and C6), 14.2 (OCH_2CH_3). IR (diethyl ether; cm^{-1} (%)): 2067.0 (5), 1931.5 (100), 1902.0 (30) [ν(C≡O)]. MS (70 eV; *m/e* ^{184}W (%)): 623 (1) [M^+], 511 (6) [$M^+ - 4$ CO]. Anal. Calcd for $C_{23}H_{21}NO_6SW$ (623.3): C, 44.28; H, 3.37; N 2.25. Found: C, 44.19; H, 3.49; N, 2.04.

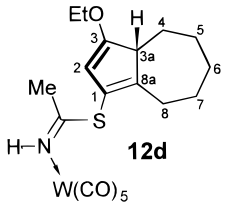
13b. ^{1}H NMR (C_6D_6): δ 7.02, 6.90, and 6.73 (2:1:2 H, Ph). ^{13}C NMR (C_6D_6): δ 132.2, 131.9, and 128.9 (CH each, 1:2:2, Ph), 118.7 (C_q, CN).

(3a*R)-Pentacarbonyl[thioacetimidic acid (3-ethoxy-4,5,6,7,8-pentahydro-3a*H*-azulen-1-yl) ester-*N*]tungsten (12d) and (3a*R**,8a*S**)-Pentacarbonyl(3-ethoxy-4,5,6,7,8,-**

(13) Data sets were collected with Nonius MACH3 and KappaCCD diffractometers, equipped with a Nonius FR591 rotating anode generator. Programs used: data collection EXPRESS (Nonius BV, 1994) and COLLECT (Nonius BV, 1998), data reduction MolEN (K. Fair, Enraf-Nonius BV, 1990) and Denzo-SMN (Otwinowski, Z.; Minor, W. *Methods Enzymol.* **1997**, *276*, 307−326), absorption correction for CCD data SORTAV (Blessing, R. H. *Acta Crystallogr.* **1995**, *A51*, 33−37. Blessing, R. H. *J. Appl. Crystallogr.* **1997**, *30*, 421−426), structure solution SHELXS-97 (Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467−473), structure refinement SHELXL-97 (Sheldrick, G. M. Universität Göttingen, 1997), graphics DIAMOND (Brandenburg, K. Universität Bonn, 1997).

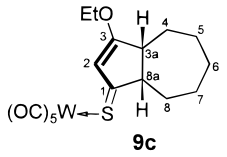
8a-hexahydro-3a*H*-azulene-1-thione-*S*)tungsten (9c). Pentacarbonyl[3-(cyclohept-1-enyl)-1-ethoxy-2-propyn-1-ylidene]-tungsten (**1c**; 250 mg, 0.50 mmol) was reacted with thioacetamide (**10a**; 38 mg, 0.50 mmol) as described above to give compound **12d** (273 mg, 95%, $R_f = 0.4$ in *n*-pentane/dichloromethane 3:1, mp 63 °C). Thermolysis of compound **12d** in dichloromethane to 50 °C (5 h) gave thione complex **9c** (90%, red crystals from diethyl ether/*n*-pentane, mp 82 °C, $R_f = 0.7$ in *n*-pentane/dichloromethane 3:1) and acetonitrile (**13b**) (identified by its ^{13}C NMR and MS).

12d.



^{1}H NMR (C_6D_6): δ 7.85 (1 H, s, NH), 4.64 (1 H, s, 2-H), 3.45 (2 H, m, OCH_2), 2.74 (1 H, dd, 3a-H), 1.51 and 0.99 (1 H each, m each, diastereotopic 8-H_2); 2.24 and 2.08, 1.02 and 1.53, 1.21 and 1.38, 1.39 and 1.38 (1 H each, m each, diastereotopic 4-H_2–7-H_2), 1.44 (3 H, s, CH_3), 1.09 (3 H, t, OCH_2CH_3). ^{13}C NMR (C_6D_6): δ 202.6 and 198.5 [C_q each, *trans*- and *cis*-CO of $W(CO)_5$], 190.4 (C_q, C=N), 166.8 (C_q, C3), 150.9 (C_q, C1), 122.8 (C_q, C8a), 100.3 (CH, C2), 65.6 (OCH_2), 54.9 (CH, C3a), 30.8 (CH_2, C8); 29.9, 29.4, 29.3, and 27.2 (CH_2 each, C4–C7), 27.9 (CH_3), 14.4 (OCH_2CH_3). IR (diethyl ether; cm^{-1} (%)): 2067.6 (5), 1931.9 (100), 1902.3 (30) [ν(C≡O)]. MS (70 eV; *m/e* ^{184}W (%)): 575 (4) [M^+], 491 (6) [$M^+ - 3$ CO], 435 (6) [$M^+ - 5$ CO]. Anal. Calcd for $C_{19}H_{21}NO_6SW$ (575.3): C, 39.65; H, 3.65; N, 2.43. Found: C, 39.45; H, 3.71; N, 2.25.

