Bicyclic Cyclopentadienes with N,S Substituents[‡]

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Bicyclic cyclopentadienes **5b**,**c** and **12b**,**c** in which an N,S-chelating group is attached to the cyclopentadiene ring were obtained in good chemical yields by reaction of [1-alkynyl-2-(1-cycloalkenyl)]carbene complexes **1a**–**d** (M = W, Cr) with pyridine-2(1*H*)-thione (**2a**) and *N*-phenylthioacetamide (**2b**), respectively. Tetrahydroindene **5b** was shown to react with [2-(1-cycloalkenyl)ethynyl]carbene complexes **1a**–**c** to give pentacyclic compounds **10a**–**c** by formation of a [4+2] cycloadduct and the subsequent π-cyclization of its 1-tungsta-1,3,5-hexatriene unit.

Introduction

(1-Alkynyl)carbene complexes $(OC)_5M{=}C(OEt)C{\equiv}CR$ (M = W, Cr; R = aryl, alkenyl) have been applied as stoichiometric reagents in a number of high-yielding transformations of potential use in organic synthesis.[1] Prominent examples involve the formation of cyclopentadienes by π-cyclization of 1-metalla-1,3,5-hexatrienes,[2,3] which were derived from (1-alkynyl)carbene complexes, e.g. by addition of enamines[4] or by addition of a variety of different protic nucleophiles NuH [e.g. $RC{=}NR(R'CO)CH_2$,[5] R_2NH,[6,7] R_2PH,[8] RC(=O)OH and ROH,[8,9] RC(=X)SH (X = O, NH, NR)[10] and RSH[11]].[6,12] The latter procedure was shown to be well suited for the generation of highly reactive bicyclic cyclopentadienes, such as tetrahydropentalenes[5,6] or tetrahydroindenes,[7,8] and most notable also for the attachment of *anionic* substituents to the cyclopentadiene ring, which is not achieved by more conventional routes.

We recently reported on the generation of novel chelate ligands in which an enaminone unit is connected to a bicyclic cyclopentadiene.[5] We now find that also N,S-chelating groups can be easily attached to cyclopentadienes to give chelate ligands of potential usefulness.

(Pyridylthio)cyclopentadienes

Reaction of [2-(1-cycloalkenyl)ethynyl]carbene complexes **1b**−**d** with 1 equiv. of pyridine-2(1*H*)-thione (**2a**) at 20 °C gave metal complexes **3b**−**d**. The latter were obtained in yields of 87−93% by crystallization directly from the reaction mixture (Scheme 1). Reaction of (1-alkynyl)carbene complexes **1b**−**d** with 2 equiv. of compound **2a** afforded metal-free compounds **5b**−**d** and [pyridine-2(1*H*)-thione]$M(CO)_5$ (**6a,b**; M = W, Cr) in good yields by ligand disengagement from the metal compounds **3b**−**d**. Ligand disengagement from compounds **3b**−**d** with trimethylamine oxide and subsequent chromatography of the reaction mixture on silica gel did not give compounds **5b**−**d** but α,β-unsaturated cyclopentenones **4** instead, by hydrolysis of the enol ether unit (Scheme 1). It should be noted that the reaction of [2-(1-cyclopentenyl)ethynyl]carbene complex **1a** with compound **2a** led to an untractable mixture of products, due to the thermal instability of the resulting tetrahydropentalene.

If the reaction of [2-(1-cycloalkenyl)ethynyl]carbene complexes **1** with 1 equiv. of pyridine-2(1*H*)-thione (**2a**) was performed in the presence of triethylamine, it afforded compounds **7**, which are isomers of compounds **3**. It should be noted that the tetrahydropentalene derivative **7a** was reasonably stable, whilst the corresponding isomer **3a** could not be isolated (Scheme 2).

[4 + 2] Cycloadducts of Cyclopentadienes 5 to (1-Alkynyl)carbene Complexes 1

On first sight it is surprising that compounds **5** could be generated and isolated in the presence of a (1-alkynyl)carbene complex **1**, since the electron-rich 1,3-diene unit of compounds **5** is expected to react with the dienophilic C≡C bond of a metal complex **1** in a [4+2] cycloaddition.[9,13] We could indeed demonstrate that a [4+2] cycloaddition of this type takes place, even though it is very slow. Thus tetrahydroindene **5b** was shown to react with [2-(1-cycloalk-

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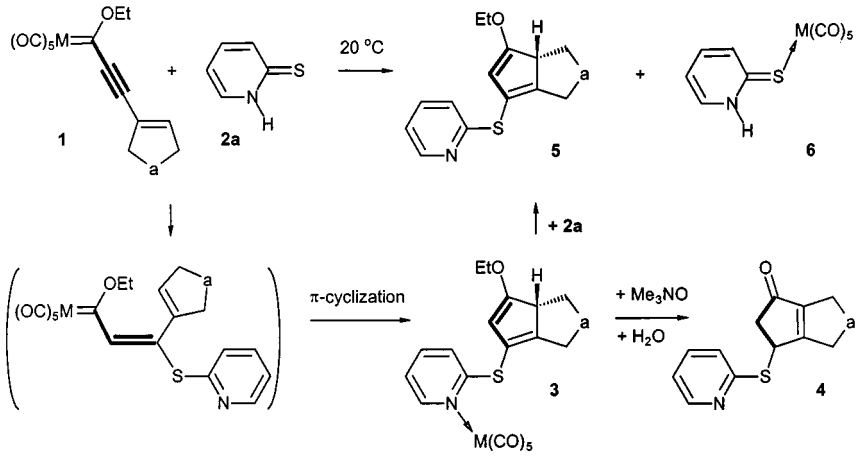
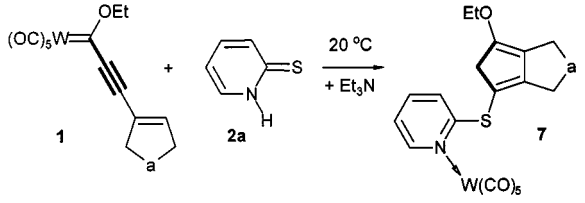


1, 3–5	M	a	Yield of 3 (%)[a]	Yield of 4 (%)[b]	Yield of 5 (%)[b]
a	W	CH_2	[c]	[c]	[c]
b	W	CH_2CH_2	87	76	70
c	W	$CH_2CH_2CH_2$	93	73	71
d	Cr	CH_2CH_2	92	–	76[d]

[a] Chemical yield obtained by crystallisation. [b] Chemical yield obtained by chromatography. [c] No stable product isolated. [d] Compound **5d** is identical with compound **5b**.

Scheme 1. 1-Pyridylthio cyclopentadienes **5** derived from [2-(1-cycloalkenyl)ethynyl)]carbene complexes **1**



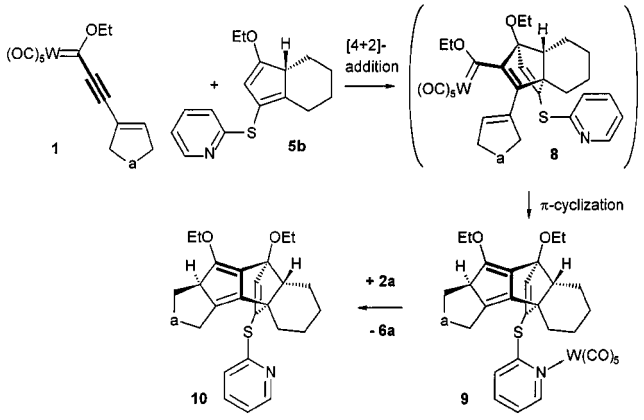
7	a	Yield of 7 (%)[a]
a	CH_2	82
b	CH_2CH_2	87
c	$CH_2CH_2CH_2$	77

[a] Chemical yields obtained by crystallization.

