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Thiocarbene and alkoxycarbene tungsten complexes exhibit typically different reaction paths ☆

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Abstract

The condensation of (butyl)thiocarbene tungsten complex [$(OC)_5W{=}C(SEt)Bu$] (**1a**) with an α,β-unsaturated *secondary* acid amide $R^2CH{=}CHC({=}O)NHR^1$ **4** in the presence of $POCl_3/Et_3N$ gives cyclopentadienimines **12**, whereas the isostructural alkoxycarbene complex [$(OC)_5W{=}C(OEt)Bu$] (**1c**) under similar conditions affords a (*N*-enamino)ethoxycarbene compound **9**. Furthermore, condensation of the (methyl)thiocarbene tungsten complex [$(OC)_5W{=}C(SEt)Me$] (**1b**) with an amide **4** yields cyclopentenimines **19** and allenylidene complexes **20**, whereas the corresponding ethoxycarbene complex [$(OC)_5W{=}C(OEt)CH_3$] (**1d**) forms 4-*NH*-amino-1-tungsta-1,3,5-hexatrienes **16** under similar conditions.

Keywords: Thiocarbene complexes; Tungsten; Cyclopentadienes; Cyclopentenes

1. Introduction

Fischer alkoxycarbene [1] and aminocarbene [2] complexes have found wide application in organic synthesis [3], whereas thiocarbene complexes have gained much less attention [4–7]. The reaction patterns of thiocarbene complexes known so far are different from those of aminocarbene complexes, but closely related to those of alkoxycarbene compounds in so far as, for example, addition of isocyanides to both thiocarbene and alkoxycarbene complexes gives ketenimine complexes and metal-free ketenimines [4b,8a], addition of phosphines affords ylides [8b], addition of aminoalkynes [4d,9] to (aryl)thiocarbene complexes produces (alkenyl)aminocarbene complexes and indenes [9], and addition of terminal alkynes to (aryl)thiocarbene complexes affords naphthalenes [4d]. Alerted by the observation that (alkenyl)thiocarbene complexes [4d] unexpectedly underwent a base-induced conversion to allenes [10], a transformation that could not be induced with isostructural (alkenyl)ethoxycarbene compounds, our attention was focused more closely to reactivity differences between thiocarbene and alkoxycarbene complexes [11].

2. Results and discussion

Fischer (alkyl)ethoxycarbene are well known to undergo condensation reactions with aldehydes [12a,12b], ketones [13], acid chlorides [12a,14], imines [15], aminoacetales [16], and acid amides [17]. We now report on striking differences in condensation reactions of isostructural thiocarbene and ethoxycarbene complexes with α,β-unsaturated *secondary* acid amides **4**.

2.1. Condensation of thiocarbene complex **1a** with α,β-unsaturated secondary acid amides **4a–e**

To a mixture of thiocarbene complex **1a** and an imidoyl chloride **5a–e**, generated *in situ* from an α,β-unsaturated *secondary* acid amides **4a–e** and $POCl_3/Et_3N$ at ambient temperature, was added triethylamine at −40 °C to give a

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[1] Crystal structure analysis.

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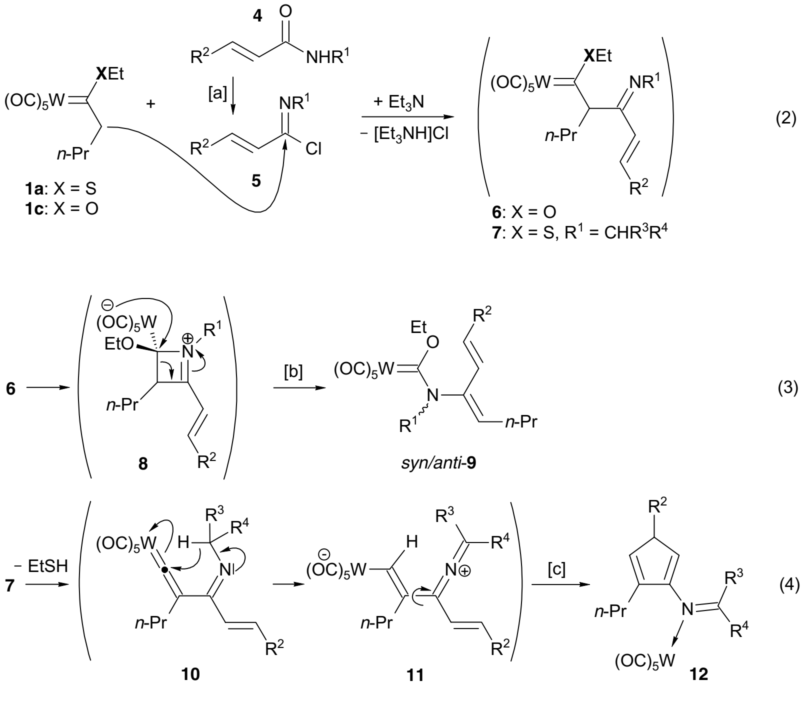
cyclopentadienimine complex **12a**–**e**, which could be isolated by chromatography on silica gel.

Whereas base-induced condensation reactions of ethoxycarbene complexes **1c**,**d** are readily performed at ambient temperature, thiocarbene complexes **1a**,**b** would rearrange under such conditions to vinyl thioethers **2a**,**b** and **3a**,**b** (Eq. (1)) rather than form a condensation product. In order to obtain reasonable yields of condensation products from a thiocarbene complex and an imidoyl chloride **5** (generated *in situ* from an acid amide **4** with $POCl_3/Et_3N$ in *ca.* 48 h at 20 °C according to ^1H NMR measurements) the reaction must be initiated under carefully controlled conditions by addition of triethylamine at −40 °C.

$$\begin{aligned}&(CO)_5W=\underset{\mathbf{1}}{C}(XEt)CH_2R\\&\xrightarrow{NEt_3\,(cat.)}(OC)_5W\leftarrow\underset{\mathbf{2}}{(EtX)CH}=CHR\\&\xrightarrow[-W(CO)_6]{+CO}\underset{\mathbf{3}}{(EtX)CH}=CHR\qquad(1)\end{aligned}$$

1–3	**a**	**b**	**c**	**d**
X	S	S	O	O
R	*n*-Pr	H	*n*-Pr	H

Based on the type of reaction products, the thiocarbene complex **1a** adds to *secondary* imidoyl chlorides **5** preferentially in 1,2-fashion to give a β-iminocarbene complex **7** (Scheme 1). Products resulting from 1,4-addition were not detected in this, but were found in related reactions with α,β-unsaturated *tertiary* acid amides [18]. The reactivity patterns of (β-imino)thiocarbene complexes **7** are typically different from those of (β-imino)ethoxycarbene complexes **6**. Whilst compounds **6** undergo a metalla(di-π-methane) rearrangement to (*N*-enamino)ethoxycarbene complexes **9**, [17d,19] the isostructural compounds **7** quite unexpectedly afforded cyclopentadienimines **12** (Scheme 1). The formation of compounds **12** from complexes **7** is highly regio- and stereoselective. According to experimental results and theoretical calculations, alkoxycarbene complexes **6** seem to prefer an associative reaction (involving a nucleo-philic addition to the carbene carbon atom), whereas thiocarbene complexes **7** preferentially undergo a dissociative reaction

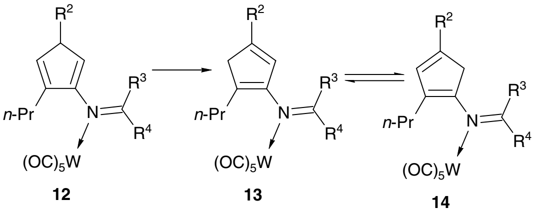


4–14	R¹	R²	R³R⁴	**12**	**13**	**14**	**13**:**14**[e]
a	*i*-Pr	Ph	Me_2	–	44	11	4:1
b	*c*-C_6H_{11}	Ph	C_5H_{10}	–	30	3	10:1
c	CH(Et)Me	Ph	EtMe	–	39	25	1.5:1
d	*i*-Pr	Me	Me_2	32	29[d]	3[d]	10:1
e	*c*-C_6H_{11}	Me	C_5H_{10}	34	31[d]	3[d]	10:1

[a] $POCl_3/NEt_3$, 48 h, 20°C; [b] metalla(di-π-methane)skeletal rearrangement; [c] π-cyclization; [d] formed by base-induced rearrangement of compound **12**; [e] product ratio according to NMR measurements.

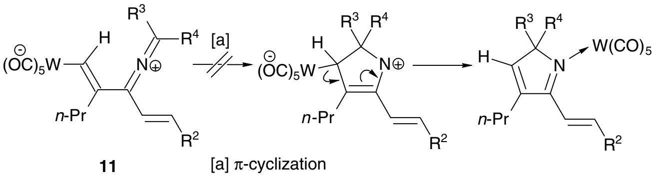
Scheme 1. (*N*-Enamino)ethoxycarbene complexes **9** and cyclopentadienimine complexes **12**–**14** by condensation of ethoxycarbene complex **1c** and thiocarbene complex **1a**, respectively, with α,β-unsaturated *secondary* acid amides **4**.

(by elimination of thiol to give vinylidene compounds **10**) [11]. It is suggested that cyclopentadienimines **12** are derived from vinylidene compounds **10** in straight-forward reactions by hydride transfer to give iminium carbonylmetalates **11**, which undergo π-cyclization to compounds **12**. Based on a series of NMR analyses of product mixtures, it appears that compounds **12** are generated as single isomers, which rearrange during work-up to produce mixtures of compounds **13** and **14** (Eq. (5)).



(5)

It should be noted that the intermediate **11** does not collapse to form a pyrrole complex by an α-cyclization (Eq. (6)), as it has been observed in related reactions of thiocarbene complexes with imidoyl chlorides [11], but is sufficiently long-lasting to allow for rotation around the central C–C bond (s. Scheme 1), as requisite for formation of the π-cyclization product **12** in a thermodynamically controlled process.