9c.

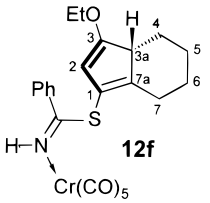


^{1}H NMR (C_6D_6): δ 6.49 (1 H, s, 2-H), 3.50 (OCH_2), 2.50 and 2.35 (1 H each, m each, 3a-H and 8a-H); 1.53 and 1.39, 1.40 and 1.26 (1 H, m each, diastereotopic 4-H_2 and 8-H_2); 1.27 and 1.04, 1.24 and 1.02, 1.12 and 0.99 (1 H, m each, diastereotopic 5-H_2–7-H_2), 0.83 (3 H, t, OCH_2CH_3). ^{13}C NMR (C_6D_6): δ 236.2 (C_q, C=S), 202.0 and 198.5 [C_q each, *trans*- and *cis*-CO of $W(CO)_5$], 194.9 (C_q, C3), 120.6 (CH, C2), 69.3 (OCH_2), 57.5 and 52.2 (CH each, C3a and C8a), 31.8 and 30.9 (CH_2 each, C4 and C8); 28.1, 27.8, and 27.4 (CH_2 each, C5–C7), 13.7 (OCH_2CH_3). IR (diethyl ether; cm^{-1} (%)): 2067.1 (5), 1941.3 (100), 1912.6 (30) [ν(C≡O)]. MS (70 eV; *m/e* ^{184}W (%)): 534 (31) [M^+], 478 (56) [$M^+ - 2$ CO], 394 (19) [$M^+ - 5$ CO]. Anal. Calcd for $C_{17}H_{18}O_6SW$ (534.4): C, 38.17; H, 3.37. Found: C, 38.13; H, 3.38.

(3a*R,8a*S**)-Pentacarbonyl(3-ethoxy-4,5,6,6a-tetrahydro-3a*H*-pentalene-1-thione-*S*)chromium (9d).** Pentacarbonyl[3-(cyclopent-1-enyl)-1-ethoxy-2-propyn-1-ylidene]chromium (**1d**; 170 mg, 0.50 mmol) was reacted with thiobenzamide (**10b**; 69 mg, 0.50 mmol) as described above in diethyl ether at 20 °C (20 min). Chromatography with *n*-pentane/dichloromethane (3:1) gave compound **9d** (163 mg, 87%, $R_f = 0.6$ in *n*-pentane/diethyl ether 10:1, mp 70 °C, red crystals from diethyl ether/*n*-pentane). ^{1}H NMR (C_6D_6): δ 6.30 (1 H, s, 2-H), 3.43 (3-OCH_2), 2.88 and 2.58 (1 H each, m each, 3a-H and 6a-H); 1.71 and 1.41, 1.44, and 1.11 (1 H each, m each, diastereotopic 4-H_2 and 6-H_2), 1.16 and 0.94 (1 H each, m each, diastereotopic 5-H_2), 0.84 (3 H, t, OCH_2CH_3). ^{13}C NMR (C_6D_6): δ 239.7 (C_q, C=S), 223.8 and 216.8 [C_q each, *trans*- and *cis*-CO of $Cr(CO)_5$], 194.9 (C_q, C3), 119.3 (CH, C2), 69.6 (OCH_2), 58.9 and 52.0 (CH each, C3a and C6a), 33.3 and 28.3 (CH_2 each, C4 and C6), 24.1 (CH_2, C5), 14.0 (OCH_2CH_3). IR (diethyl ether; cm^{-1} (%)): 2061.2 (5), 1939.6 (100), 1916.1 (30) [ν(C≡O)]. MS (70 eV; *m/e* (%)): 374 (9) [M^+], 262 (13) [$M^+ - 4$ CO], 234 (100) [$M^+ - 5$ CO]. Anal. Calcd for $C_{15}H_{14}O_6SCr$ (374.3): C, 48.13; H, 3.74. Found: C, 47.51; H, 3.86.

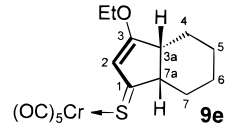
(3a*R)-Pentacarbonyl[thiobenzimidic acid (3-ethoxy-4,5,6,7-tetrahydro-3a*H*-inden-1-yl) ester-*N*]chromium (12f) and (3a*R**,7a*S**)-Pentacarbonyl(3-ethoxy-3a,4,5,6,7,7a-hexahydroindene-1-thione-*S*)chromium (9e).** Pentacarbonyl[3-(cyclohex-1-enyl)-1-ethoxy-2-propyn-1-ylidene]chromium (**1e**; 178 mg, 0.50 mmol) was reacted with thiobenzamide (**10b**; 69 mg, 0.50 mmol) as decribed above to give compound **12f** (201 mg, 82%, $R_f = 0.5$ in *n*-pentane/diethyl ether 10:1, yellow crystals, mp 118 °C). Thermolysis of compound **12f** (98 mg, 0.20 mmol) in dichloromethane at 50 °C, 5 h and subsequent chromatograpgy on silica gel with *n*-pentane/diethyl ether (10:1) gave compound **9e** (73 mg, 95%, $R_f = 0.7$ in *n*-pentane/diethyl ether 10:1, red crystals, mp 107 °C).