Scheme 2. Formation of isomers **7** of compounds **3** from [2-(1-cycloalkenyl)ethynyl)carbene complexes **1** in the presence of a base

enyl)ethynyl]carbene complexes **1a–c** to give pentacyclic complexes **9a–c** in good yields and with high diastereoselectivity. The reaction involves the formation of a [4+2] cycloadduct **8** and the π-cyclization of its 1-tungsta-1,3,5-hexatriene unit (Scheme 3). The regiochemistry of the [4+2] cycloaddition appears to be orbital-controlled in line with expectation for the interaction of a 1-ethoxy-3-thio-1,3-butadiene unit in compound **5b** with the polarized C≡C bond in compound **1**. Addition to the outer side of the "bowl-shaped" molecule **5b** is controlled by steric factors. Furthermore, based on earlier studies on the π-cyclization[6] of the 1-tungsta-1,3,5-hexatriene unit of compound **8** the hydrogen atom at the newly generated stereocenter must "point to the inside" of the product **9**. The reason, why compound **5b** can be prepared according to the route outlined in Scheme 1 is due to the fact that [4+2] cycloadducts **8** are generated quite slowly (within ca. 20 h at 20 °C) for steric reasons, much slower than tetrahydroindene **5b** is generated from its starting component **1b** (at 20 °C within ca. 10 min; Scheme 1). The pentacyclic complexes **9a–c** could be most conveniently prepared by crystallization directly from the reaction mixture, if proper solvents were applied. The compounds could as well be isolated by column chromatography on silica gel. Disengagement of the metal unit to give compounds **10a–c** was conveniently achieved by interaction with pyridine-2(1*H*)-thione (**2a**; Scheme 3).

Compounds **9** and **10** were identified by ^1H and ^{13}C NMR spectra on the basis of $^1J(C,H)$, $^2J(C,H)$, and $^3J(C,H)$ decoupling experiments. Diagnostically useful are the signals of the bridgehead, the olefinic, and the diastereotopic OCH_2 protons, which each appear in a narrow range, e.g. **9b**: 8-H: δ = 2.88; 12-H: δ = 2.38; 18-H: δ = 6.53; 9-OCH_2: δ = 4.02 and 4.14; 11-OCH_2: δ = 3.28 and 3.54. A typical shift to lower field was observed for the metal-free compounds **10** compared to the complexes **9**, e.g. **9b/10b**: 4- and 5-H of Py: δ = 6.47 and 5.82/6.82 and 6.38; 18-H: δ = 6.53/6.77; C-18: δ = 148.5/141.4). The chemical shifts of the bridgehead carbon atoms are characteristically observed at quite low field, e.g. **9a**: δ = 71.5; **9b**: δ = 71.3; **9c**: δ = 70.8.[9] More structural details could be obtained by a crystal structure analysis of compound **9b** (Figure 1). From the molecular geometry of compound **9b** it is obvious that the C≡C bond of compound **1** has been added from the *exo* side of the 1,3-diene unit. The striking down-field chemical



9,10	a	Yield of 9 (%)[a]	Yield of 10 (%)[b]
a	CH_2	64	–
b	CH_2CH_2	82	77
c	$CH_2CH_2CH_2$	78	71

[a] Chemical yields obtained by crystallization. [b] Isolated yields after column chromatography.

Scheme 3. Pentacyclic compounds **9** by [4+2] cycloaddition of [(1-alkynyl)carbene]tungsten complexes **1a–c** to tetrahydroindene **5b** and subsequent π-cyclization of the 1-tungsta-1,3,5-hexatriene unit resulting thereof

shift of the bridgehead carbon signals (see above) is attributed to the distortion of the corresponding tetrahedral configuration of C16 (C15–C16–C11 112.7, C15–C16–C26 118.7, C11–C16–C26 94.3) and C23 (C18–C23–C22 111.1, C18–C23–C24 102.6, C22–C23–C24 116.9).

(Iminoacylthio)cyclopentadienes

The reaction given in Scheme 1 was extended to the formation of (iminoacylthio)tetrahydroindenes **12b** and

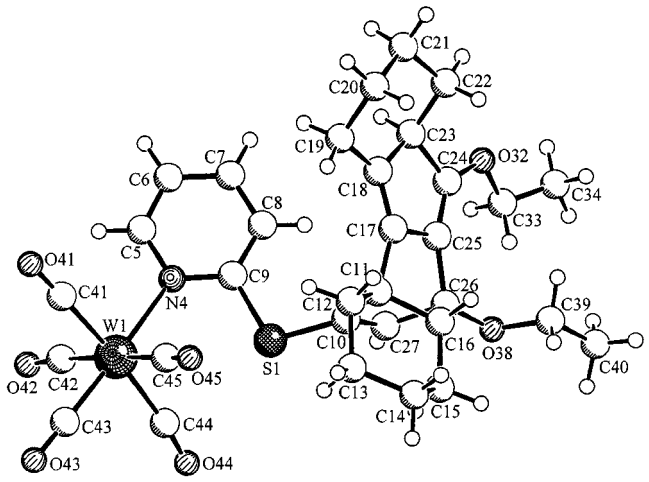
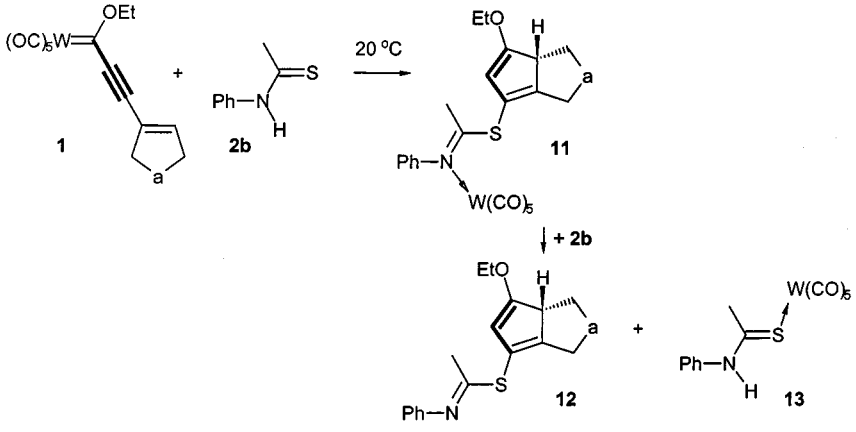


Figure 1. Molecular structure of pentacyclic compound **9b**; selected bond lengths [Å] and angles [°]: W1–N4 2.301(2), C9–S1 1.764(3), C10–C27 1.331(4), C10–C11 1.542(4), C10–S1 1.765(3), C11–C12 1.519(4), C11–C17 1.524(4), C11–C16 1.562(4), C16–C26 1.562(4), C17–C18 1.337(4), C17–C25 1.489(4), C18–C19 1.503(4), C18–C23 1.516(4), C22–C23 1.518(5), C23–C24 1.523(4), C24–C25 1.343(4), C24–O32 1.360(4), C25–C26 1.547(4), C26–O38 1.410(3), C26–C27 1.517(4); C9–N4–C5 116.4(2), C9–N4–W1 126.76(18), C5–N4–W1 116.67(18), N4–C5–C6 124.0(3), C5–C6–C7 118.7(3), C8–C7–C6 118.8(3), C27–C10–C11 108.9(2), C27–C10–S1 125.7(2), C11–C10–S1 125.4(2), C12–C11–C17 120.5(2), C12–C11–C10 118.3(2), C17–C11–C10 102.6(2), C12–C11–C16 113.8(2), C17–C11–C16 99.2(2), C10–C11–C16 98.8(2), C15–C16–C11 112.7(2), C15–C16–C26 118.7(2), C11–C16–C26 94.3(2), C18–C17–C25 111.4(2), C18–C17–C11 142.1(3), C25–C17–C11 106.3(2), C17–C18–C19 133.8(3), C17–C18–C23 108.4(3), C19–C18–C23 117.8(3), C18–C23–C22 111.1(3), C18–C23–C24 102.6(2), C22–C23–C24 116.9(3), C25–C24-O32 133.8(3), C25–C24–C23 110.6(3), O32–C24–C23 115.7(3), C24–C25–C17 107.1(2), C24–C25–C26 148.6(3), C17–C25–C26 104.0(2), O38–C26–C27 110.7(2), O38–C26–C25 121.0(2), C27–C26–C25 102.8(2), O38–C26–C16 119.1(2), C27–C26–C16 100.7(2), C25–C26–C16 99.5(2), C10–C27–C26 107.7(2), C9–S1–C10 104.7(1)



12	a	Yield of 11 (%)	Yield of 12 (%) [a]
a	CH_2	[b]	[b]
b	CH_2CH_2	96[11]	76
c	$CH_2CH_2CH_2$	94[11]	73

[a] Isolated yields after column chromatography. [b] Compound was not prepared.