(6)

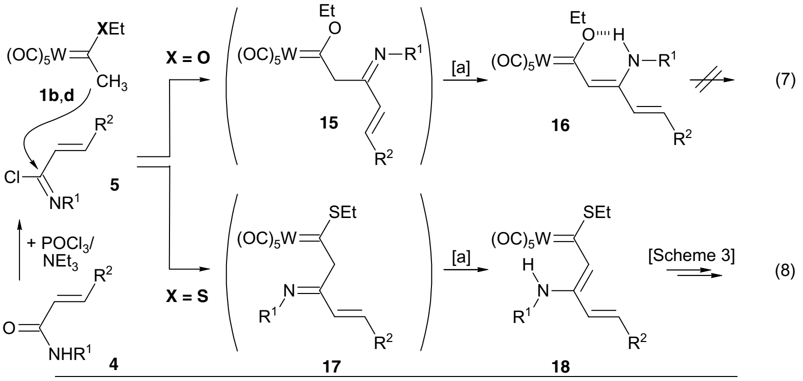
2.2. Condensation of (methyl)thiocarbene complex 1b with α,β-unsaturated secondary acid amides 4

The condensation of the (methyl)thiocarbene complex **1b**, and (methyl)ethoxycarbene complex **1d**, respectively, with an α,β-unsaturated *secondary* amide **4** takes a course significantly different from that observed with the corresponding (butyl)thiocarbene complex **1a**, and (butyl)ethoxycarbene complex **1c**, respectively (s. Scheme 1), except for the first step, resulting in formation of a (β-imino)thiocarbene complex **15**, and (β-imino)ethoxycarbene complex **17**, respectively (Scheme 2).

Ethoxycarbene complexes **15** form metallahexatrienes **16** which are stabilized by a hydrogen bridge [17d], whereas the thiocarbene complexes **17** lack this type of stabilization and therefore readily undergo π-cyclization to cyclopentenimine complexes **19** (Eq. (9), Scheme 3), and – in competition – an elimination of thiol to yield (deep blue) allenylidene complexes **20** (Eq. (10), Scheme 3) [20]. The conformation required for the π-cyclization of compounds **18** is readily achieved due to the high flexibility of the carbon backbone of this highly polar iminium carbonylmetalate.

2.3. Structure elucidation

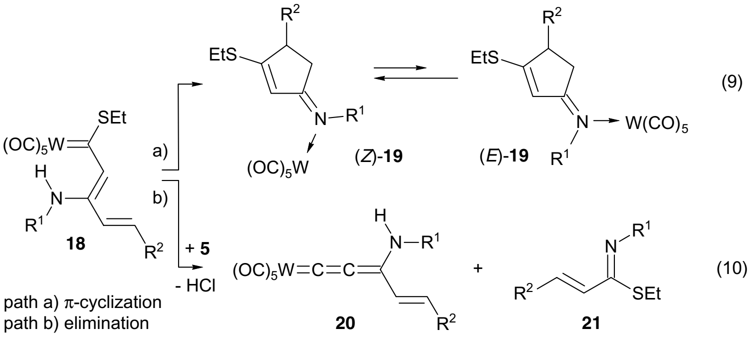
The molecular structures of the cyclopentadienes **12**, **13** and **14** are based on ^1H and ^{13}C NMR data. Compounds **12** can be distinguished from compounds **13** and **14** due to the presence of two olefinic protons. The methylene unit of the cyclopentadienes **13** and **14** exhibits an AB system (**13d**: $\delta_H = 3.07$ and 2.94, $^2J = 22.7$ Hz; **14d**: $\delta_H = 3.42$ and 2.76, $^2J = 22.7$ Hz). The A_1-bands in the IR spectra of compounds **12**–**14** (e.g. **13a**: $\tilde{\nu} = 2068.5\ cm^{-1}$) are in a range



4–18	a	b	D	f	g	h	i	j	K
R^1	*i*-Pr	*c*-C_6H_{11}	*i*-Pr	Me	*n*-Pr	Allyl	Ph	Me	*n*-Pr
R^2	Ph	Ph	Me	Ph	Ph	Ph	Ph	Me	Me
5 [%]	quant.[c]	[b]	[b]	[b]	85[c]	[b]	[b]	[b]	[b]
18 [%][d]	–	36	21	49	56	–	–	–	–

[a] 1,3 H-shift; [b] NMR data were not recorded; [c] NMR data were recorded from 1:1 mixtures of amides and $POCl_3$ (yield estimated based on ^1H NMR measurements); [d] isolated chemical yield.

Scheme 2. 4-Amino-1-tungsta-1,3,5-hexatrienes **16** and 4-amino-1-tungsta-1,3,5-hexatrienes **18**, respectively, by condensation of (methyl)ethoxycarbene complexes **1d** and (methyl)thiocarbene complexes **1b**, respectively, with α,β-unsaturated *secondary* acid amides **4**.



18–21	R^1	R^2	19[a]	(*E*/*Z*)-19	20[a]	21[a]
a	*i*-Pr	Ph	53	[c]	12	10
b	*c*-C_6H_{11}	Ph	36[b]	[c]	17	[e]
d	*i*-Pr	Me	21[b]	[c]	–	–
f	Me	Ph	35	2:3	22	[e]
g	*n*-Pr	Ph	56[b]	3:4	31	[e]
h	Allyl	Ph	22	7:10	11	[e]
i	Ph	Ph	2	[c]	[d]	37
j	Me	Me	26	2:3	–	–
k	*n*-Pr	Me	11	9:10	–	–

[a] isolated chemical yields; [b] corresponds to the yield of compound **18**; [c] *E*/*Z*-**19** equilibration not observed; [d] facile decomposition; [e] could not be isolated due to hydrolysis on silica gel.

Scheme 3. Competition between the π-cyclization of 4-amino-1-tungsta-1,3,5-hexatrienes **18** to cyclopentenimines **19**, and the elimination of ethanethiol to allenylidene complexes **20**.

expected for a $W(CO)_5$ unit coordinated to the nitrogen of an imino function [21]. The configurational assignment of the structures **13** and **14** is based on NOE experiments. Irradiation of the methylene protons of the cyclopentadiene **13a** results in a positive enhancement of the signal of the $CH_2CH_2CH_3$ protons. The high-field signal of the two $N(CH_3)_2$ proton signals is observed on irradiation of the olefinic C*H* proton. Compound **14a** shows the corresponding NOEs between the CH_2 group and the high-field signal of the two $N(CH_3)_2$ proton signals as well as between the olefinic proton and the $CH_2CH_2CH_3$ protons. This assignment corresponds to chemical shifts observed for compounds **13c** and **14c**. The (*Z*)-configuration is prevailing for steric reasons and the low-field NCH_3 proton signals can be assigned to the (*E*)-isomers in which the methyl group is directed towards the $W(CO)_5$ unit.

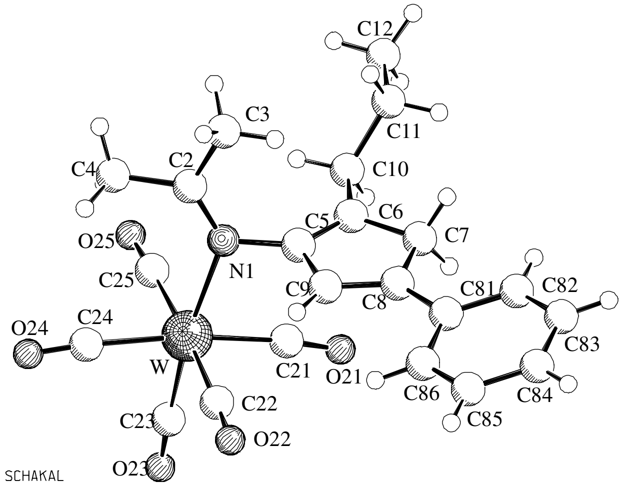


Fig. 1. Molecular structure of the cyclopentadienimine complex **13a** with selected bond lengths (Å), bond angles (°) and dihedral angles (deg): W–N1 2.286(2), N1–C2 1.289(4), N1–C5 1.446(4), C5–C6 1.340(4), C6–C7 1.511(4), C7–C8 1.495(4), C8–C9 1.361(4), C9–C5 1.460(4), C8–C81 1.465(4), C5–N1–C2 116.9(3), C5–N1–W 111.0(2), W–N1–C2 132.2(2), N1–C2–C3 123.4(3), N1–C2–C4 121.2(3), C3–C2–C4 115.3(3), N1–C5–C9 122.2(3), N1–C5–C6 126.3(3), C6–C5–C9 111.5(3), C5–C6–C7 107.0(3), C6–C7–C8 104.8(3), C7–C8–C9 108.3(3), C8–C9–C5 108.5 (3), W–N1–C5–C6 94.2(3), W–N1–C5–C9 –82.8(3), C5–N1–C2–C4 178.4(3), C5–N1–C2–C3 –2.9(4), C9–C5–C6–C7 0.5(3), C7–C8–C9–C5 –0.3(3), C7–C8–C81–C82 –170.0(3).