12f.



^{1}H NMR (C_6D_6): δ 8.62 (1 H, s, NH), 7.11–6.36 (5 H, Ph), 4.88 (1 H, s, 2-H), 3.55 (2 H, broad, OCH_2), 2.21 and 0.78 (1 H each, m each, diastereotopic 7-H_2), 2.60 and 1.67, 1.58 and 0.81, 1.41 and 0.97 (1 H each, m each, diastereotopic 4-H_2–6-H_2), 1.10 (3 H, broad, OCH_2CH_3). ^{13}C NMR (C_6D_6): δ 221.3 and 214.8 [C_q each, *trans*- and *cis*-CO of $Cr(CO)_5$], 195.5 (C_q, C=N), 170.4 (C_q, C3), 152.2 (C_q, C1), 138.0 (C_q, *i*-C Ph), 131.5, 129.1, and 127.7 (CH each, 1:2:2, Ph), 117.1 (C_q, C7a), 98.3 (CH, C2), 66.0 (OCH_2), 52.3 (CH, C3a), 30.3 (CH_2, C7); 29.5, 26.7, and 24.7 (CH_2 each, C4–C6), 14.3 (OCH_2CH_3). IR (diethyl ether; cm^{-1} (%)): 2060.5 (5), 1929.6 (100), 1906.2 (30) [ν(C≡O)]. MS (70 eV; *m/e* (%)): 491 (9) [M^+], 388 (14) [M^+ – PhCN], 379 (24) [$M^+ - 4$ CO], 351 (18) [$M^+ - 5$ CO]. Anal. Calcd for $C_{23}H_{21}NO_6SCr$ (491.5): C, 56.16; H, 4.27; N, 2.85. Found: C, 56.06; H, 4.22; N, 3.11.

9e.



^{1}H NMR (C_6D_6): δ 6.38 (1 H, s, 2-H), 3.44 (OCH_2), 2.45 and 2.25 (1 H each, m each, 3a-H and 7a-H), 1.66 and 1.56, 1.35 and 1.27 (1 H each, m each, diastereotopic 4-H_2 and 7-H_2); 1.08 (4 H, m, 5-H_2 and 6-H_2), 0.81 (3 H, t, OCH_2CH_3). ^{13}C NMR (C_6D_6): δ 239.1 (C_q, C=S), 223.9 and 217.2 [C_q each, *trans*- and *cis*-CO of $Cr(CO)_5$], 195.8 (C_q, C3), 117.0 (CH, C2), 69.4 (OCH_2), 53.8 and 46.4 (CH each, C3a and C7a), 28.5 and 25.0 (CH_2 each, C4 and C7), 20.8 and 20.9 (CH_2 each, C5 and C6), 14.0 (OCH_2CH_3). IR (diethyl ether; cm^{-1} (%)): 2061.8 (5), 1939.6 (100), 1916.2 (30) [ν(C≡O)]. MS (70 eV; *m/e* (%)): 388 (7) [M^+], 276 (13) [$M^+ - 4$ CO], 248 (80) [$M^+ - 5$ CO]. Anal. Calcd for $C_{16}H_{16}O_6SCr$ (388.4): C, 49.44; H, 4.12. Found: C, 49.12; H, 3.93.

Pentacarbonyl[thioacetimidic acid (3-ethoxy-4,5,6,7,8-pentahydro-3a*H*-azulen-1-yl) ester-*N*]chromium (12g) and Pentacarbonyl(3-ethoxy-4,5,6,7,8,8a-hexahydro-3a*H*-azulene-1-thione-*S*)chromium (9f). Pentacarbonyl[3-(cyclohept-1-enyl)-1-ethoxy-2-propyn-1-ylidene]chromium (**1f**; 184 mg, 0.50 mmol) was reacted with thioacetamide (**10a**; 38 mg, 0.50 mmol) to give compound **12g** (199 mg, 90%, $R_f = 0.4$ in

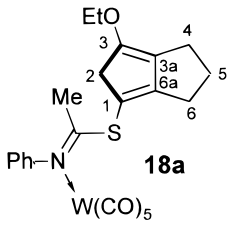
n-pentane/diethyl ether 1:10, yellow crystals, mp 69 °C). Thermolysis of compound **12g** (98 mg, 0.20 mmol) in dichloromethane at 50 °C (5 h) and subsequent chromatography on silica gel with *n*-pentane/diethyl ether 10:1 affords compound **9f** (76 mg, 95%, R_f = 0.7 in *n*-pentane/diethyl ether 10:1, red crystals, mp 85 °C).