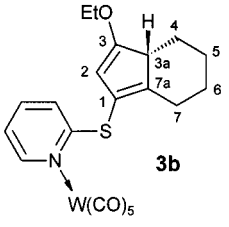
Scheme 4. Generation of cyclopentadienes **12** bearing iminoacylthiolate substituents

hexahydroazulenes **12c** from the corresponding [2-(1-cycloalkenyl)alkynyl]carbene complexes **1b,c** and *N*-phenylthioacetamide (**2b**) (Scheme 4).

Experimental Section

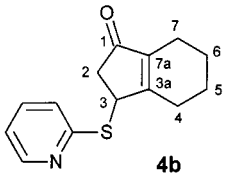
General: All operations were performed under argon. All solvents were dried and distilled prior to use. All ^{1}H and ^{13}C NMR spectra were routinely recorded with Bruker ARX 300 and AM 360 instruments. ^1J(H,C)-, ^2J(H,C)-, and ^3J(H,C) decoupling experiments were performed with a Varian 400 instrument, if not indicated otherwise. 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 also stained by iodine vapor. R_f values refer to TLC tests. Chromatographic purifications were performed on Merck Kieselgel 100. Pentacarbonyl(3-cycloalkenyl-1-ethoxy-2-propyn-1-ylidene)tungsten and -chromium compounds **1a−d** were prepared according to ref.[6]

Pentacarbonyl[3-ethoxy-1-(2-pyridylthio)-4,5,6,7-tetrahydro-3a*H*-indene-*N*]tungsten (3b), 3-(2-Pyridylthio)-2,3,4,5,6,7-hexahydroinden-1-one (4b), (3a*R)-1-Ethoxy-3-(2-pyridylthio)-4,5,6,7-tetrahydro-3a*H*-indene (5b), Pentacarbonyl[pyridine-2(1*H*)-thione-*S*]tungsten (6a):** To pentacarbonyl(3-cyclohexenyl-1-ethoxy-2-propyn-1-ylidene)tungsten (**1b**) (243 mg, 0.50 mmol) in 2 mL of diethyl ether in a 5-mL screw-top vessel was added 1 equiv. of pyridine-2(1*H*)-thione (**2a**) (55 mg, 0.50 mmol) with stirring at 20 °C. A color change from brown to yellow was instantly observed. After 5 min, the mixture was diluted with 1 mL of *n*-hexane and cooled to2 −0 °C to give yellow crystals of compound **3b**, which were isolated after 12 h by centrifugation, washed with 1 mL of pre-cooled *n*-pentane/diethyl ether (1:1) and dried in vacuo (15 Torr, 20 °C) (260 mg, 87%, R_f = 0.3 in *n*-pentane/diethyl ether, 10:1, m.p. 115 °C). Reaction of compound **1b** (243 mg, 0.50 mmol) with 2 equiv. of pyridine-2(1*H*)-thione (**2a**) (110 mg, 1.00 mmol) in dichloromethane at 20 °C, 6 h and subsequent fast chromatography of the mixture on silica gel in the presence of air (column 20 × 2 cm) with *n*-pentane/diethyl ether (5:1) afforded a colorless main fraction with compound **5b** (63 mg, 70%, R_f = 0.4 in *n*-pentane/diethyl ether, 4:1) and another fraction containing yellow pentacarbonyl[pyridine-2(1*H*)-thione-*S*]tungsten (**6a**). Reaction of pentacarbonyl[3-ethoxy-1-(2-pyridylthio)-4,5,6,7-tetrahydro-3a*H*-indene-*N*]tungsten (**3b**) (298 mg, 0.50 mmol) in 2 mL of dichloromethane with trimethylamine oxide (150 mg, 4.00 mmol) with stirring at 20 °C, and chromatography after 10 h on silica gel with *n*-pentane/diethyl ether, 1:3, gave colorless compound **4b** (93 mg, 76%, R_f = 0.4 in *n*-pentane/diethyl ether, colorless oil).



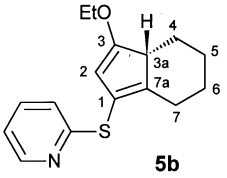
3b

3b: ^{1}H NMR (C_6D_6): δ = 8.59 and 7.00 (1 H each, "d" each, 3-H and 6-H Py), 6.67 and 5.95 (1 H each, "t" each, 4-H and 5-H Py), 4.80 (s, 1 H, 2-H), 3.45 (m, 2 H, OCH_2), 2.83 (dd, 1 H, 3a-H), 2.59 (m, 1 H), 2.29 (m, 1 H), 1.76 (m, 1 H), 1.61 (m, 1 H), 1.46 (m, 1 H), 0.93 (m, 3 H), 1.07 (t, 3 H, OCH_2CH_3). ^{13}C NMR (C_6D_6): δ = 202.7 and 199.6 [C_q each, *trans*- and *cis*-CO of $W(CO)_5$], 169.2 and 167.9 (C_q each, C2 Py and C3); 157.2, 138.9, 123.2, and 119.5 (CH each, Py), 148.2 (C_q, C1), 120.8 (C_q, C7a), 99.4 (CH, C2), 65.6 (OCH_2), 51.6 (CH, C3a); 31.3, 29.0, 26.6, and 24.9 (CH_2 each, C4 − C7), 14.4 (OCH_2CH_3). IR (diethyl ether): $\tilde{\nu}$ (%) = 2060.8 (5), 1931.5 (100), 1901.5 cm^{-1} (30) [ν(C≡O)]. MS (70 eV); *m*/*z* (%) [^{184}W]: 597 (15) [M^+], 485 (48) [M^+ − 4 CO], 457 (60) [M^+ − 5 CO]. $C_{21}H_{19}NO_6SW$ (597.3): calcd. C 42.19, H 3.18, N 2.34; found C 42.11, H 3.28, N 2.15.



4b

4b: ^{1}H NMR (C_6D_6): δ = 8.57, 6.83, and 6.46 (1:2:1 H; "d", m, "t", Py), 4.92 (m, 1 H, 3-H), 2.93 and 2.52 (1:1 H, m each, ^2J = 18.8, ^3J = 6.6 and 1.8, respectively; diastereotopic 2-H_2), 2.09 (m, 2 H, 7-H_2), 2.34 and 1.92 (1:1 H, m each, ^2J = 19.8, ^3J = 5.8 and 5.5, 4-H_2), 1.27 (m, 4 H, 5-H_2 and 6-H_2). ^{13}C NMR (C_6D_6): δ = 203.6 (C_q, C1), 158.8 (C_q, C2 Py), 169.1 and 141.3 (C_q each, C3a and C7a), 149.5, 135.8, 122.5, and 119.6 (CH each, Py), 44.5 (CH_2, C3), 44.2 (CH, C2), 26.3 (CH_2, C4), 20.9 (CH_2, C7), 22.3 and 21.6 (CH_2 each, C5 and C6). IR (diethyl ether): $\tilde{\nu}$ (%) = 1705.4 cm^{-1} (80) [ν(C=O)]. MS (70 eV); *m*/*z* (%) = 245 (100) [M^+].