The cyclopentadienimine complex **13a** was characterized also by a crystal structure analysis (Fig. 1). The cyclopentadiene ring of compound **13a** is almost planar [C9–C5–C6–C7 0.5(3)°, C7–C8–C9–C5 –0.3(3)°]. The five-membered ring and the plane comprised by the atoms W, N and C2 are strongly distorted against each other [W–N1–C5–C6–94.2(3)°, W–N1–C5–C9–82.8(3)°]. The C=N bond distance of 1.289(4) Å in compound **13a** is shorter than in the iminium carbonylmetalate **18b** [C5–N1 1.328(3) Å]. Compounds **18**, **19** and **20** are easily distinguished by the position of the A_1-bands in the IR spectra: compounds **18** (e.g. **18f**: $\tilde{\nu} = 2060.9\ \mathrm{cm}^{-1}$), characteristical of 1-tungsta-1,3,5-hexatrienes, compounds **19** (e.g. (*Z*)-**19g**: $\tilde{\nu} = 2065.8\ \mathrm{cm}^{-1}$), characteristical of σ-coordination to C=NR group. The very small A_1-bands of the allenylidene complexes **20f–e** are shifted to exceptionally high wave numbers in a very nar-

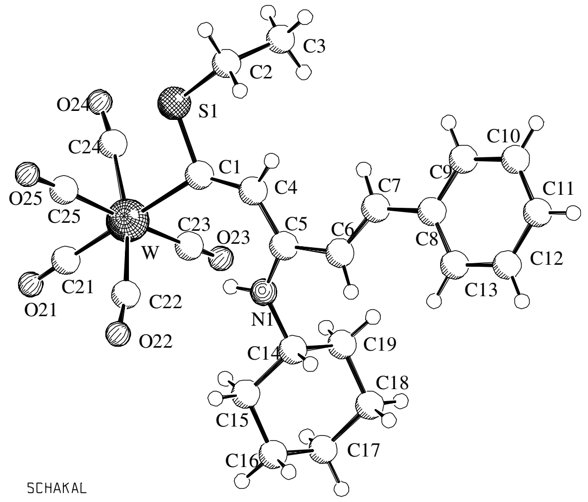


Fig. 2. Molecular structure of the 4-amino-1-tungsta-1,3,5-hexatriene **18b** with selected bond lengths (Å), bond angles (°) and dihedral angles (°): W–C1 2.280(3), C1–C4 1.390(4), C4–C5 1.417(4), C5–C6 1.469(4), C6–C7 1.332(4), C7–C8 1.466(4), C5–N1 1.328(3), N1–C14 1.473(3), C1–S1 1.742(3), W–C1–S 106.7(1), S–C1–C4 116.2(2), W–C1–C4 137.0(2), C1–C4–C5 129.0(3), C4–C5–N1 122.8(2), C6–C5–N1 117.7(2), C4–C5–C6 119.5(2), C5–C6–C7 123.9 (3), C6–C7–C8 127.1(3), C5–N1–C14 128.6(2), W–C1–C4–C5 3.6(4), S–C1–C4–C5 179.2(2), C1–C4–C5–N1 0.1(4), C1–C4–C5–C6 –178.5(2), C4–C5–C6–C7 –26.4(4), C5–C6–C7–C8 179.3(3), C6–C7–C8–C9 180.0(3), C4–C5–N1–C14 175.0(2), C5–N1–C14–C15 162.5(3).

row range of 2082.8 to 2083.0 cm^{-1} (e.g. **20f**: $\tilde{\nu} = 2083.0$ cm^{-1}) [22]. The configuration of compounds (*Z*)-**19** and (*E*)-**19** was assigned by NOE experiments of compounds **19f** and **19j**. While the (*Z*)-isomers showed NOE between *N*-CH$_3$ and the C*H*$_2$ group of the cyclopentene ring, the expected NOE of the (*E*)-isomer between N-CH$_3$ and the olefinic C*H* proton could also be observed (see Fig. 2).

The ligand backbone W–C1–C4–C5–N1 of compound **18b** is essentially planar. Its bond angles W–C1–C4 (137.0(2)°), C1–C4–C5 (129.0(3)°), C4–C5–N1 (122.8(2)°) and C5–N1–C14 (128.6(2)°) are above 120°. The N*H* proton is located between two neighbouring carbonyl carbon atoms. This 4-amino-1,3,5-metallatriene shows a carbiminium carbonylmetalate unit, which is characterized by a pattern of alternating bond distances of the W–C=C–C=N$^+$ backbone [W–C1 2.280(3) Å, C1–C4 1.390(4) Å, C4–C5 1.417(4) Å, C5–N1 1.328(3) Å]. The W–C1–C4–C5 portion [dihedral angle 3.6(4)°] and the C1–C4–C5–N1 portion [dihedral angle 0.1(4)°] of the molecule both adopt a *cis* configuration. The C4–C5–C6–C7 unit [dihedral angle −26.4(4)°] exhibits a *cisoidal* arrangement.

3. Conclusion

The reactivity patterns of alkylcarbene complexes **1a**–**d** with α,β-unsaturated *secondary* acid amides R^{2}CH=CHC(=O)NHR^1 **4** in the presence of POCl$_3$/Et$_3$N have been unravelled, and it has been shown that β-iminocarbene complexes are key-intermediates in these reactions. The reactivity of a (β-imino)*thio*carbene complexes is significantly different from that of an isostructural (β-imino)*ethoxy*carbene complex. Furthermore, fundamental changes in reactivities are observed also within the groups of (β-imino)heterocarbene complexes derived from methylcarbene, and alkylcarbene complexes other than methylcarbene complexes, respectively. The condensation of (*n*-butyl)thiocarbene complex [(OC)$_5$W=C(SEt)(*n*-Bu)] (**1a**) with α,β-unsaturated *secondary* acid amides **4** yields cyclopentadienimine complexes **12**–**14** (reaction initiated by 1,2-addition and subsequent π-cyclization), whereas the (methyl)thiocarbene complex [(OC)$_5$W=C(SEt)CH$_3$] (**1b**) under similar conditions affords cyclopentenimine complexes **19** and allenylidene complexes **20** (reaction initiated by 1,2-addition and aubsequent hydrogen shift). The formation of different products from β-iminocarbene complexes is attributed to minor differences in activation energies of the single steps involved in the multistep-reaction sequences. In line with theoretical predictions [11], the observation of allenylidene complexes **20** indicates that a dissociative reaction step is favoured with thiocarbene complexes over an associative process.

4. Experimental

All operations were carried out under an atmosphere of argon. All solvents were dried and distilled prior to use. All ^{1}H and ^{13}C NMR spectra were routinely recorded in CDCl$_3$ or C$_6$D$_6$ on a Bruker ARX 300 instrument. COSY, HMQC, HMBC, TOCSY and NOE experiments were performed on either a Bruker AMX 400, a Varian 500 Inova or a Varian 600 unity plus instrument. The chemical shifts are given in ppm with TMS ($\delta = 0$ ppm) and the residue signal of CDCl$_3$ and C$_6$D$_6$ ($\delta = 77$ and 128 ppm) as the internal standards for ^{1}H and ^{13}C NMR spectra. IR spectra were measured on a Bruker Vector 22 FT-IR spectrometer. EI and ESI mass spectra were obtained on a double-focussing Sektorfeld-MS MAT8200 (Thermo-Finnigan-MAT, Bremen) and QUATTRO LCZ (Waters-Micromass, Manchester, UK) spectrometers. HRMS spectra were determined on a MicroTof (Bruker Daltronics, Bremen) instrument with loop injection; for mass calibration sodium formate clusters were used. Elemental analyses were determined on an elementar vario EL III instrument. Analytical TLC plates, Merck TLC aluminium sheets Silica gel 60 F$_{254}$, were viewed by UV light (254 nm) and stained by iodine. R_f values refer to TLC tests. Merck Silica gel 60 F was used for column chromatography. Flash chromatography was performed under an argon atmosphere. Compound **1a** was prepared according to the literature [11].

4.1. Pentacarbonyl[1-(ethylsulfanyl)eth-1-ylidene]tungsten (1b)

(The procedure given is an adjustment of the procedure presented by Aumann and Schröder [4b] to the special requirements of (alkyl)thiocarbene complexes of tungsten; see Eq. (1)). To pentacarbonyl[1-(ethoxy)eth-1-ylidene]-

tungsten (**1d**, 7.92 g, 20.0 mmol) and sodiumcarbonate (2.12 g, 20.0 mmol) in 150 mL dry methanol in a 250-mL round bottom flask is added ethanethiol (1.4 mL, 22.1 mmol) at −40 °C. The progress of the reaction can be monitored by TLC or by IR measurements. On addition of phosphoric acid (2.16 g, 22.0 mmol) after 3 h stirring at −40 °C the color of the solution turns from yellow to red. After addition of 75 mL of water the red carbene complex is extracted with *n*-pentane. Crystallization on dry ice yields analytically pure compound **1b** (7.00 g, 85%, $R_f = 0.3$ in *n*-pentane) in a 10:1 *Z*/*E*-ratio.

(*Z*)-**1b**

(E)-**1b**

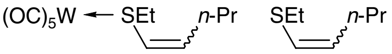
4.1.1. Data for (Z)-*1b* {(E)-*1b*, ca. 10%}

^{1}H NMR (300 MHz, CDCl$_3$, 298 K): δ 3.37 {3.43} (s, 3H; CCH$_3$), 3.02 {3.64} (q, ^3J(H,H) = 7.5 Hz {7.5 Hz}, 2H; SCH_2CH$_3$), 1.37 {1.54} (t, ^3J(H,H) = 7.5 Hz {7.5 Hz}, 3H; SCH$_2$CH_3); ^{13}C NMR (75 MHz, CDCl$_3$, 298 K): δ 332.2 {[23]} (C$_q$; W=C), 207.3 and 197.6 {[23]} [each C$_q$, 1:4, *trans*- and *cis*-CO; W(CO)$_5$], 47.7 {51.8} (CH$_3$; C*C*H$_3$), 37.2 {42.4} (CH$_2$; S*C*H$_2$CH3), 11.5 {12.4} (CH$_3$; SCH$_2$*C*H$_3$); IR (cyclohexane) [cm^{-1} (%)]: $\tilde{\nu}$ = 2066.4 (40) {2058.9 (4)}, 2058.9 (2), 1950.0 (100) [ν(C≡O)]; MS (70 eV): *m*/*z* for ^{184}W (%): 412 (20) [*M*]$^+$, 486 (10) [*M* − CO]$^+$, 328 (35), 298 (35), 270 (100), 127 (50); elemental analysis (%) calcd for C$_9$H$_8$O$_5$SW (412.1): C, 26.23; H, 1.96; found: C, 26.05; H, 1.70%.

4.2. Pentacarbonyl[1-(ethylsulfanyl)pent-1-ene, S-W]-tungsten (*2a*), 1-(ethylsulfanyl)pent-1-ene (*3a*)

To pentacarbonyl[1-(ethylsulfanyl)but-1-ylidene]tungsten(0) (**1a**, 113 mg, 0.25 mmol) in 1 mL of CH$_2$Cl$_2$ is added triethylamine (10 mg, 0.1 mmol). Within 15 min at 20 °C the solution turned from dark red to yellow. Solvent was removed to give a 5:1 mixture of isomeric compounds (*Z*)-**2a** and (*E*)-**2a** [R_f (1*Z*)-**2a** = 0.5, R_f (1*E*)-**2a** = 0.4 in *n*-pentane, yellow oil], which are spontaneously transformed into compounds **3a** by addition of one equivalent of pyridine.