12g. ^{1}H NMR (C_6D_6): δ 7.37 (1 H, s, NH), 4.66 (1 H, s, 2-H), 3.47 (2 H, m, OCH_2), 2.75 (1 H, dd, 3a-H), 1.53 and 0.90 (1 H each, m each, diastereotopic 8-H_2); 2.29 and 2.07, 1.53 and 1.02, 1.36 and 1.20, 1.34 and 1.32 (1 H each, m each, diastereotopic 4-H_2−7-H_2), 1.45 (3 H, s, CH_3), 1.10 (3 H, t, OCH_2CH_3). ^{13}C NMR (C_6D_6): δ 221.4 and 215.4 [C_q each, *trans*- and *cis*-CO of $Cr(CO)_5$], 190.7 (C_q, C═N), 166.7 (C_q, C3), 150.6 (C_q, C1), 122.8 (C_q, C8a), 100.4 (CH, C2), 65.5 (OCH_2), 54.8 (CH, C3a), 30.8 (CH_2, C8); 29.9, 29.4, 29.3, and 27.2 (CH_2 each, C4−C7), 28.7 ($SCCH_3$), 14.4 (OCH_2CH_3). IR (diethyl ether; cm^{-1} (%)): 2062.5 (5), 1930.6 (100), 1906.8 (30) [ν(C≡O)]. MS (70 eV; *m*/*e* (%)): 443 (4) [M^+], 359 (5) [$M^+ - 3$ CO], 303 (8) [$M^+ - 5$ CO]. Anal. Calcd for $C_{19}H_{21}NO_6SCr$ (443.4): C, 51.46; H, 4.77; N, 3.16. Found: C, 51.51; H, 5.01; N, 2.93.

9f. ^{1}H NMR (C_6D_6): δ 6.49 (1 H, s, 2-H), 3.53 (OCH_2), 2.54 and 2.41 (1 H each, m each, 3a-H and 8a-H); 1.55 and 1.38, 1.40 and 1.25 (1 H, m each, diastereotopic 4-H_2 and 8-H_2); 1.27 and 1.04, 1.23 and 1.02, 1.12 and 0.98 (1 H each, m each, diastereotopic 5-H_2−7-H_2), 0.88 (3 H, t, OCH_2CH_3). ^{13}C NMR (C_6D_6): δ 238.4 (C_q, C═S), 223.6 and 216.9 [C_q each, *trans*- and *cis*-CO of $Cr(CO)_5$], 195.2 (C_q, C3), 118.0 (CH, C2), 69.1 (OCH_2), 58.6 and 51.8 (CH each, C3a and C8a), 32.0 and 30.9 (CH_2 each, C4 and C8); 28.2, 27.8, and 27.4 (CH_2 each, C5−C7), 13.7 (OCH_2CH_3). IR (diethyl ether; cm^{-1} (%)): 2061.3 (5), 1939.7 (100), 1616.0 (30) [ν(C≡O)]. MS (70 eV; *m*/*e* (%)): 402 (25) [M^+], 346 (56) [$M^+ - 2$ CO], 262 (19) [$M^+ - 5$ CO]. Anal. Calcd for $C_{17}H_{18}O_6SCr$ (402.4): C, 50.70; H, 4.47. Found: C, 50.54; H, 4.57.

Pentacarbonyl[*N*-phenyl-thioacetimidic acid (3-ethoxy-2,4,5,6-tetrahydropentalen-1-yl) ester-*N*]tungsten (18a). Pentacarbonyl[3-(cyclopent-1-enyl)-1-ethoxy-2-propyn-1-ylidene]-tungsten (**1a**; 236 mg, 0.50 mmol) was reacted with (*N*-phenyl)-thioacetamide (**16**; 76 mg, 0.50 mmol) in 2 mL of dichloromethane in the presence of 1 equiv of triethylamine with stirring at 20 °C (20 min). Fast chromatography on silica gel afforded yellow compound **18a** (277 mg, 89%, R_f = 0. 4 in *n*-pentane/diethyl ether 10:1, mp 92 °C).

18a.