5b

5b: ^{1}H NMR (C_6D_6): δ = 8.33 and 7.12 (1 H each, d each, 3-H and 6-H Py), 6.98 and 6.47 (1 H each, t each, 4-H and 5-H Py), 5.14 (s, 1 H, 2-H), 3.49 (m, 2 H, OCH_2), 2.71 (dd, 1 H, 3a-H); 3.00, 2.36, 1.88, 1.63, and 1.50 (1 H each, m each), 1.13−0.89 (m, 3 H) (4-H_2−7-H_2), 1.06 (t, 3 H, OCH_2CH_3). ^{13}C NMR (C_6D_6): δ 168.1 (C_q, C2 Py), 162.2 (C_q, C3), 149.9, 136.0, 120.8, and 119.2 (CH each, C3−C6 Py), 144.9 (C_q, C1), 121.3 (C_q, C7a), 101.5 (CH, C2), 65.3 (OCH_2), 51.6 (CH, C3a), 31.5, 29.0, 26.8, and 25.2 (CH_2 each, C4−C7), 14.4 (OCH_2CH_3). MS (70 eV); *m*/*z* (%): 273 (41) [M^+], 244 (100) [M^+ − Et]. $C_{16}H_{19}NOS$ (273.4): calcd. C 70.23, H 6.95, N 5.12; found C 69.51, H 7.22, N 4.79.

6a: ^{1}H NMR (C_6D_6): δ = 10.20 (1 H, NH), 7.11, 6.09, 5.75, and 5.40 (1 H each, m each, 3-H − 6-H Py). ^{13}C NMR (C_6D_6): δ = 201.2 and 198.5 [C_q each, *trans*- and *cis*-CO of $W(CO)_5$], 193.1 (C_q, C1), 138.2, 136.5, 132.0, and 114.6 (CH each, Py). MS (70 eV); *m*/*z* (%) [^{184}W]: 435 (15) [M^+], 407 (10) [M^+ − CO], 351 (30) [M^+ − 3 CO], 323 (30) [M^+ − 4 CO], 295 (30) [M^+ − 5 CO], 111 (65) [M^+ − $W(CO)_5$].

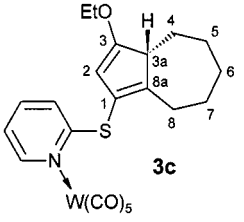
(3a*R)-Pentacarbonyl[3-ethoxy-1-(2-pyridylthio)-4,5,6,7-tetrahydro-3a*H*-indene-*N*]chromium (3d) and Pentacarbonyl[pyridine-2(1*H*)-thione-*S*]chromium (6b):** Pentacarbonyl(3-cyclohexenyl-1-ethoxy-2-propyn-1-ylidene)chromium (**1d**) (177 mg, 0.50 mmol) was treated with pyridine-2(1*H*)-thione (**2a**) (55 mg, 0.50 mmol) in diethyl ether at 20 °C, 30 min as described above to give yellow crystals of com-

pound **3d** (233 mg, 92%, R_f = 0.5 in *n*-pentane/diethyl ether, 4:1, m.p. 108 °C). Reaction of compounds **1d** and **2a** in dichloromethane in a molar ratio of 1:2 at 20 °C for 4 h and subsequent fast chromatography of the mixture on silica gel (column 20 × 2 cm) with *n*-pentane/diethyl ether, 5:1, afforded colorless compound **5b** in 76% yield and pentacarbonyl[pyridine-2(1*H*)-thione-*S*]chromium **6b**.

3d: ^{1}H NMR (C_6D_6): δ = 8.43, 6.95, 6.64, and 5.97 (1 H each, m broad each, 3-H−6-H Py), 4.81 (s, 1 H, 2-H), 3.45 (m, 2 H, OCH_2), 2.61 (1 H, dd broad, 3a-H); 2.83, 2.31, 1.93−0.85 (m, 8 H) (1:1:4, m each, 4-H_2−7-H_2), 1.05 (t, 3 H, OCH_2CH_3). ^{13}C NMR (C_6D_6): δ = 221.9 and 214.9 [C_q each, *trans*- and *cis*-CO of $Cr(CO)_5$], 169.1 and 156.2 (C_q each, C2 Py and C3), 147.8, 136.5, 121.2, and 118.8 (CH each, Py), 145.0 (C_q, C1), 120.7 (C_q, C7a), 99.6 (CH, C2), 65.6 (OCH_2), 51.7 (CH, C3a), 31.4, 29.0, 26.6, and 25.6 (CH_2 each, C4−C7), 14.3 (OCH_2CH_3). IR (diethyl ether): $\tilde{\nu}$ (%) = 2061.7 (5), 1929.8 (100), 1988.9 cm^{-1} (30) [ν(C≡O)]. MS (70 eV), *m*/*z* (%) = 465 (8) [M^+], 381 (80) [M^+ − 3 CO], 271 (100) [M^+ − $Cr(CO)_5$]. $C_{21}H_{19}CrNO_6S$ (465.4): calcd. C 54.14, H 4.08, N 3.01; found C 54.35, H 4.20, N 3.38.

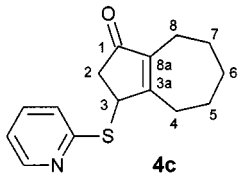
6b: ^{1}H NMR (C_6D_6): δ = 10.32 (1 H, NH), 7.12, 6.09, 5.78, and 5.39 (1 H each, m each, Py). ^{13}C NMR (C_6D_6): δ = 219.8 and 213.5 [C_q each, *trans*- and *cis*-CO of $Cr(CO)_5$], 193.9 (C_q, C2), 138.3, 136.7, 132.0, and 114.6 (CH each, Py). MS (70 eV); *m*/*z* (%): 303 (15) [M^+], 163 (20) [M^+ − 5 CO], 111 (65) [M^+ − $Cr(CO)_5$].

Pentacarbonyl[3-ethoxy-1-(2-pyridylthio)-4,5,6,7,8-pentahydro-3a*H*-azulene-*N*]tungsten (3c), 3-(2-Pyridylthio)-2,3,4,5,6,7-heptahydroazulen-1-one (4c) and (3a*R)-1-Ethoxy-3-(2-pyridylthio)-4,5,6,7,8-pentahydro-3a*H*-azulene (5c):** Pentacarbonyl(3-cycloheptenyl-1-ethoxy-2-propyn-1-ylidene)tungsten (**1c**) (250 mg, 0.50 mmol) was treated with pyridine-2(1*H*)-thione (**2a**) (55 mg, 0.50 mmol) in 2 mL of diethyl ether as described above to give compound **3c** (284 mg, 93%, R_f = 0.4 in *n*-pentane/diethyl ether, 10:1, m.p. 102 °C). Reaction of compound **1c** (250 mg, 0.50 mmol) with 2 equiv. of compound **2a** (111 mg, 1.00 mmol) in dichloromethane, 20 °C, 6 h gave compound **5c** (109 mg, 71%, R_f = 0.5 in *n*-pentane/diethyl ether, 5:1, colorless oil). Compound **3c** (305 mg, 0.50 mmol) in 2 mL of dichloromethane was treated with trimethylamine oxide (150 mg, 4.0 mmol) as described above to afford compound **4c** (96 mg, 73%, R_f = 0.4 in *n*-pentane/diethyl ether, 3:2, colorless oil).



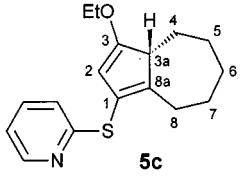
3c

3c: ^{1}H NMR (C_6D_6): δ = 8.61 and 7.98 (1 H each, d each, 3-H and 6-H Py), 6.67 and 5.94 (1 H each, t each, 4-H and 5-H Py), 4.78 (s, 1 H, 2-H), 3.45 (m, 2 H, OCH_2), 2.90 (dd, 1 H, 3a-H), 2.45, 2.39, 2.13, 1.58−1.01 (1:1:1:7 H, m each, 4-H_2−8-H_2), 1.07 (t, 3 H, OCH_2CH_3). ^{13}C NMR (C_6D_6): δ 202.7 and 199.7 [C_q each, *trans*- and *cis*-CO of $W(CO)_5$], 167.6 and 167.4 (C_q each, C2 Py and C3); 157.3, 136.9, 123.1, and 119.5 (CH each, Py), 151.1 (C_q, C1), 123.7 (C_q, C8a), 99.4 (CH, C2), 65.6 (OCH_2), 55.1 (CH, C3a); 30.9, 29.9, 29.4, and 27.5 (1:1:2:1, C4−C7), 14.4 (OCH_2CH_3). IR (diethyl ether): $\tilde{\nu}$ (%) = 2061.0 (5), 1931.2 (100), 1901.1 cm^{-1} (30) [ν(C≡O)]. MS (70 eV); *m*/*z* (%) [^{184}W]: 527 (2) [M^+ − 3 CO], 258 (33) [M^+ − $W(CO)_5$]. $C_{22}H_{21}NO_6SW$ (611.3): calcd. C 43.22, H 3.46, N 2.29; found C 43.23, H 3.44, N 2.01.