(*E*/*Z*)-**2a**



(E/Z)-**3a**

4.2.1. Data for (Z)-*2a*{(E)-*2a*}

^{1}H NMR (400 MHz, CDCl$_3$, 300 K): δ 5.97 {6.10} (dt, ^3J(H,H) = 8.8 Hz {14.7 Hz}, ^3J(H,H) = 7.4 Hz {7.1 Hz}, 1H; 2-H), 5.88 {5.86} (dt, ^3J(H,H) = 8.8 Hz {14.7 Hz}, ^4J(H,H) = 1.3 Hz {1.4 Hz}, 1H; 1-H), 2.84 {2.84} (q, ^3J(H,H) = 7.4 Hz {7.4 Hz}, 2H; SCH$_2$), 2.30 {2.21} (m, 2H; 3-H$_2$), 1.47 {1.47} (m, 2H; 4-H$_2$), 1.28 {1.29} (t, ^3J(H,H) = 7.4 Hz {7.4 Hz}, 3H; SCH$_2$CH_3), 0.96 {0.94} (t, ^3J(H,H) = 7.1 Hz {7.4 Hz}, 3H; 5-H$_3$); ^{13}C NMR (100 MHz, CDCl$_3$, 300 K): δ 200.2 and 197.1 {200.4 and 197.2} [each C$_q$, 1:4, *trans*- and *cis*-CO; W(CO)$_5$], 140.2 {142.6} (CH; C2), 124.3 {122.9} (CH; C1), 40.1 {39.6} (CH$_2$; SCH$_2$), 31.0 {34.3} (CH$_2$; C3), 22.0 {21.9} (CH$_2$; C4), 14.8 {14.3} (SCH$_2$CH$_3$), 13.6 {13.5} (CH$_3$; C5); IR (cyclohexane) [cm^{-1} (%)]: $\tilde{\nu}$ = 2074.0 (10), 1939.9 (100), 1928.7 (40) [ν(C≡O)]; IR (diffuse reflexion) [cm^{-1} (%)]: $\tilde{\nu}$ = 2073.3 (10), 1890.0 (100) [ν(C≡O)], 1454.1 (5); MS (70 eV): *m*/*z* for ^{184}W (%): 454.0 (30) [*M*]$^+$, 426.0 (10) [*M* − CO]$^+$, 370.0 (10) [*M* − 3CO]$^+$, 341.0 (100); HRMS (ESI) calcd for C$_{12}$H$_{14}$SO$_5$WNa [*M* + Na]$^+$: 476.9963; found: 476.9948.

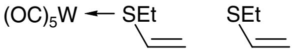
4.2.2. Data for (Z)-*3a* {(E)-*3a*}

^{1}H NMR (400 MHz, CDCl$_3$, 300 K): δ 5.93 {5.92} (dt, ^3J(H,H) = 9.4 Hz {15.1 Hz}, ^4J(H,H) = 1.4 Hz {1.4 Hz}, 1H; 1-H), 5.57 {5.63} (dt, ^3J(H,H) = 9.4 Hz {15.1 Hz}, ^3J(H,H) = 7.2 Hz {7.0 Hz}, 1H; 2-H), 2.66 {2.65} (q, ^3J(H,H) = 7.4 Hz {7.4 Hz}, 2H; SCH$_2$), 2.09 {2.06} (m, 2H; 3-H$_2$), 1.41 {1.41} (m, 2H; 4-H$_2$), 1.28 {1.27} (t, ^3J(H,H) = 7.4 Hz {7.4 Hz}, 3H; SCH$_2$CH_3), 0.91 {0.91} (t, ^3J(H,H) = 7.4 Hz {7.4 Hz}, 3H; 5-H$_3$); ^{13}C NMR (100 MHz, CDCl$_3$, 300 K): δ 129.4 {130.8} (CH; C2), 124.5 {122.4} (CH; C1), 31.0 {35.1} (CH$_2$; C3), 27.6 {26.6} (CH$_2$; SCH$_2$), 22.0 {22.3} (CH$_2$; C4), 15.3 {14.4} (SCH$_2$CH$_3$), 13.5 {13.3} (CH$_3$; C5).

4.3. Pentacarbonyl[(ethylsulfanyl)ethene, S–W]tungsten (0) (*2b*), (ethylsulfanyl)ethene (*3b*)

To pentacarbonyl[1-(ethylsulfanyl)eth-1-ylidene]tungsten(0) (**1b**, 103 mg, 0.25 mmol) in 1 mL of CH$_2$Cl$_2$ is added triethylamine (10 mg, 0.1 mmol). After 4 h, 20 °C the solution turns from red to yellow. Evaporation of solvent gives compound **2b** (R_f = 0.3 in *n*-pentane, yellow oil) as the only product, which is transformed into compound **3b** by addition of one equivalent of pyridine.

2b



3b

4.3.1. Data for *2b*

^{1}H NMR (400 MHz, C$_6$D$_6$, 300 K): δ 5.47 (dd, ^3J(H,H) = 16.3 Hz, ^3J(H,H) = 9.3 Hz, 1H; 1-H), 4.91 (d, ^2J(H,H) = 0.8 Hz, ^3J(H,H) = 16.3 Hz, 1 H; *cis*-2-H), 4.79 (d, ^2J(H,H) = 0.8 Hz, ^3J(H,H) = 9.3 Hz, 1H; *trans*-2-H), 2.06 (q, ^3J(H,H) = 7.3 Hz, 2H; SCH$_2$), 0.62 (t, ^3J(H,H) = 7.3 Hz, 3H; SCH$_2$CH_3); ^{13}C NMR (100 MHz, CDCl$_3$, 300 K): δ 202.0 and 197.4 [each C$_q$, 1:4, *trans*- and *cis*-CO; W(CO)$_5$], 132.0 (CH; C1), 121.9 (CH; C2), 38.2 (CH$_2$; SCH$_2$), 13.9 (SCH$_2$CH$_3$); IR (cyclohexane) [cm^{-1} (%)]: $\tilde{\nu}$ = 2075.1 (10), 1941.9 (100), 1930.9 (40) [ν(C≡O)]; MS-ESI (ESI): *m*/*z* (%) = 411.1 (100) [*M* − H]$^-$.

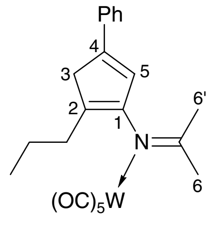
4.3.2. Data for ***3b***

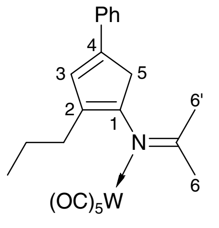
^{1}H NMR (400 MHz, C_6D_6, 300 K): δ 6.17 (dd, ^3J(H,H) = 16.7 Hz, ^3J(H,H) = 10.2 Hz, 1H; 1-H), 5.02 (d, ^3J(H,H) = 10.2 Hz, 1H; *cis*-2-H), 4.98 (d, ^3J(H,H) = 16.7 Hz, 1H; *trans*-2-H), 2.31 (q, ^3J(H,H) = 7.4 Hz, 2H; SCH_2), 0.99 (t, ^3J(H,H) = 7.4 Hz, 3H; SCH_2CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 300 K): δ 132.9 (CH; C1), 110.1 (CH; C2), 25.3 (CH_2; SCH_2), 14.1 (SCH_2CH_3).

*4.4. Pentacarbonyl[isopropylidene-(4-phenyl-2-propyl-cyclopenta-1,4-dienyl)-amine, N-W]tungsten(0) (**13a**), pentacarbonyl[isopropylidene-(4-phenyl-2-propyl-cyclopenta-1,3-dienyl)- amine, N-W]tungsten(0) (**14a**)*

(*E*)-*N*-Isopropyl-3-phenyl-acrylimidoyl chloride (**5a**) (generated *in situ* by addition of (2*E*)-*N*-isopropyl-3-phenyl acrylamide (**4a**, 378 mg, 2.0 mmol) to phosphorous oxychloride (306 mg, 2.0 mmol) in dry dichloromethane (2 mL) in a 3-mL screw-top vessel at 20 °C, 48 h) was added to pentacarbonyl[1-(ethylsulfanyl)but-1-ylidene]tungsten(0) (**1a**, 454 mg, 1.0 mmol) in dry dichloromethane (3 mL). A color change to dark blue is observed while triethylamine (404 mg, 4.0 mmol) is added at −40 °C. On warming to 20 °C after 10 min, the color fades to yellow. Evaporation of the solvent and flash chromatography at 20 °C on silica gel (40 × 1 cm, 10:1 *n*-pentane/diethyl ether) affords a bright yellow 4:1 mixture of compounds **13a** (260 mg, 46%, R_f = 0.5 in 10:1 *n*-pentane/diethyl ether) and **14a** (65 mg, 12%, R_f = 0.4 in 10:1 *n*-pentane/diethyl ether). A more polar colorless fraction contained compound **21a** (105 mg, 45%, R_f = 0.3 in *n*-pentane/diethyl ether 10:1).