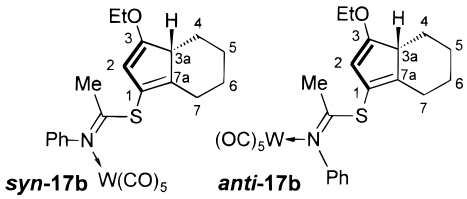


18a

^{1}H NMR (400 MHz, C_6D_6): δ 6.99, 6.79, and 6.42 (2:1:2, *m*-, *p*-, *o*-H Ph), 3.65 (2 H, m, OCH_2), 3.13 (2 H, s, 2-H_2), 2.17 and 1.80 (4:2, m each, 4-H_2−6-H_2), 1.50 (s, 3 H, CH_3), 1.04 (3 H, t, OCH_2CH_3). ^{13}C NMR (400 MHz, C_6D_6): δ 203.9 and 199.6 [C_q each, *trans*- and *cis*-CO of $W(CO)_5$], 189.9 (C_q, C═N), 170.2 (C_q, C3), 158.2 (C_q, C1), 155.5 (C_q, *i*-C Ph), 129.9, 126.1, and 121.1 (2:1:2, *m*-, *p*-, *o*-C Ph), 124.1 and 102.5 (C_q each, C3a and C6a), 65.9 (OCH_2), 49.9 (CH_2, C2); 30.1, 26.2, and 25.9 (CH_2 each, C4−C7), 21.6 ($NCCH_3$), 15.1 (OCH_2CH_3). IR (diethyl ether; cm^{-1} (%)): 2067.1 (5), 1932.0 (100), 1901.2 (30) [ν(C≡O)]. MS (70 eV; *m*/*e* ^{184}W (%)): 539 (0.3) [$M^+ - 3$ CO], 483 (0.4) [$M^+ - 5$ CO], 299 (5) [$M^+ - W(CO)_5$], 118 (100). Anal. Calcd for $C_{23}H_{21}NO_6SW$ (623.3): C, 44.32; H, 3.40; N, 2.25. Found: C, 44.32; H, 3.59; N, 1.70.

Pentacarbonyl[*N*-phenylthioacetimidic acid (3-ethoxy-4,5,6,7-tetrahydro-3a*H*-inden-1-yl) ester-*N*]tungsten (*syn*-17b and *anti*-17b) and Pentacarbonyl[*N*-phenylthioacetimidic acid (3-ethoxy-4,5,6,7-tetrahydro-3a*H*-inden-1-yl) ester-*N*]tungsten (18b). Pentacarbonyl[3-(cyclohex-1-enyl)-1-ethoxy-2-propyn-1-ylidene]tungsten (**1b**; 243 mg, 0.50 mmol) was reacted with (*N*-phenyl)thioacetamide (**16**; 76 mg, 0.50 mmol) in diethyl ether at 20 °C (25 min). A yellow precipitate was produced, collected by centrifugation, washed two times with *n*-pentane, and dried in vacuo (15 Torr, 20 °C) to give almost clean compound *syn*-**17b** (305 mg, 96%, R_f = 0.3 in *n*-pentane/dichloromethane 3:1, mp 110 °C). Compound *syn*-**17b** was transformed into a 2:1 mixture of *syn*- and *anti*-**17b** in benzene at 50 °C after 3 h, which could not be separated by chromatography on silica gel, since they exist in dynamic equilibrium, but were analyzed instead as mixtures by NMR spectra at 600 MHz. Reaction of compounds **1b** and **16** in the presence of 1 equiv of triethylamine at 20 °C (20 min) afforded compound **18b** (264 mg, 83%, R_f = 0.3 in *n*-pentane/diethyl ether 10:1, mp 106 °C).

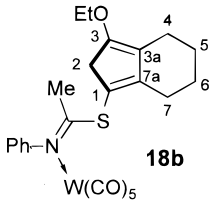
syn-**17b** (*anti*-**17b**).