4c

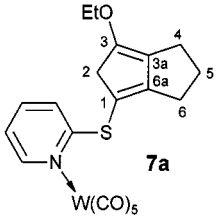
4c: ^{1}H NMR (C_6D_6): δ = 8.19, 6.80, and 6.42 (1:2:1 H, Py), 4.92 (m, 1 H, 3-H), 2.92 and 2.52 (1 H each, m each, AB system ^2J = 17.0 Hz, 2-H_2), 2.28 and 1.36 (4:6 H, m each) (4-H_2−8-H_2). ^{13}C NMR (C_6D_6): δ = 203.6 (C_q, C1), 158.9 (C_q, C2 Py), 171.3 and 145.4 (C_q each, C3a and C7a), 149.6, 135.9, 122.6, and 119.7 (CH each, Py), 46.1 (CH, C3), 45.0 (CH_2, C2), 31.6, 26.7, 26.6, and 23.8 (2:1:1:1, CH_2 each, C4−C8). MS (70 eV); *m*/*z* (%): 259 (100) [M^+]. $C_{15}H_{17}NOS$ (259.4): calcd. C 69.46, H 6.61, N 5.40; found C 69.44, H 6.56, N 5.20.



5c

5c: ^{1}H NMR (C_6D_6): δ = 8.35 and 7.12 (1 H each, d each, 3-H and 6-H Py), 7.00 and 6.50 (1 H each, dd each, 4-H and 5-H Py), 5.13 (s, 1 H, 2-H), 3.50 (m, 2 H, OCH_2), 2.70 (dd, 1 H, 3a-H); 3.04, 2.54, 2.19, 1.56, 1.37, and 1.18 (1:1:1:3:3:1 H, m each, 4-H_2−8-H_2), 1.07 (t, 3 H, OCH_2CH_3). ^{13}C NMR (C_6D_6): δ = 166.3 (C_q, C2 Py), 161.7 (C_q, C3), 149.9, 136.0, 121.0, and 119.3 (CH each, Py), 147.5 (C_q, C1), 124.2 (C_q, C8a), 110.3 (CH, C2), 65.3 (OCH_2), 54.7 (CH, C3a), 31.1, 29.3, 29.5, 29.4, and 27.9 (CH_2 each, C4−C7), 14.5 (OCH_2CH_3). MS (70 eV); *m*/*z* (%): 287 (28) [M^+], 258 (100) [M^+ − Et]. $C_{17}H_{21}NOS$ (287.4): calcd. C 71.08, H 7.32, N 4.88; found C 71.24, H 7.32, N 4.63.

Pentacarbonyl[3-ethoxy-1-(2-pyridylthio)-2,4,5,6-tetrahydropentalene-*N*]tungsten (7a): To pentacarbonyl(3-cyclopentenyl-1-ethoxy-2-propyn-1-ylidene)tungsten (**1a**) (236 mg, 0.50 mmol) and triethylamine (50 mg, 0.50 mmol) in 1 mL of dichloromethane was added dropwise pyridine-2(1*H*)-thione (**2a**) (55 mg, 0.50 mmol) in 1 mL of dichloromethane at 0 °C while stirring. The solvent was removed after 20 min at 0 °C by a stream of argon, and the residue was dissolved in very little diethyl ether/*n*-pentane, 2:1, and placed at2 −0 °C to afford yellow crystals of compound **7a** (239 mg, 82%, R_f = 0.3 in *n*-pentane/diethyl ether, 10:1, m.p. 85 °C).

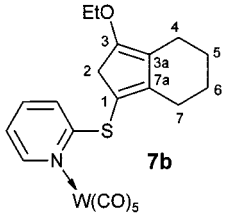


7a

7a: ^{1}H NMR (400 MHz, C_6D_6): δ = 8.53 and 6.76 (1 H each, "d" each, 3-H and 6-H Py), 6.61 and 5.91 (1 H, each, "t" each, 4-H and 5-H Py), 3.70 (m, 2 H, OCH_2), 2.16 (s, 2 H, 2-H_2); 2.26, 2.12,

and 1.83 (2:2:2, m each, 4-H_2−6-H_2), 1.06 (t, 3 H, OCH_2CH_3). ^{13}C NMR (C_6D_6): δ = 202.8 and 199.7 [C_q each, *trans*- and *cis*-CO of $W(CO)_5$], 170.3 and 170.2 (C_q each, C2 Py and C3), 158.0 (C_q, C1), 157.1, 136.8, 122.4, and 119.2 (CH each, Py), 121.2 and 102.0 (C_q each, C3a and C6a), 66.0 (OCH_2), 48.3 (CH_2, C2), 30.3 and 26.0 (1:2, CH_2 each, C4−C6), 15.2 (OCH_2CH_3). IR (diethyl ether): ṽ (%) = 2067.2 (5), 1931.5 (100), 1900.5 cm^{-1} (30) [ν(C≡O)]. MS (70 eV); *m/z* (%) [^{184}W]: 499 (0.5) [M^+ − 3 CO], 259 (21) [M^+ − $W(CO)_5$], 230 (100) [M^+ − $W(CO)_5$ − Et]. $C_{20}H_{17}NO_6SW$ (583.3): calcd. C 41.19, H 2.94, N 2.40; found C 41.23, H 3.27, N 2.25.

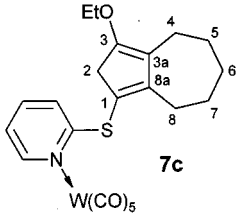
Pentacarbonyl[3-ethoxy-1-(2-pyridylthio)-4,5,6,7-tetrahydro-2*H*-indene-*N*]tungsten (7b): Pentacarbonyl(3-cyclohexenyl-1-ethoxy-2-propyne-1-ylidene)tungsten (**1b**) (243 mg, 0.50 mmol) was treated with pyridine-2(1*H*)-thione (**2a**) (55 mg, 0.50 mmol) in 2 mL of dichloromethane in the presence of triethylamine (50 mg, 0.50 mmol) as described above to afford yellow compound **7b** (260 mg, 87%, R_f = 0.3 in *n*-pentane/diethyl ether, 10:1, m.p. 82 °C).



7b

7b: ^1H NMR (C_6D_6): δ = 8.57 and 6.61 (1 H each, "d" each, 3-H and 6-H Py), 6.60 and 5.92 (1 H, each, "t" each, 4-H and 5-H Py), 3.42 (m, 2 H, OCH_2), 2.68 (s, 2 H, 2-H); 2.36, 2.25, and 1.37 (2:2:4 H, m each, 4-H_2−7-H_2), 1.07 (t, 3 H, OCH_2CH_3). ^{13}C NMR (C_6D_6): δ = 202.8 and 199.7 [C_q each, *trans*- and *cis*-CO of $W(CO)_5$], 170.0 (C_q, C-3), 161.9 (C_q, C2 Py), 159.1 (C_q, C1); 157.3, 136.8, 122.1, and 119.2 (CH each, Py), 116.5 and 106.4 (C_q each, C3a and C7a), 65.8 (OCH_2), 40.6 (CH_2, C2); 25.5, 23.1, and 21.9 (1:2:1, C4 − C7), 15.2 (OCH_2CH_3). IR (diethyl ether): ṽ (%) = 2067.0 (5), 1931.5 (100), 1902.5 cm^{-1} (30) [ν(C≡O)]. MS (70 eV); *m/z* (%) [^{184}W]: 597 (15) [M^+], 485 (50) [M^+ − 4 CO], 457 (60) [M^+ − 5 CO]. $C_{21}H_{19}NO_6SW$ (597.3): calcd. C 42.23, H 3.21, N 2.35; found C 42.11, H 3.17, N 2.13.