13a





14a

*4.4.1. Spectroscopic data of **13a** (obtained from a 4:1 mixture of compounds **13a** and **14a**)*

^{1}H NMR (300 MHz, $CDCl_3$, 303 K): δ 7.48 (m, 2H; *o*-CH Ph), 7.33 (m, 2 H; *m*-CH Ph), 7.22 (m, 1H; *p*-CH Ph), 6.59 (s, 1H; 5-H, NOE (+) with 6′-NCH_3), 3.59 and 3.52 (AB system, ^2J(H,H) = 23.0 Hz, 2H; 3-H_2, NOE (+) with $CH_2CH_2CH_3$), 2.52 (s, 3H; 6-H_3), 2.18 (m, 2H; $CH_2CH_2CH_3$), 2.02 (s, 3H; 6′-H_3), 1.60 (m, 2H; $CH_2CH_2CH_3$), 0.99 (t, 3H; $CH_2CH_2CH_3$); ^{13}C NMR (75 MHz, $CDCl_3$, 303 K): δ 202.6 and 198.5 [each C_q, 1:4, *trans*- and *cis*-CO; $W(CO)_5$], 184.0 (C_q; C=N), 152.3 (C_q; C1), 144.9 (C_q; C4), 135.4 (C_q; *i*-C Ph), 128.8 (CH; *m*-C Ph), 127.3 (CH; *p*-C Ph), 126.5 (C_q; C2), 124.9 (CH; C5), 124.8 (CH; *o*-C Ph), 40.5 (CH_2; C3), 31.9 (CH_3; C6), 29.7 ($CH_2CH_2CH_3$), 23.7 (CH_3; C6′), 22.0 ($CH_2CH_2CH_3$), 14.7 ($CH_2CH_2CH_3$); IR (cyclohexane) [cm^{-1} (%)]: $\tilde{\nu}$ = 2068.5 (10), 1969.4 (5), 1927.9 (100), 1913.1 (40) [ν(C≡O)]; HRMS (ESI) calcd for $C_{22}H_{21}NO_5WNa$ $[M + Na]^+$: 586.0825; found: 586.0859; HRMS (ESI) calcd for $C_{20}H_{20}NO_3W$ $[M - 2CO - H]^-$: 506.0961; found: 506.0996; elemental analysis (%) calcd for $C_{22}H_{21}NO_5W$ (563.1): C, 46.91; H, 3.76; N, 2.49; found: C, 46.98; H, 3.81; N, 2.36%.

4.4.2. Molecular structure analysis of bf 13a (code 3339.AUM)

Formula $C_{22}H_{21}NO_5W$, M_r = 563.25 g mol^{-1}, yellow crystal, 0.25 × 0.20 × 0.10 mm, a = 10.061(1), b = 10.615(1), c = 11.743(1) Å, α = 71.60(1)°, β = 82.21(1)°, γ = 68.48(1)°, V = 1106.8(2) Å^3, ρ_{calcd} = 1.690 g cm^{-3}, μ = 52.49 cm^{-1}, empirical absorption correction ($0.354 \leqslant T \leqslant 0.622$), Z = 2, triclinic, space group $P\bar{1}$ (no. 2), λ = 0.71073 Å, T = 198 K, ω and φ scans, 7275 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda]_{max}$ = 0.66 Å^{-1}, 5219 independent (R_{int} = 0.021) and 4869 observed reflections [$I \geqslant 2\sigma(I)$], 265 refined parameters, R = 0.023, wR_2 = 0.057, max./min. residual electron density 0.71/–1.41 e Å^{-3}, hydrogen atoms calculated and refined as riding atoms [24].

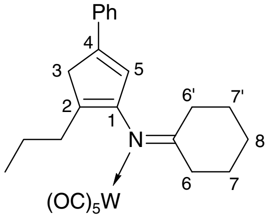
4.4.3. Data for ***14a***

^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ 7.44 (m, 2H; *o*-CH Ph), 7.33 (m, 2H; *m*-CH Ph), 7.20 (m, 1H; *p*-CH Ph), 6.73 (s, 1H; 3-H, NOE (+) with $CH_2CH_2CH_3$), 3.89 and 3.28 (AB system, ^2J(H,H) = 22.7 Hz, 2H; 5-H_2, NOE (+) with 6′-NCH_3 on irradiation at 3.28), 2.52 (s, 3H; 6-H_3), 2.10 (m, 2H; $CH_2CH_2CH_3$), 2.02 (s, 3H; 6′-H_3), 1.60 (m, 2 H; $CH_2CH_2CH_3$), 0.99 (t, 3H; $CH_2CH_2CH_3$); ^{13}C NMR (100 MHz, $CDCl_3$, 300 K): δ 202.4 and 198.4 [each C_q, 1:4, *trans*- and *cis*-CO; $W(CO)_5$], 184.8 (C_q; C=N), 151.8 (C_q; C1), 139.4 (C_q; C4), 135.1 (C_q; *i*-C Ph), 130.1 (C_q; C2), 128.7 (CH; *m*-CH Ph), 127.3 (CH; C3), 127.0 (CH; *p*-CH Ph), 124.6 (CH; *o*-CH Ph), 41.1 (CH_2; C5), 32.0 (CH_3; C6), 28.8 ($CH_2CH_2CH_3$), 23.9 (CH_3; C6′), 20.9 ($CH_2CH_2CH_3$), 14.5 ($CH_2CH_2CH_3$).

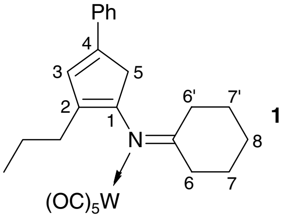
*4.5. Pentacarbonyl[cyclohexylidene-(4-phenyl-2-propyl-cyclopenta-1,4-dienyl)-amine, N-W]tungsten(0) (**13b**), pentacarbonyl[cyclohexylidene-(4-phenyl-2-propyl-cyclopenta-1,3-dienyl)- amine, N-W]tungsten(0) (**14b**)*

(*E*)-*N*-Cyclohexyl-3-phenyl-acrylimidoyl chloride (**5b**), generated *in situ* from (2*E*)-*N*-cyclohexyl-3-phenyl acrylamide (**4b**, 458 mg, 2.0 mmol) and phosphorous oxychloride (306 mg, 2.0 mmol) in dry dichloromethane (2 mL) at 20 °C, 48 h in a 3-mL screw-top vessel, was added to pentacarbonyl[1-(ethylsulfanyl)but-1-ylidene]tungsten(0) (**1a**, 454 mg, 1.0 mmol) in dry dichloromethane (3 mL). Triethylamine (404 mg, 4.0 mmol) was added at −40 °C and the mixture turned dark blue. The color faded to yellow on warming to 20 °C after 10 min. Evaporation of the solvent and flash chromatography at 20 °C on silica gel (40 × 1 cm, 10:1 *n*-pentane/diethyl ether) afforded a bright yellow 10:1 mixture of compounds **13b** (183 mg, 30%, $R_f = 0.6$ in 10:1 *n*-pentane/diethyl ether) and **14b** (18 mg, 3%, $R_f = 0.5$ in 10:1 *n*-pentane/diethyl ether).

13b



14b



4.5.1. Data for **13b**

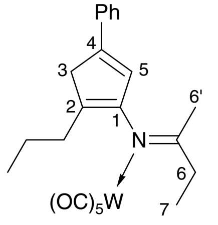
^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ 7.48 (m, 2H; *o*-CH Ph), 7.33 (m, 2H; *m*-CH Ph), 7.22 (m, 1H; *p*-CH Ph), 6.59 (s, 1H; 5-H), 3.55 (s, 2H; 3-H_2), 2.89 (m, 2H; 6-H_2), 2.37 (m, 2H; 6′-H_2), 1.93 and 1.67 (each m, 2:4 H; 7-, 7′- and 8-CH_2), 2.18 (m, 2H; $CH_2CH_2CH_3$), 1.55 (m, 2H; $CH_2CH_2CH_3$), 0.99 (t, 3H; $CH_2CH_2CH_3$); ^{13}C NMR (100 MHz, $CDCl_3$, 300 K): δ 202.8 and 198.5 [each C_q, 1:4, *trans*- and *cis*-CO; $W(CO)_5$], 189.6 (C_q; C=N), 151.4 (C_q; C1), 144.6 (C_q; C4), 135.4 (C_q; *i*-C Ph), 128.7 (CH; *m*-C Ph), 127.2 (CH; *p*-C Ph), 126.6 (C_q; C2), 125.5 (CH; C5), 124.8 (CH; *o*-C Ph), 42.1 (CH_2; C6), 40.5 (CH_2; C3), 33.0 (CH_2; C6′), 29.7 ($CH_2CH_2CH_3$), 27.9 and 27.7 (CH_2; C7 and C7′), 25.1 (CH_2; C8), 22.2 ($CH_2CH_2CH_3$), 14.6 ($CH_2CH_2CH_3$); IR (cyclohexane) [cm^{-1} (%)]: $\tilde{\nu} =$ 2068.0 (10), 1968.5 (3), 1939.7 (25), 1928.2 (100), 1911.6 (40) [ν(C≡O)]; MS (70 eV): *m/z* for ^{184}W (%): 603.3 (2) $[M]^+$, 547 (5) $[M - 2CO]^+$, 279 (50) $[M - W(CO)_5]^+$, 250 (100) $[M - W(CO)_5 - C_2H_5]^+$; HRMS (ESI) calcd for $C_{23}H_{24}NO_3W$ $[M - 2CO - H]^-$: 546.1264; found: 546.1292; elemental analysis (%) calcd for $C_{25}H_{25}NO_5W$ (544.3): C 49.77, H 4.18, N 2.32; found C 49.83, H 4.22, N 2.17.

4.5.2. Data for **14b**

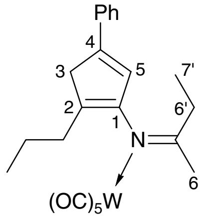
^{1}H NMR (300 MHz, $CDCl_3$, 303 K; for phenyl and cyclohexyl signals see **13b**): δ 6.73 (s, 1H; 3-H), 4.01 and 3.18 (AB system, ^2J(H,H) = 22.6 Hz, 2H; 5-H_2), 0.88 (t, 3H; $CH_2CH_2CH_3$); ^{13}C NMR (75 MHz, $CDCl_3$, 303 K): δ 202.6 and 198.4 [each C_q, 1:4, *trans*- and *cis*-CO; $W(CO)_5$], 190.6 (C_q; C=N), 150.9 (C_q; C1), 139.2 (C_q; C4), 135.2 (C_q; *i*-C Ph), 130.2 (C_q; C2), 128.6 (CH; *m*-CH Ph), 127.4 (CH; C3), 126.9 (CH; *p*-CH Ph), 124.5 (CH; *o*-CH Ph), 42.3 (CH_2; C6), 41.7 (CH_2; C5), 33.3 (CH_2; C6′), 28.8 ($CH_2CH_2CH_3$), 27.9 and 27.7 (CH_2; C7 and C7′), 25.8 (CH_2; C8), 21.2 ($CH_2CH_2CH_3$), 14.5 ($CH_2CH_2CH_3$); for IR and MS data see compound **13b**.