***syn*-17b** ***anti*-17b**

^{1}H NMR (600 MHz, C_6D_6): δ 6.99, 6.80, and 6.46 (7.11, 6.87, and 6.85) (2:1:2 *m*-, *p*-, and *o*-H Ph), 4.85 (4.69) (1 H, s, 2-H), 3.46 (3.46) (2 H, m, OCH_2), 2.47 (2.45) (1 H, dd, 3a-H), 2.84 (2.50) (1 H, m), 2.22 (2.22) (1 H, m), 1.71 (1.77) (1 H, m), 1.66 (2.54) (3 H, s, N═CCH_3), 1.63 (1.66) (1 H, m), 1.41 (1.53) (1 H, m), 0.89 (0.79) (3 H, m), 1.08 (1.07) (3 H, t, OCH_2CH_3). ^{13}C NMR (C_6D_6): δ 203.8 and 199.6 (203.2 and 199.2) [C_q each, *trans*- and *cis*-CO of $W(CO)_5$], 187.5 (185.0) (C_q, C═N), 168.8 (168.7) (C_q, C3), 155.3 (155.2) (C_q, *i*-C Ph), 148.1 (147.5) (C_q, C1); 129.4, 126.3, and 121.0 (129.6, 126.9, and 121.0) (2:1:2 *m*-, *p*-, and *o*-C Ph), 121.4 (121.5) [C_q, C7a], 100.3 (100.2) (CH, C2), 65.6 (65.6) (OCH_2), 51.7 (51.2) (CH, C3a); 31.1, 28.7, 26.6, and 24.8 (31.0, 28.6, 26.3, and 24.7) (CH_2 each, C4−C7), 22.2 (29.7) (N═CCH_3), 14.3 (14.4) (OCH_2CH_3). IR (diethyl ether; cm^{-1} (%)): 2061.3 (5), 1931.7 (100), 1901.8 (30) [ν(C≡O)]. MS (70 eV; *m*/*e* ^{184}W (%)): 637 (14) [M^+], 525 (47) [$M^+ - 4$ CO], 497 (55) [$M^+ - 5$ CO]. Anal. Calcd for $C_{24}H_{23}NO_6SW$ (637.4): C, 45.21; H, 3.61; N, 2.20. Found: C, 45.28; H, 3.68; N, 1.86.

18b.



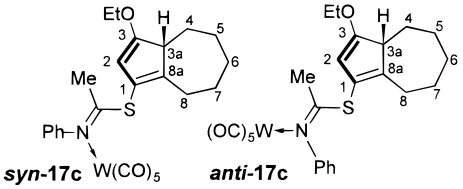
18b

^{1}H NMR (400 MHz, C_6D_6): δ 6.99, 6.79, and 6.47 (2:1:2, *m*-, *p*-, *o*-H Ph), 3.38 (2 H, m, 3-OCH_2), 2.60 (2 H, s, 2-CH_2), 2.27 and 1.31 (4:2, m each, 4-H−7-H), 1.42 (s, 3 H, CH_3), 1.02 (3 H, t, 3-OCH_2CH_3). ^{13}C NMR (C_6D_6): δ 203.9 and 199.7 [C_q each, *trans*- and *cis*-CO of $W(CO)_5$], 189.4 (C_q, C═N), 162.0 (C_q, C3), 158.9 (C_q, C1), 155.5 (C_q, *i*-C Ph); 129.4, 126.2, and 121.1 (2:1:2, *m*-, *p*-, *o*-C Ph), 116.4 and 107.0 (C_q each, C3a and C7a), 65.8 (OCH_2), 42.0 (CH_2, C2), 25.8 and 22.9 (2:2, C4−C7), 21.7 (N═CCH_3), 15.2 (OCH_2CH_3). IR (diethyl ether; cm^{-1} (%)): 2066.9 (5), 1932.2 (100), 1902.0 (30) [ν(C≡O)]. MS (70 eV; *m*/*e* ^{184}W (%): 553 (1) [$M^+ - 3$ CO], 497 (3) [$M^+ - 5$ CO], 313 (5) [$M^+ - W(CO)_5$], 118 (100). Anal. Calcd for $C_{24}H_{23}NO_6SW$ (637.4): C, 45.23; H, 3.64; N, 2.20. Found: C, 44.46; H, 3.43; N, 1.96.

Pentacarbonyl[*N*-phenylthioacetimidic acid (3-ethoxy-4,5,6,7,8-pentahydro-3a*H*-azulen-1-yl) ester-*N*]tungsten (*syn*-17c and *anti*-17c) and Pentacarbonyl[*N*-phenylthio-

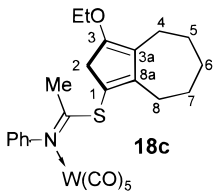
acetimidic acid (3-ethoxy-4,5,6,7,8-pentahydro-3a*H*-azulen-1-yl) ester-*N*]tungsten (18c). Pentacarbonyl[3-(cyclohept-1-enyl)-1-ethoxy-2-propyn-1-ylidene]tungsten (**1c**; 250 mg, 0.50 mmol) and (*N*-phenyl)thioacetamide (**16**; 76 mg, 0.50 mmol) was reacted as described above in diethyl ether at 20 °C (25 min) to give compound *syn*-**17c** (305 mg, 94%, R_f = 0.5 in *n*-pentane/dichloromethane 3:1, yellow crystals, mp 108 °C). Compound *syn*-**17c** was heated in benzene at 50 °C (3 h) to give a 4:5-mixture of *syn*- and *anti*-**17c**. The reaction of compounds **1c** and **16** in diethyl ether in the presence of 1 equiv of triethylamine at 20 °C (20 min) afforded compound **18c** (280 mg, 86%, R_f = 0.4 in *n*-pentane/diethyl ether 10:1, yellow crystals, mp 102 °C).

syn-**17c** (*anti*-**17c**).