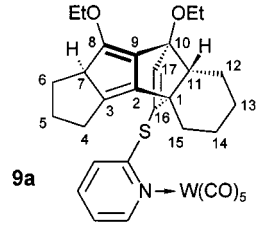
Pentacarbonyl[3-ethoxy-1-(2-pyridylthio)-4,5,6,7,8-pentahydro-3a*H*-azulene-*N*]tungsten (7c): Pentacarbonyl(3-cyclohexenyl-1-ethoxy-2-propyne-1-ylidene)tungsten (**1c**) (250 mg, 0.50 mmol) was treated with pyridine-2(1*H*)-thione (**2a**) (55 mg, 0.50 mmol) in 2 mL of diethyl ether in the presence of triethylamine (50 mg, 0.50 mmol) as described above to give yellow compound **7c** (235 mg, 77%, R_f = 0.4 in *n*-pentane/diethyl ether, 10:1, m.p. 73 °C).



7c

7c: ^1H NMR (C_6D_6): δ = 8.57 and 6.66 (1 H each, "d" each, 3-H and 6-H Py), 6.60 and 5.91 (1 H, each, "t" each, 4-H and 5-H Py), 3.35 (m, 2 H, OCH_2), 2.71 (s, 2 H, 2-H), 2.45, 1.47, and 1.38 (2:2:1, m each, 4-H_2−8-H_2), 1.01 (t, 3 H, OCH_2CH_3). ^{13}C NMR (C_6D_6): δ = 202.7 and 199.8 [C_q each, *trans*- and *cis*-CO of $W(CO)_5$], 170.3 (C_q, C3), 164.2 (C_q, C2 Py), 161.2 (C_q, C1), 157.3, 136.7, 122.8, and 119.2 (CH each, Py), 122.3 and 108.0 (C_q each, C3a and C8a), 65.8 (OCH_2), 40.4 (CH_2, C2), 32.7, 29.9, 28.9, and 25.0 (1:2:1:1, CH_2 each, C4−C8), 15.2 (OCH_2CH_3). IR (diethyl ether): ṽ (%) = 2067.8 (5), 1931.5 (100), 1902.5 cm^{-1} (30) [ν(C≡O)]. MS (70 eV); *m/z* (%) [^{184}W]: 527 (10) [M^+ − 3 CO], 471 (20) [M^+ − 5 CO], 258 (35) [M^+ − $W(CO)_5$]. $C_{22}H_{21}NO_6SW$ (611.3): calcd. C 43.22, H 3.46, N 2.29; found C 43.01, H 3.40, N 2.15.

(1*S,7*R**,10*R**,11*S**)-Pentacarbonyl{8,10-diethoxy-16-(2-pyridylthio)penta-cyclo[8.5.2.0^{1,11}.0^{2,9}.0^{3,7}]heptadeca-2,8,16-triene-*N*}-tungsten (9a):** 1-Ethoxy-3-(2-pyridylthio)-4,5,6,7-tetrahydro-3a*H*-indene (**5b**) (68 mg, 0.25 mmol) and compound **1a** (118 mg, 0.25 mmol) in 2 mL of *n*-pentane/diethyl ether, 1:1, was stirred at 20 °C. Compound **1a** was consumed completely (TLC test) after 20 h while a precipitate was formed. The latter was collected by centrifugation, washed twice with small portions of precooled *n*-pentane/diethyl ether, 2:1, each to give the condensation product **9a** (119 mg, 64%, R_f = 0.6 in *n*-pentane/diethyl ether, 3:1, m.p. 106 ° C). Ligand disengagement from compound **9a** by interaction with 1 equiv. of compound **2a** afforded a mixture of unstable compounds, which was not further characterized.

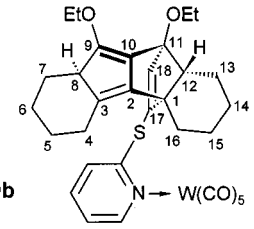


9a

9a: ^1H NMR (C_6D_6, 600 Hz): δ = 8.49 and 7.14 (1 H each, "d" each, 3-H and 6-H Py), 6.52 and 5.82 (1 H each, "t" each, 4-H and 5-H Py), 6.55 (s, 1 H, 17-H), 4.02 and 3.84 (1 H each, m each, diastereotopic 8-OCH_2), 3.65 and 3.44 (1 H each, m each, 10-OCH_2), 3.59 (dd, 1 H, 7-H), 2.39 (dd, 1 H, 11-H), 2.15, 2.03−1.90, 1.51−1.41, 1.32, 1.19, 1.11, and 0.85 (1:3:6:1:1:1 H, m each, (4-H_2−6-H_2 and 12-H_2−15-H_2), 1.19 and 1.18 (3 H each, t each, OCH_2CH_3 each). ^{13}C NMR (C_6D_6): δ = 202.6 and 199.5 [C_q each, *trans*- and *cis*-CO of $W(CO)_5$], 167.2 (C_q, C2 Py); 156.9, 136.6, 125.0, and 119.9 (CH each, Py), 151.9 (C_q, C8), 147.6 (CH, C17), 143.5 (C_q, C16), 137. 8 (C_q, C2), 130.7 (C_q, C3), 125.0 (C_q, C9), 93.6 (C_q, C10), 71.5 (CH, C11), 68.3 (8-OCH_2), 63.8 (CH, C7), 62.0 (10-OCH_2), 56.7 (C_q, C1), 31.6, 28.5, and 21.2 (CH_2 each, C4−C6), 24.7, 23.9, 23.0, and 22.2 (CH_2 each, C12−C15), 15.3 and 15.7 (OCH_2CH_3 each). $C_{31}H_{31}NO_7SW$ (745.5): calcd. C 49.95, H 4.19, N 1.88; found C 50.17, H 4.12, N 1.62. IR (diethyl ether): ṽ (%) = 2067.8 (5), 1931.6 (100), 1906.7 cm^{-1} (30) [ν(C≡O)]. MS (70 eV); *m/z* (%) [^{184}W]: 421 (10) [M^+ − $W(CO)_5$], 392 (15) [421 − C_2H_5], 311 (85) [421 − PyS].

(1*S,8*R**,11*R**,12*S**)-Pentacarbonyl{9,11-diethoxy-17-(2-pyridylthio)pentacyclo[9.5.2.0^{1,12}.0^{2,10}.0^{3,8}]octadeca-2,9,17-triene-*N*}-tungsten (9b) and (1*S**,8*R**,11*R**,12*S**)-11-Ethoxy-17-(2-pyridylthio)pentacyclo[9.5.2.0^{1,12}.0^{2,10}.0^{3,8}]octadeca-2,9,17-triene (10b):** 1-Ethoxy-3-(2-pyridylthio)-4,5,6,7-tetrahydro-3a*H*-indene (**5b**) (68 mg, 0.25 mmol) and compound **1b** (121 mg, 0.25 mmol) were treated as described above to give a yellow cycloadduct **9b** (155 mg, 82%, R_f = 0.6 in *n*-pentane/diethyl ether, 3:1, m.p. 123 °C). Reaction of compound **9b** (190 mg, 0.25 mmol) with compound **2a** (28 mg, 0.25 mmol) in dichloromethane as described above afforded compound **10b** (83 mg, 77%, R_f = 0.4 in *n*-pentane/diethyl

ether, 3:2, colorless oil). The latter compound was slowly generated also under the influence of air on a solution of the complex **9b**.