4.6. Pentacarbonyl[(1-methyl-propylidene)-(4-phenyl-2-propyl-cyclopenta-1,4- dienyl)-amine, N-W]tungsten(0) (**13c**), pentacarbonyl[(1-methyl-propylidene)-(4-phenyl-2-propyl-cyclopenta-1,3- dienyl)-amine, N-W]tungsten(0) (**14c**)

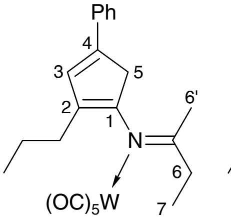
(*E*)-*N*-*sec*-Butyl-3-phenyl-acrylimidoyl chloride (**5c**), generated from (2*E*)-*N*-*sec*-butyl-3-phenyl acrylamide (**4c**, 378 mg, 2.0 mmol) with phosphorous oxychloride (306 mg, 2.0 mmol) in dry dichloromethane (2 mL) at 20 °C, 48 h in a 3-mL screw-top vessel, was added to pentacarbonyl[1-(ethylsulfanyl)but-1-ylidene]tungsten(0) (**1a**, 454 mg, 1.0 mmol) in dry dichloromethane (3 mL). Triethylamine (404 mg, 4.0 mmol) was added to the mixture at −40 °C leading to a color change from red to dark blue. On warming after 10 min to 20 °C, the color faded to yellow. Evaporation of the solvent and flash chromatography at 20 °C on silica gel (40 × 1 cm, 10:1 *n*-pentane/diethyl ether) afforded a bright yellow fraction of a 12:2:6:3 mixture of compounds (*Z*)-**13c**, (*E*)-**13c**, (*Z*)-**14c**, (*E*)-**14c** (370 mg, 64%, $R_f = 0.4$ in 50:1 *n*-pentane/diethyl ether).



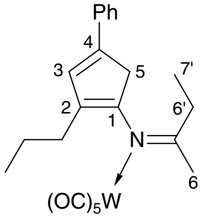
(*Z*)-**13c**



(*E*)-**13c**



(*Z*)-**14c**



(*E*)-**14c**

Data for (*E*/*Z*)-**13c** and (*E*/*Z*)-**14c** (obtained from a 13:2:6:3 mixture of compounds (*Z*)-**13c**, (*E*)-**13c**, (*Z*)-**14c**, (*E*)-**14c**; only some characteristic signals are given for minor isomers).

4.6.1. Data for (*Z*)-**13c**

^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ 7.48 (m, 2H; *o*-CH Ph), 7.31 (m, 2 H; *m*-CH Ph), 7.20 (m, 1H; *p*-CH Ph), 6.57 (s, 1H; 5-H), 3.57 and 3.50 (AB system, ^2J(H,H) = 22.8 Hz, 2H; 3-H_2), 2.78 (m, 2H; 6-H_2), 2.16 (m, 2H; $CH_2CH_2CH_3$), 1.95 (s, 3H; 6′-H_3), 1.60 (m, 2H; $CH_2CH_2CH_3$), 1.28 (t, ^3J(H,H) = 7.5 Hz, 3H; 7-H_3), 0.99 (t, ^3J(H,H) = 7.4 Hz, 3H; $CH_2CH_2CH_3$); ^{13}C NMR (100 MHz, $CDCl_3$, 300 K): δ 202.5 and 198.4 [each C_q, 1:4, *trans*- and *cis*-CO; $W(CO)_5$], 188.3 (C_q; C=N), 152.4 (C_q; C1), 144.9 (C_q; C4), 135.3 (C_q; *i*-C Ph), 128.6 (CH; *m*-C Ph), 127.1 (CH; *p*-C Ph), 126.3 (C_q; C2), 124.8 (CH; C5), 124.7 (CH; *o*-C Ph), 40.4 (CH_2; C3), 38.1 (CH_2; C6), 29.5 ($CH_2CH_2CH_3$), 22.0 ($CH_2CH_2CH_3$), 20.3 (CH3; C6′), 14.6 ($CH_2CH_2CH_3$), 11.5 (CH_3; C7); IR (cyclohexane) [cm^{-1} (%)]: $\tilde{\nu} =$ 2068.4 (10), 1969.4 (5), 1927.0 (100), 1912.4 (40) [ν(C≡O)]; HRMS (ESI) calcd for $C_{21}H_{22}NO_3W$ $[M - 2CO - H]^-$: 520.1107; found: 520.1124.

4.6.2. Data for (*E*)-**13c**

^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ 6.56 (s, 1H; 5-H), 2.45 (s, 3H; 6-H_3).

4.6.3. Data for (Z)-**14c**

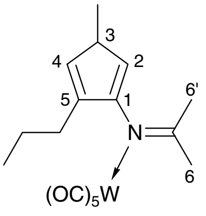
^{1}H NMR (400 MHz, CDCl$_3$, 300 K): δ 6.72 (s, 1H; 3-H), 3.96 and 3.27 (AB system, ^2J(H,H) = 22.6 Hz, 2H; 5-H$_2$), 1.93 (s, 3H; 6′-H$_3$).

4.6.4. Data for (E)-**14c**

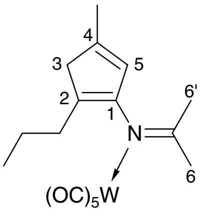
^{1}H NMR (400 MHz, CDCl$_3$, 300 K): δ 3.98 and 3.22 (AB system, ^2J(H,H) = 22.6 Hz, 2H; 5-H$_2$), 2.44 (s, 3H; 6-H$_3$).

4.7. Pentacarbonyl[isopropylidene-(3-methyl-5-propyl-cyclopenta-1,4-dienyl)- amine, N-W]tungsten(0) (**12d**), pentacarbonyl[isopropylidene-(4-methyl-2-propyl-cyclopenta-1,4-dienyl)- amine, N-W]tungsten(0) (**13d**), pentacarbonyl[isopropylidene-(4-methyl-2-propyl-cyclopenta-1,3-dienyl)- amine, N-W]tungsten(0) (**14d**)

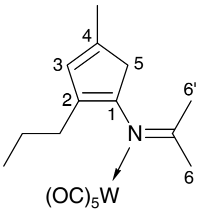
(*E*)-*N*-Isopropyl-but-2-ene-1-carboximidoyl chloride (**5d**), generated from (*E*)-but-2-enonic acid isopropylamide (**4d**, 254 mg, 2.0 mmol) with phosphorous oxychloride (306 mg, 2.0 mmol) in dry dichloromethane (2 mL) at 20 °C, 48 h in a 3-mL screw-top vessel, was added to pentacarbonyl[1-(ethylsulfanyl)but-1-ylidene]tungsten(0) (**1a**, 454 mg, 1.0 mmol) in dry dichloromethane (3 mL). At −40 °C triethylamine (404 mg, 4.0 mmol) was added leading to a color change from red to dark blue. The color faded to yellow on warming to 20 °C after 10 min. Evaporation of the solvent and flash chromatography at 20 °C on silica gel (40 × 1 cm, 10:1 *n*-pentane/diethyl ether) afforded a bright yellow 6:10:1 mixture of compounds **12d**, **13d** and **14d** (160 mg, 32%, $R_f = 0.6$ in 10:1 *n*-pentane/diethyl ether). Compound **12d** in CDCl$_3$ is transformed completely into a 10:1 mixture of compounds **13d** and **14d** in 24 h, 20 °C.



12d



13d



14d

Data for **12d**, **13d** and **14d** (obtained from a 6:10:1 mixture of compounds **12d**, **13d** and **14d**).

4.7.1. Data for **12d**

^{1}H NMR (400 MHz, CDCl$_3$, 300 K): δ 6.15 (m, 1H; 4-H), 5.60 (m, 1H; 2-H), 3.21 (m, 1H; C*H*CH$_3$), 2.50 (s, 3H; 6-H$_3$), 1.94 (s, 3H; 6′-H$_3$), 2.12 and 1.81 (each m, each 1H; C*H*$_2$CH$_2$CH$_3$), 1.62 (m, 2H; CH$_2$C*H*$_2$CH$_3$), 1.19 (d, ^3J(H,H) = 7.7 Hz, 3H; CHC*H*$_3$), 0.99 (t, ^3J(H,H) = 7.4 Hz, 3H; CH$_2$CH$_2$C*H*$_3$); ^{13}C NMR (100 MHz, CDCl$_3$, 300 K): δ 203.0 and 198.7 [each C$_q$, 1:4, *trans*- and *cis*-CO; W(CO)$_5$], 183.8 (C$_q$; C=N), 156.9 (C$_q$; C1), 140.8 (C$_q$; C5), 136.1 (CH; C4), 121.2 (CH; C2), 44.1 (CH; *C*HCH$_3$), 31.8 (CH$_3$; C6′), 28.8 (CH$_2$; *C*H$_2$CH$_2$CH$_3$), 23.6 (CH$_3$; C6), 20.7 (CH$_2$; CH$_2$*C*H$_2$CH$_3$), 14.2 (CH$_3$; CH$_2$CH$_2$*C*H$_3$), 14.0 (CH$_3$; CH*C*H$_3$); IR (cyclohexane) [cm^{-1} (%)]: $\tilde{\nu}$ = 2069.0 (10), 1969.4 (5), 1931.5 (100), 1927.1 (95), 1912.8 (40) [ν(C≡O)]; MS (70 eV): *m*/*z* for ^{184}W (%): 501 (24) [*M*]$^+$, 473 (15) [*M* − CO]$^+$, 445 (40) [*M* − 2CO]$^+$; 415 (100).