^{1}H NMR (600 MHz, C_6D_6): δ 7.01, 6.81, and 6.50 (7.12, 6.88, and 6.83) (2:1:2 *m*-, *p*-, and *o*-H Ph), 4.82 (4.68) (1 H, s, 2-H), 3.45 (3.46) (2 H, m, OCH_2), 2.78 (2.44) (1 H, dd, 3a-H), 2.45 (2.38) (2 H, m), 2.08 (2.28) (1 H, m), 1.65 (2.54) (3 H, s, $SCCH_3$), 1.51 (1.51) (3 H, m), 1.27 (1.27) (2 H, m), 1.07 (1.07) (2 H, m), 1.07 (1.07) (3 H, t, OCH_2CH_3). ^{13}C NMR (C_6D_6): δ 203.8 and 199.6 (203.0 and 199.3) [C_q each, *trans*- and *cis*-CO of $W(CO)_5$], 187.2 (184.6) (C_q, C=N), 167.1 (16.47) (C_q, C3), 155.4 (155.3) (C_q, *i*-C Ph), 151.1 (149.6) (C_q, C1); 129.4, 126.3, and 121.0 (129.3, 127.0, and 121.4) (2:1:2 *m*-, *p*-, and *o*-C Ph), 124.3 (123.7) [C_q, C8a], 100.2 (101.9) (CH, C2), 65.6 (65.6) (OCH_2), 55.0 (54.9) (CH, C3a); 30.9, 29.8, 29.7, 29.2, and 27.3 (30.7, 29.4, 29.3, 28.5, and 27.1) (CH_2 each, C4−C7), 22.1 (21.5) (CH_3), 14.3 (15.1) (OCH_2CH_3). IR (diethyl ether; cm^{-1} (%)): 2068.3 (5), 1931.1 (100), 1901.8 (30) [ν(C≡O)]. MS (70 eV; *m*/*e* ^{184}W (%)): 651 (0.25) [M^+], 567 (2) [$M^+ - 3$ CO], 511 (5) [$M^+ - 5$ CO]. Anal. Calcd for $C_{25}H_{25}NO_6SW$ (651.4): C, 46.08; H, 3.84; N, 2.15. Found: C, 45.98; H, 3.89; N, 2.02.

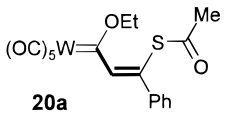
18c.



^{1}H NMR (C_6D_6): δ 7.01, 6.81, and 6.48 (2:1:2, *m*-, *p*-, *o*-H Ph), 3.37 (2 H, m, OCH_2), 2.66 (2 H, s, 2-H_2); 2.47, 2.33, and 1.42 (2:2:6, m each, 4-H−8-H), 1,47 (s, 3 H, CH_3), 1.03 (3 H, t, OCH_2CH_3). ^{13}C NMR (C_6D_6): δ 203.9 and 199.7 [C_q each, *trans*- and *cis*-CO of $W(CO)_5$], 189.4 (C_q, C=N), 163.9 (C_q, C3), 161.3 (C_q, C1), 155.6 (C_q, C-*i* Ph), 129.5, 126.2, and 121.1 (2:1:2, *m*-, *p*-, *o*-C Ph), 122.8 and 108.4 (C_q each, C3a and C8a), 65.8 (OCH_2), 42.1 (CH_2, C2), 32.6, 30.1, 29.8, 28.6, and 24.9 (CH_2 each, C4−C7), 21.5 (N=CCH_3), 15.2 (OCH_2CH_3). IR (diethyl ether; cm^{-1} (%)): 2067.0 (5), 1932.0 (100), 1902.5 (30) [ν(C≡O)]. MS (70 eV; *m*/*e* ^{184}W (%)): 567 (2) [$M^+ - 3$ CO], 511 (10) [$M^+ - 5$ CO]. X-ray crystal structure analysis of compound *syn*-**18c** (code 1224.AUM: formula $C_{25}H_{25}NO_6SW$, M = 651.37, yellow crystal 0.35 × 0.30 × 0.15 mm, a = 8.757(1) Å, b = 10.516(1) Å, c = 14.976(1) Å, α = 74.03(1)°, β = 79.35(1)°, γ = 75.46(1)°, V = 1273.5(2) Å^3, ρ_{calcd} = 1.699 g cm^{-3}, μ = 46.57 cm^{-1}, empirical absorption correction via SORTAV (0.293 ≤ T ≤ 0.542), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 0.710 73 Å, T = 198 K, ω and φ scans, 8586 reflections collected (±h, ±k, ±l), (sin θ)/λ = 0.65 Å^{-1}, 5820 independent (R_{int} = 0.025) and 5511 observed reflections ($I \geq 2\sigma(I)$), 309 refined parameters, R1 = 0.022, wR2 = 0.053, maximum residual electron density 1.34 (−1.07) e Å^{-3}close to tungsten, hydrogens calculated and refined as riding atoms.[13]