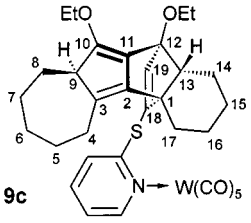
9b

9b: ^{1}H NMR (C_6D_6, 600 Hz): δ = 8.49 and 6.98 (1 H each, d each, 3-H and 6-H Py), 6.47 and 5.82 (1 H, each, t each, 4-H and 5-H Py), 6.53 (s, 1 H, 18-H), 4.14 and 4.03 (1 H each, m each, diastereotopic 9-OCH_2), 3.54 and 3.28 (1 H each, m each, 11-OCH_2), 2.88 (dd, 1 H, 8-H), 2.38 (dd, 1 H, 12-H), 2.47 and 1.52 (1 H each, m each), 1.52 and 1.34 (1 H each, m each), 1.34 and 0.79 (1 H each, m each), 1.34 (m, 2 H) (13-H_2−16-H_2); 2.46 and 1.26 (1 H each, m each), 2.21 and 1.45 (1 H each, m each), 1.62 and 1.09 (1 H each, m each) (4-H_2−7-H_2), 1.21 and 1.09 (3 H each, t each, OCH_2CH_3 each). ^{13}C NMR (C_6D_6): δ = 202.6 and 199.5 [C_q each, *trans*- and *cis*-CO of $W(CO)_5$], 167.6 (C_q, C2 Py); 156.8, 136.5, 124.7, and 119.8 (CH each, Py), 153.7 (C_q, C9), 148.5 (CH, C18), 143.1 (Cq, C17), 137.4 (C_q, C2), 124.2 (C_q, C3), 117.8 (C_q, C10), 93.2 (C_q, C11), 71.3 (CH, C12), 68.5 (9-OCH_2), 61.7 (11-OCH_2), 61.2 (CH, C8), 57.7 (C_q, C9), 56.5 (C_q, C1), 31.9, 28.5, 26.0, and 25.6 (CH_2 each, C7−C9), 25.8, 24.0, 23.0, and 22.3 (CH_2 each, C13−C16), 15.6 and 15.3 (OCH_2CH_3 each). $C_{32}H_{33}NO_7SW$ (759.5): calcd. C 50.60, H 4.38, N 1.84; found C 50.37, H 4.22, N 1.71. IR (diethyl ether): $\tilde{\nu}$ (%) = 2066.4 (5), 1930.1 (100), 1904.1 cm^{-1} (30) [ν(C≡O)]. MS (70 eV); *m*/*z* (%) [^{184}W]: 435 (10) [M^+ − $W(CO)_5$], 406 (30) [435 − C_2H_5], 377 (70) [406 − C_2H_5], 325 (90) [435 − PyS]. X-ray crystal structure analysis of compound **9b** (code 1227.AUM), formula $C_{32}H_{33}NO_7SW$, M = 759.50 $gmol^{-1}$, 0.20 × 0.15 × 0.10 mm, a = 9.579(1), b = 10.972(1), c = 15.491(1) Å, α = 82.61(1), β = 80.04(1), γ = 73.59(1)°, V = 1532.8(2) $Å^3$, $D_{calcd.}$ = 1.646 gcm^{-3}, μ = 38.84 cm^{-1}, empirical absorption correction with SORTAV (0.511≤ T ≤ 0.697), Z = 2, triclinic, space group $P\bar{1}$ (no. 2), λ = 0.71073 Å, T = 198 K, ω and θ scans, 10358 reflections collected (±h, ±k, ±l), $[(\sin\Theta)/\lambda]_{max}$ = 0.65 $Å^{-1}$, 6971 independent reflections (R_{int} = 0.023) and 6415 observed reflections [I ≥ 2σ(I)], 381 refined parameters, R = 0.025, wR^2 = 0.057, max. residual electron density 0.68 (−0.96) $eÅ^{-3}$, positions of hydrogen atoms calculated and refined as riding atoms.

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC-172958. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033, E-mail: deposit@ccdc.cam.ac.uk].[14]

10b: ^{1}H NMR (C_6D_6, 600 Hz): δ = 8.23 and 7.02 (1 H each, "d" each, 3-H and 6-H Py), 6.82 and 6.38 (1 H, each, "t" each, 4-H and 5-H Py), 6.77 (s, 1 H, 18-H), 4.18 and 4.06 (1 H each, m each, diastereotopic 9-OCH_2), 3.68 and 3.43 (1 H each, m each, 11-OCH_2), 2.92 (dd, 1 H, 8-H), 2.44 (dd, 1 H, 12-H); 2.46 (m, 2 H), 1.69 (m, 3 H), 1.46 (m, 6 H), 1.30 (m, 1 H), 1.10 (m, 3 H) (4-H_2−7-H_2 and 13-H_2−16-H_2), 1.22 and 1.14 (3 H each, t each, OCH_2CH_3 each). ^{13}C NMR (C_6D_6): δ = 160.9 (C_q, C2 Py), 149.6, 136.0, 122.0, and 120.0 (CH each, Py), 152.6 (C_q, C9), 141.4 (CH, C18), 143.4 (C_q, C17), 137.7 (C_q, C2), 123.6 (C_q each, C3), 119.5 (C_q each, C10), 93.4 (C_q, C11), 70.1 (CH, C12), 68.4 (9-OCH_2), 61.5 (11-OCH_2), 61.0 (CH, C8), 57.6 (C_q, C9), 56.3 (C_q, C1), 31.9, 28.7, 26.7, and 26.3 (CH_2 each, C4−C7), 25.7, 24.3, 23.3, and 22.4 (CH_2 each, C13−C16), 15.6 and 15.4 (OCH_2CH_3 each). HSMS; $C_{27}H_{33}NO_2S$: calcd. 435.22320; found 435.22157. MS (70 eV); *m*/*z* (%): 435 (10) [M^+], 406 (22) [M^+ − C_2H_5], 325 (100) [M^+ − PyS].

(1*S,9*R**,12*R**,13*S**)-Pentacarbonyl{10,12-diethoxy-18-(2-pyridylthio)pentacyclo[10.5.2.0^{1,13}.0^{2,11}.0^{3,9}]nonadeca-2,10,18-triene-*N*}tungsten (9c) and (1*S**,9*R**,12*R**,13*S**)-12-Ethoxy-18-(2-pyridylthio)pentacyclo[10.5.2. 0^{1,13}.0^{2,11}.0^{3,9}]nonadeca-2,10,18-triene (10c):** 1-Ethoxy-3-(2-pyridylthio)-4,5,6,7-tetrahydro-3a*H*-indene (**5b**) (68 mg, 0.25 mmol) and compound **1c** (125 mg, 0.25 mmol) were treated as described above to give a yellow cycloadduct **9c** (150 mg, 78%, R_f = 0.7 in *n*-pentane/diethyl ether, 3:1, m.p. 118 °C). Reaction of compound **9c** (193 mg, 0.25 mmol) with compound **2a** (28 mg, 0.25 mmol) in dichloromethane as described above afforded compound **10b** (78 mg, 71%, R_f = 0.5 in *n*-pentane/diethyl ether, 3:2, colorless oil).



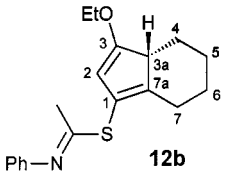
9c

9c: ^{1}H NMR (C_6D_6, 600 Hz): δ = 8.53 and 6.82 (1 H each, "d" each, 3-H and 6-H Py), 6.50 and 5.87 (1 H, each, "t" each, 4-H and 5-H Py), 6.51 (s, 1 H, 19-H), 4.13 and 4.05 (1 H each, m each, diastereotopic 10-OCH_2), 3.53 and 3.50 (1 H each, m each, 12-OCH_2), 3.30 (dd, 1 H, 9-H), 2.36 (dd, 1 H, 13-H); 2.39 (m, 1 H), 2.25 (m, 2 H), 1.90 (m, 1 H), 1.74 (m, 1 H), 1.68−1.48 (m, 9 H), 1.21 (m, 2 H), 1.18 (m, 1 H), 0.88 (m, 1 H) (4-H_2−8-H_2 and 14-H_2−17-H_2), 1.21 and 1.09 (3 H each, t each, OCH_2CH_3 each). ^{13}C NMR (C_6D_6): δ = 202.5 and 199.5 [C_q each, *trans*- and *cis*-CO of $W(CO)_5$], 167.8 (C_q, C2 Py), 156.9, 136.5, 124.5, and 119.8 (CH each, Py), 152.2 (C_q, C10), 148.9 (CH, C19), 145.6 (C_q, C18), 136.8 (C_q, C2), 127.5 (C_q, C3), 117.1 (C_q, C11), 93.2 (C_q, C12), 70.8 (CH, C13), 68.4 (10-OCH_2), 61.6 (12-OCH_2), 61.2 (C_q, C10), 57.7 (CH, C9), 56.8 (C_q, C1), 31.4, 30.7, 30.1, 28.1 and 28.5 (CH_2 each, C4−C8), 25.9, 23.8, 23.0, and 22.3 (CH_2 each, C14−C17), 15.6 and 15.3 (OCH_2CH_3 each). $C_{33}H_{35}NO_7SW$ (773.6): calcd. C 51.24, H 4.56, N 1.81; found C 51.50, H 5.04, N 1.60. IR (diethyl ether): $\tilde{\nu}$ (%) = 2067.8 (5), 1931.2 (100), 1905.9 cm^{-1} (30) [ν(C≡O)]. MS (70 eV); *m*/*z* (%) [^{184}W]: 449 (10) [M^+ − $W(CO)_5$], 420 (25) [449 − C_2H_5], 339 (100) [449 − PyS].