4.7.2. Data for **13d**

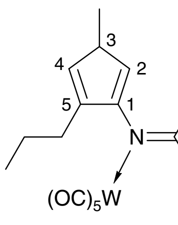
^{1}H NMR (400 MHz, CDCl$_3$, 300 K): δ 5.84 (s, br, 1H; 5-H), 3.07 and 2.94 (AB system, ^2J(H,H) = 22.7 Hz, 2H; 3-H$_2$), 2.46 [s, 3H; 6-H$_3$], 1.97 [s, 3H; 6′-H$_3$], 2.05 (m, 2H; C*H*$_2$CH$_2$CH$_3$), 2.03 ("d", ^3J(H,H) = 1.6 Hz, br, 3H; CHC*H*$_3$), 1.48 (m, 2H; CH$_2$C*H*$_2$CH$_3$), 0.95 (t, ^3J(H,H) = 7.3 Hz, 3H; CH$_2$CH$_2$C*H*$_3$); ^{13}C NMR (100 MHz, CDCl$_3$, 300 K): δ 202.9 and 198.5 [each C$_q$, 1:4, *trans*- and *cis*-CO; W(CO)$_5$], 183.3 (C$_q$; C=N), 151.6 (C$_q$; C1), 143.7 (C$_q$; *C*CH$_3$), 125.3 (CH; C5), 124.0 (C$_q$; C2), 44.0 (CH$_2$; C3), 31.7 (CH$_3$; C6′), 29.5 (CH$_2$; *C*H$_2$CH$_2$CH$_3$), 23.5 (CH$_3$; C6), 22.0 (CH$_2$; CH$_2$*C*H$_2$CH$_3$), 16.3 (CH$_3$; CH*C*H$_3$), 14.6 (CH$_3$; CH$_2$CH$_2$*C*H$_3$); IR (cyclohexane) [cm^{-1} (%)]: $\tilde{\nu}$ = 2068.5 (10), 1969.0 (3), 1931.1 (100), 1926.4 (95), 1911.1 (40) [ν(C≡O)]; HRMS (ESI) calcd for C$_{17}$H$_{19}$NO5WNa [*M* + Na]$^+$: 524.0668; found: 524.0662; HRMS (ESI) calcd for C$_{15}$H$_{19}$NO$_3$W [*M* − 2CO − H]$^-$: 444.0793; found: 444.0803.

4.7.3. Data for **14d**

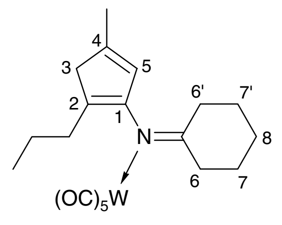
^{1}H NMR (400 MHz, CDCl$_3$, 300 K): δ 5.94 (s, br, 1H; 3-H), 3.42 and 2.76 (AB system, ^2J(H,H) = 22.7 Hz, 2H; 5-H$_2$), 2.46 [s, 3H; 6-H$_3$], 1.96 [s, 3H; 6′-H$_3$], for data of CC*H*$_3$ and *n*-propyl see **13d** due to strong overlap; ^{13}C NMR (100 MHz, CDCl$_3$, 300 K): δ 202.8 and 198.4 [each C$_q$, 1:4, *trans*- and *cis*-CO; W(CO)$_5$], 184.2 (C$_q$; C=N), 150.3 (C$_q$; C1), 137.3 (C$_q$; *C*CH$_3$), 129.0 (C$_q$; C2), 127.3 (CH; C3), 44.7 (CH$_2$; C5), 32.0 (CH$_3$; C6′), 28.8 (CH$_2$; *C*H$_2$CH$_2$CH$_3$), 23.7 (CH$_3$; C6), 22.8 (CH$_2$; CH$_2$*C*H$_2$CH$_3$), 15.9 (CH$_3$; CH*C*H$_3$), 14.5 (CH$_3$; CH$_2$CH$_2$*C*H$_3$); for IR and MS data see **13d**.

4.8. Pentacarbonyl[cyclohexylidene-(3-methyl-5-propyl-cyclopenta-1,4-dienyl)- amine, N-W]tungsten(0) (**12e**), pentacarbonyl[cyclohexylidene-(4-methyl-2-propyl-cyclopenta-1,4-dienyl)- amine, N-W]tungsten(0) (**13e**), pentacarbonyl[cyclohexylidene-(4-methyl-2-propyl-cyclopenta-1,3-dienyl)- amine, N-W]tungsten(0) (**14e**)

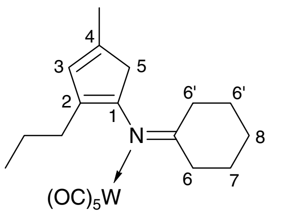
(*E*)-*N*-Cyclohexyl-but-2-ene-1-carboximidoyl chloride (**5e**), generated from (*E*)-but-2-enonic acid cyclohexylamide (**4e**, 334 mg, 2.0 mmol) and phosphorous oxychloride (306 mg, 2.0 mmol) as described above, was added to pentacarbonyl[1-(ethylsulfanyl)but-1-ylidene]tungsten(0) (**1a**, 454 mg, 1.0 mmol) in dry dichloromethane (3 mL). Work-up as described above afforded a bright yellow 10:1 mixture of compounds **12e** and **13e** (186 mg, 34%, $R_f = 0.7$ in 10:1 *n*-pentane/diethyl ether). Compound **12e** in CDCl$_3$ is slowly transformed into a 10:1 mixture of compounds **13e** and **14e**.



12e



13e



14e

Data for **12e**, **13e** and **14e** (NMR and MS data of a 3:10:1 mixture of compounds **12e**, **13e** and **14e**).

4.8.1. *Data for* **12e**

^{1}H NMR (400 MHz, CDCl$_3$, 300 K): δ 6.13 (m, 1H; 4-H), 5.61 (m, 1H; 2-H), 3.20 (m, 1H; C*H*CH$_3$), 2.90 (m, 2H; 6-H$_2$), 2.32 (m, 2H; 6′-H$_2$), 2.16 and 1.80 (each m, each 1H; C*H*$_2$CH$_2$CH$_3$), 1.61 (m, 2H; CH$_2$C*H*$_2$CH$_3$), 1.19 (d, ^{3}J(H,H) = 7.7 Hz, 3H; CHC*H*$_3$), 0.99 (t, ^{3}J(H,H) = 7.4 Hz, 3H; CH$_2$CH$_2$C*H*$_3$); ^{13}C NMR (100 MHz, CDCl$_3$, 300 K): δ 203.2 and 198.7 [each C$_q$, 1:4, *trans*- and *cis*-CO; W(CO)$_5$], 189.2 (C$_q$; C=N), 155.9 (C$_q$; C1), 141.2 (C$_q$; C5), 135.7 (CH; C4), 122.2 (CH; C2), 44.0 (CH; *C*HCH$_3$), 42.0 (CH$_2$; C6), 33.2 (CH$_3$; C6′), 28.8 (CH$_2$; *C*H$_2$CH$_2$CH$_3$), 27.7 and 27.5 (CH$_2$; C7 and C7′), 25.0 (CH$_2$; C8), 20.8 (CH$_2$; CH$_2$*C*H$_2$CH$_3$), 14.2 (CH$_3$; CH$_2$CH$_2$*C*H$_3$), 14.1 (CH$_3$; CH*C*H$_3$); IR (cyclohexane) [cm^{-1} (%)]: $\tilde{\nu}$ = 2068.5 (10), 1968.7 (5), 1930.7 (100), 1926.6 (95), 1911.2 (40) [ν(C≡O)]; HRMS (ESI) calcd for C$_{20}$H$_{23}$NO$_5$WNa [M + Na]$^+$: 564.0981; found: 564.0972; HRMS (ESI) calcd for C$_{18}$H$_{22}$NO$_3$W [M − 2CO − H]$^-$: 484.1160; found: 484.1161.

4.8.2. *Data for* **13e**

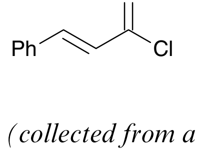
^{1}H NMR (400 MHz, CDCl$_3$, 300 K): δ 5.84 (s, br, 1H; 5-H), 3.07 and 2.95 (AB system, ^{2}J(H,H) = 22.8 Hz, 2H; 3-H$_2$), 2.83 [m, 2H; 6-H$_2$], 2.32 [s, 2H; 6′-H$_2$], 2.13 and 2.00 (m, 2H; C*H*$_2$CH$_2$CH$_3$), 2.03 ("d", ^{3}J(H,H) = 1.5 Hz, br, 3H; CHC*H*$_3$), 1.89 and 1.66 (each m, 2:4 H; 7-, 7′- and 8-CH$_2$), 1.51 and 1.38 (each m, each 1H; CH$_2$C*H*$_2$CH$_3$), 0.94 (t, ^{3}J(H,H) = 7.3 Hz, 3H; CH$_2$CH$_2$C*H*$_3$); ^{13}C NMR (100 MHz, CDCl$_3$, 300 K): δ 203.0 and 198.5 [each C$_q$, 1:4, *trans*- and *cis*-CO; W(CO)$_5$], 188.9 (C$_q$; C=N), 150.7 (C$_q$; C1), 143.3 (C$_q$; *C*CH$_3$), 126.0 (CH; C5), 124.2 (C$_q$; C2), 44.1 (CH$_2$; C3), 42.0 (CH$_2$; C6), 32.8 (CH$_2$; C6′), 29.5 (CH$_2$; *C*H$_2$CH$_2$CH$_3$), 27.8 and 27.6 (CH$_2$; C7 and C7′), 22.2 (CH$_2$; CH$_2$*C*H$_2$CH$_3$), 16.3 (CH$_3$; CH*C*H$_3$), 14.6 (CH$_3$; CH$_2$CH$_2$*C*H$_3$); IR (cyclohexane) [cm^{-1} (%)]: $\tilde{\nu}$ = 2067.7 (10), 1968.2 (5), 1930.5 (100), 1925.8 (95), 1909.5 (40) [ν(C≡O)]; HRMS (ESI) calcd for C$_{20}$H$_{23}$NO$_5$WNa [M + Na]$^+$: 564.0981; found: 564.0977; HRMS (ESI) calcd for C$_{18}$H$_{22}$NO$_3$W [M − 2CO − H]$^-$: 484.1106; found: 484.1120; elemental analysis (%) calcd for C$_{20}$H$_{23}$NO$_5$W (541.3): C, 44.38; H, 4.28; N, 2.59; found: C, 44.49; H, 4.18; N, 2.50%.