Pentacarbonyl[3-(*S*-thioacetyl)-1-ethoxy-3-phenyl-2-propen-1-ylidene]tungsten (20a). Pentacarbonyl(3-phenyl-1-ethoxy-2-propyn-1-ylidene)tungsten (**19**; 241 mg, 0.50 mmol) in 1 mL of *n*-hexane was added dropwise to a solution of thioacetic acid (**6a**; 38 mg, 0.50 mmol) and triethylamine (40 mg, 0.40 mmol) in 1 mL of diethyl ether. The mixture was stirred for 3 h at 20 °C and separated by rapid chromatography on silica gel (column 20 × 2 cm) with *n*-pentane/dichloromethane (5:1) to give a brown fraction containing compound **20a** (198 mg, 71%, R_f = 0.4 in dichloromethane/*n*-pentane 1:3, mp 82 °C).

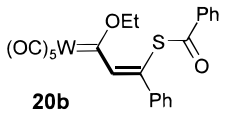
20a.



^{1}H NMR (C_6D_6): δ 7.33 (1 H, s, 2-H); 7.56, 7.10, and 7.05 (2:1:2, Ph), 4.45 (2 H, q, OCH_2), 1.72 (3 H, s, $COCH_3$), 1.14 (3 H, t, OCH_2CH_3). ^{13}C NMR (C_6D_6): δ 312.2 (W=C), 203.6 and 197.3 [C_q each, *trans*- and *cis*-CO of $W(CO)_5$], 196.5 (3-SCO), 149.3 (C_q, C3), 142.8 (C_q, *i*-C Ph), 140.0 (CH, C2), 129.4, 128.8, and 127.9 (2:1:2, CH each, Ph), 79.2 (OCH_2), 29.9 ($COCH_3$), 14.5 (OCH_2CH_3). IR (diethyl ether; cm^{-1} (%)): 2068.0 (10), 1976.3 (5), 1947.0 (100) [ν(C≡O)]. MS (70 eV; *m*/*e* ^{184}W (%)): 558 (2) [M^+], 446 (3) [$M^+ - 4$ CO], 418 (7) [$M^+ - 5$ CO]. Anal. Calcd for $C_{18}H_{14}O_7SW$ (558.2): C, 38.69; H, 2.51. Found C, 38.45; H, 2.47.

Pentacarbonyl[3-(*S*-thiobenzoyl)-1-ethoxy-3-phenyl-2-propen-ylidene]tungsten (20b). Pentacarbonyl(3-phenyl-1-ethoxy-2-propyn-1-ylidene)tungsten (**19**; 241 mg, 0.50 mmol) was reacted with thiobenzoic acid (**6b**; 69 mg, 0.50 mmol) as described above in diethyl ether/*n*-hexane (1:1) for 6 h at 20 °C. Fast chromatography on silica gel (column 20 × 2 cm) with *n*-pentane/dichloromethane (5:1) gave compound **20b** (211 mg, 68%, R_f = 0.3 in dichloromethane/*n*-pentane 1:3, brown solid).

20b.



^{1}H NMR (C_6D_6): δ 7.50 (1 H, s, 2-H); 7.82, 7.00, and 6.92 (2:1:2, m each, 3-thiobenzoyl); 7.56, 7.09, and 7.06 (2:1:2, 3-Ph), 4.45 (2 H, q, OCH_2), 1.06 (3 H, t, OCH_2CH_3). ^{13}C NMR (C_6D_6): δ 310.9 (W=C), 204.2 and 197.3 [C_q each, *trans*- and *cis*-CO of $W(CO)_5$], 195.8 (C=O), 150.3 (C_q, C3), 143.0 and 136.7 (*i*-C each, Ph each), 140.1 (CH, C2), 133.8, 128.9, and 127.8 (1:2:2, CH each, 3-thiobenzoyl), 129.4, 128.8, and 128.0 (2:1:2, CH each, 3-Ph), 78.6 (OCH_2), 13.8 (OCH_2CH_3). IR (diethyl ether; cm^{-1} (%)): 2068.4 (10), 1975.4 (5), 1947.4 (100) [ν(C≡O)]. MS (70 eV; *m*/*e* ^{184}W (%)): 620 (2) [M^+], 536 (3) [$M^+ - 3$ CO], 508 (4) [$M^+ - 4$ CO]. Anal. Calcd for $C_{23}H_{16}O_7SW$ (620.3): C, 44.49; H, 2.58. Found C, 44.35; H, 2.65.

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Supporting Information Available: Details of the X-ray crystal structure analyses. This material is available free of charge via the Internet at http://pubs.acs.org.

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