10c: ^{1}H NMR (C_6D_6, 600 Hz): δ = 8.22 and 6.95 (1 H each, "d" each, 3-H and 6-H Py), 6.83 and 6.40 (1 H, each, "t" each, 4-H and 5-H Py), 6.73 (s, 1 H, 19-H), 4.16 and 4.09 (1 H each, m each, diastereotopic 10-OCH_2), 3.66 and 3.44 (1 H each, m each, 12-OCH_2), 3.27 (dd, 1 H, 9-H), 2.38 (dd, 1 H, 13-H), 2.48 (m, 1 H), 2.25 (m, 2 H), 1.68 (m, 3 H), 1.52 (m, 6 H), 1.34 (m, 4 H), 1.13 (m, 1 H), 0.95 (m, 1 H) (4-H_2−8-H_2 and 14-H_2−17-H_2), 1.22 and 1.13 (3 H each, t each, OCH_2CH_3 each). ^{13}C NMR (C_6D_6): δ = 161.1 (C_q, C2 Py), 149.6, 135.9, 122.8, and 120.0 (CH each, Py), 151.2 (C_q, C10), 146.2 (C_q, C18), 142.1 (CH, C19), 137.7 (C_q, C2), 126.9 (C_q, C3), 119.5 (C_q, C11), 93.5 (C_q, C12), 69.5 (CH, C13), 68.3 (10-OCH_2), 61.5 (12-OCH_2), 61.0 (C_q, C10), 67.6 (CH, C9), 56.7 (C_q, C1), 31.5, 30.8, 30.0, 28.7, and 28.1 (CH_2 each, C4−C8), 26.2, 24.2, 23.3, and 22.6 (CH_2 each, C14−C17), 15.7 and 15.4

(OCH_2CH_3 each). HSMS; $C_{28}H_{35}NO_2S$: calcd. 449.23886; found 449.23696. MS (70 eV); *m/z* (%): 449 (12) [M^+], 420 (26) [$M^+ - C_2H_5$], 339 (90) [$M^+ - PyS$].

(3a*R)-3-Ethoxy-4,5,6,7-tetrahydro-3a*H*-inden-1-yl (1*E*)-*N*-Phenylethanimidothioate (12b) and Pentacarbonyl(*N*-phenylthioacetamide-*S*)tungsten (13):** Pentacarbonyl(3-cyclohexenyl-1-ethoxy-2-propyne-1-ylidene)tungsten (**1b**) (243 mg, 0.50 mmol) was treated with 2 equiv. of *N*-phenylthioacetamide (**2b**) (151 mg, 1.00 mmol) in 2 mL of dichloromethane 20 °C, 6 h with stirring as described above to give compound **12b** (127 mg, 75%, R_f = 0.4 in *n*-pentane/diethyl ether, 5:1, colorless oil) and yellow compound **13**.

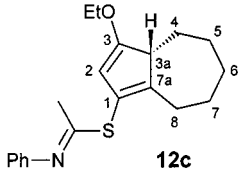


12b

12b: ^{1}H NMR (C_6D_6): δ = 7.25, 7.20, and 7.01 (2:2:1, Ph), 4.50 (s, 1 H, 2-H), 3.51 (m, 2 H, OCH_2), 2.88 (dd, 1 H, 3a-H), 2.58 (m, 1 H), 2.41 (s, 3 H, CH_3), 2.30 (m, 1 H), 1.84 (m, 1 H), 1.66 (m, 1 H), 0.92 (m, 3 H), 1.08 (t, 3 H, OCH_2CH_3). ^{13}C NMR (C_6D_6): δ = 168.0 (C_q, C=N), 164.1 (C_q, C3), 151.4 and 145.2 (C_q, C1 and *i*-C Ph), 129.3, 124.0, and 120.3 (2:1:2, Ph), 121.4 (C_q, C7a), 102.1 (CH, C2), 65.4 (OCH_2), 51.5 (CH, C3a), 31.1, 28.6, 26.5, and 25.0 (CH_2 each, C4−C7), 26.3 (CH_3), 14.4 (OCH_2CH_3). MS (70 eV); *m/z* (%): 313 (8) [M^+], 118 (100) [$CH_3C{=}NPh]^+$. $C_{19}H_{23}NOS$ (313.5): calcd. C 72.74, H 7.34, N 4.47; found C 72.76, H 7.56, N 4.38.

13: ^{1}H NMR (C_6D_6): δ = 9.29 (1 H, broad, NH), 6.95 and 6.52 (3:2, m each, Ph), 1.82 (s, 3 H, CH_3). ^{13}C NMR (C_6D_6): δ = 201.5 and 198.6 [C_q each, *trans*- and *cis*-CO of $W(CO)_5$], 202.3 (C_q, C=S), 137.3 (C_q, *i*-C Ph), 129.9, 128.6 and 124.4 (2:1:2, Ph), 28.0 (CH_3). MS (70 eV); *m/z* (%) [^{184}W]: 475 (5) [M^+], 335 (20) [M^+ − 5 CO] and 151 (40) [$M^+ - W(CO)_5$].

(3a*R)-3-Ethoxy-3a,4,5,6,7,8-hexahydroazulen-1-yl (1*E*)-*N*-Phenylethanimidothioate (12c):** Pentacarbonyl(3-cycloheptenyl-1-ethoxy-2-propyn-1-ylidene)tungsten (**1c**) (250 mg, 0.50 mmol) was treated with *N*-phenylthioacetamide (**2b**) (151 mg, 1.00 mmol) in 2 mL of dichloromethane as described above to give compound **12c** (127 mg, 73%, R_f = 0.5 in *n*-pentane/diethyl ether, 5:1, colorless oil) together with complex **13**.



12c

12c: ^{1}H NMR (C_6D_6): δ = 7.25, 7.15, and 6.95 (2:2:1, Ph), 4.97 (s, 1 H, 2-H), 3.50 (m, 2 H, OCH_2), 3.28 (m, 1 H), 2.84 (m, 1 H), 2.43 (m, 2 H), 2.38 (s, 3 H, $S{=}CCH_3$), 2.12 (m, 1 H), 1.86 (m, 1 H), 1.54 (m, 1 H), 1.26 (m, 2 H), 1.11 (m, 1 H), 1.08 (t, 3 H, OCH_2CH_3). ^{13}C NMR (C_6D_6): δ = 166.3 (C_q, C=N), 163.6 (C_q, C3), 151.4 and 145.2 (C_q, C1 and *i*-C Ph), 129.3, 124.0, and 120.3 (2:1:2, Ph), 120.5 (C_q, C8a), 101.9 (CH, C2), 65.3 (OCH_2), 54.7 (CH, C3a), 31.4, 30.0, 29.6, 29.4, and 27.4 (CH_2 each, C4−C8), 26.4 (CH_3), 14.5 (OCH_2CH_3). MS (70 eV); *m/z* (%): 327 (10) [M^+], 118 (100) [$CH_3C{=}NPh]^+$. $C_{20}H_{25}NOS$ (327.5): calcd. C 73.35, H 7.69, N 4.28; found C 72.86, H 7.96, N 3.98.

Acknowledgments

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