4.8.3. *Data for* **14e**

^{1}H NMR (400 MHz, CDCl$_3$, 300 K): δ 5.94 (s, br, 1H; 3-H), 3.44 and 2.69 (AB system, ^{2}J(H,H) = 22.6 Hz, 2H; 5-H$_2$), for data of CC*H*$_3$, *n*-propyl and cyclohexyl see **13e** due to strong overlap; ^{13}C NMR (100 MHz, CDCl$_3$, 300 K): δ 202.9 and 198.4 [each C$_q$, 1:4, *trans*- and *cis*-CO; W(CO)$_5$], 189.9 (C$_q$; C=N), 149.4 (C$_q$; C1), 137.6 (C$_q$; *C*CH$_3$), 129.1 (C$_q$; C2), 127.4 (CH; C3), 45.3 (CH$_2$; C5), 42.3 (CH$_3$; C6′), 33.0 (CH$_3$; C6), 28.8 (CH$_2$; *C*H$_2$CH$_2$CH$_3$), 27.7 and 27.0 (each CH$_2$; C7 and C7′), 25.0 (CH$_2$; C8), 21.1 (CH$_2$; CH$_2$*C*H$_2$CH$_3$), 15.9 (CH$_3$; CH*C*H$_3$), 14.8 (CH$_3$; CH$_2$CH$_2$*C*H$_3$); for IR and MS data see **13e**.

4.9. *(E)-N-Isopropyl-3-phenyl-acrylimidoyl chloride (**5a**), pentacarbonyl[(3-ethylsulfanyl-4-phenyl-cyclopent-2-enylidene)-isopropyl- amine, N-W]tungsten(0) [(1 Z)-**19a** and (1E)-**19a**], pentacarbonyl[3-(isopropylamino)-5-phenyl-penta-1,2,4-triene-1- ylidene]tungsten(0) (**20a**), (E)-N-isopropyl-3-phenyl-thioacrylimidic acid ethyl ester (**21a**)*

(*E*)-*N*-Isopropyl-3-phenyl-acrylimidoyl chloride (**5a**), generated as described above from (2*E*)-*N*-isopropyl-3-phenyl acrylamide (**4a**, 378 mg, 2.0 mmol) and phosphorous oxychloride (306 mg, 2.0 mmol), was reacted with pentacarbonyl[1-(ethylsulfanyl)eth-1-ylidene]tungsten(0) (**1b**, 412 mg, 1.0 mmol). Work-up gave a colorless compound **21a** (23 mg, 10%, R_f = 0.5 in 10:1 *n*-pentane/diethyl ether) and a thermolabile red compound (R_f = 0.4 in 10:1 *n*-pentane/diethyl ether) which was transformed into compound (*Z*)-**19a** (310 mg, 53%, R_f = 0.7 in 10:1 *n*-pentane/diethyl ether, yellow oil) within 30 min. Equilibration of (*Z*)-**19a** and (*E*)-**19a** (R_f = 0.5 in 10:1 *n*-pentane/diethyl ether) is accompanied by strong decomposition. ^{1}H NMR data of (*E*)-**19a** were collected from a sample freshly chromatographed and very dilute. A more polar dark red to violet fraction contained compound **20a** (64 mg, 12%, R_f = 0.5 in 1:1:1 *n*-pentane/diethyl ether/dichloromethane, violet oil).



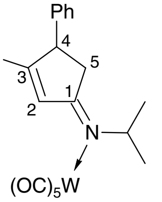
5a

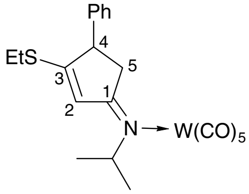
4.9.1. *Data for* **5a** *(collected from a 1:1 mixture of amid and phosphorous oxychloride in CDCl$_3$ after completion of the reaction at 20 °C, 6 h)*

^{1}H NMR (400 MHz, CDCl$_3$, 300 K): δ 7.99 (d, ^{3}J(H,H) = 15.2 Hz, 1H; PhC*H*), 7.77 (d, ^{3}J(H,H) = 15.2 Hz, 1H; PhCH=C*H*), 7.77 (m, 2H; *o*-CH Ph), 7.54 (m, 1H; *p*-CH Ph), 7.46 (m, 2H; *m*-CH Ph), 4.54 (sept., ^{3}J(H,H) = 6.6 Hz;

2H; NCH), 1.55 [d, ^3J(H,H) = 6.6 Hz, 6H; NCH(CH_3)$_2$]; ^{13}C NMR (100 MHz, CDCl$_3$, 300 K): δ 165.7 (C$_q$; C=N), 154.4 (CH; Ph*C*H), 133.2 (CH; *p*-C Ph), 132.2 (C$_q$; *i*-C Ph), 129.9 (CH; *o*-C Ph), 129.1 (CH; *m*-C Ph), 117.3 (CH; PhCH=*C*H), 53.5 (CH; NCH), 20.6 [NCH(*C*H$_3$)$_2$].

(*Z*)-**19a**

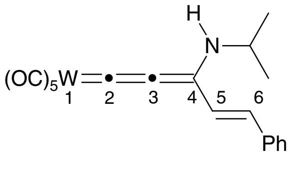




(*E*)-**19a**

*4.9.2. Data for (Z)-**19a**{(E)-**19a**} (obtained from a 2:3 Z/E mixture)*

^{1}H NMR (400 MHz, CDCl$_3$, 300 K): δ 7.36 {7.36} (m, 2H; *m*-CH Ph), 7.30 {7.30} (m, 1 H; *p*-CH Ph), 7.13 {7.13} (m, 2H; *o*-CH Ph), 6.89 {6.32} (d, ^4J(H,H) = 1.4 Hz {1.3 Hz}, 1H; 2-H), 4.08 {3.98} (m, 1H; 4-H), 3.82 {4.36} (sept. {br}, ^3J(H,H) = 6.6 Hz, 1H; NCH), 3.35 {3.45} (dd, ^2J(H,H) = 17.7 Hz {17.8 Hz}, ^3J(H,H) = 7.6 Hz {7.5 Hz}, 1H; *cis*-5-H$_2$), 2.96 {2.86} (q, ^3J(H,H) = 7.5 Hz {7.5 Hz}, 2H; SCH_2CH$_3$), 2.77 {2.99} (dd, ^2J(H,H) = 17.7 Hz {17.8 Hz}, ^3J(H,H) = 2.6 Hz {2.4 Hz}, 1H; *trans*-5-H$_2$), 1.38 {1.32} (t, ^3J(H,H) = 7.5 Hz, 3H; SCH$_2$CH_3), 1.29 and 1.27 {1.41 and 1.40} [each d, ^3J(H,H) = 6.6 Hz {6.6 Hz}, 3H; NCH(CH_3)$_2$]; ^{13}C NMR (100 MHz, CDCl$_3$, 300 K): δ 201.7 and 199.4 [C$_q$, 1:4, *trans*- and *cis*-CO; W(CO)$_5$], 182.5 (C$_q$; C=N), 172.5 (C$_q$; C3), 141.0 (C$_q$; *i*-C Ph), 129.1 (CH; *m*-C Ph), 128.2 (CH; C2), 127.8 (CH; *p*-C Ph), 127.1 (CH; *o*-C Ph), 60.4 (CH; NCH), 52.1 (CH; C4), 41.9 (CH$_2$; C5), 27.1 (S*C*H$_2$CH$_3$), 23.8 and 23.7 [NCH(*C*H$_3$)$_2$], 13.3 (SCH$_2$*C*H$_3$); IR (cyclohexane) [cm^{-1} (%)]: $\tilde{\nu}$ =2065.7 (30), 1962.4 (5), 1927.1 (100), 1918.3 (95), 1908.0 (95) [ν(C≡O)], 1569.7 (10), 1545.4 (10) [ν(C=C) and ν(C=N)]; IR (diffuse reflexion) [cm^{-1} (%)]: $\tilde{\nu}$ = 2064.4 (10), 1965.8 (4), 1875.5 (100), 1568.3 (7), 1544.0 (15), 1494.5 (1), 1454.0 (3), 1304.5 (1), 1172.8 (1); HRMS (ESI) calcd for $C_{21}H_{21}NSO_5WNa$ [M + Na]$^+$: 606.0543; found: 606.0513.

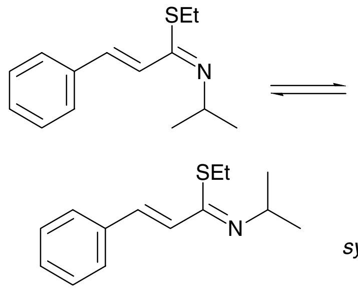


20a

*4.9.3. Data for **20a***

^{1}H NMR (400 MHz, CDCl$_3$, 300 K): δ 9.52 (s, br, 1H; NH), 7.98 (d, ^3J(H,H) = 15.3 Hz, 1H; PhC*H*), 7.53 (m, 2H; *o*-CH Ph), 7.34 (m, 1H; *p*-CH Ph), 7.31 (m, 2H; *m*-CH Ph), 6.95 (m, ^3J(H,H) = 15.3 Hz, 1H; PhCH=C*H*), 4.62 (m, 1H; NCH), 1.40 (d, ^3J(H,H) = 6.6 Hz, 6H; NCH(CH_3)$_2$); ^{13}C NMR (100 MHz, CDCl$_3$, 300 K): δ 203.3 and 197.4 [C$_q$, 1:4, *trans*- and *cis*-CO; W(CO)$_5$], (C$_q$; W=C),[25] 151.6 (C$_q$; C4), 150.1 (CH; C6), 134.3 (C$_q$; *i*-C Ph), 131.2 (CH; *p*-CH Ph), 129.1 (CH; *m*-CH Ph), 128.7 (CH; *o*-CH Ph), 121.8 (CH; C5), 112.2 (C$_q$; C3), 50.3 (NCH), 21.7 (NCH(*C*H$_3$)$_2$); IR (dichloromethane) [cm^{-1} (%)]: $\tilde{\nu}$ = 3365.9 (5) [ν(N–H)], 2082.8 (1), 1993.7 (25), 1929.4 (100) [ν(C≡O)], 1625.9 (10), 1540.1 (10), 1467.1 (10), 1452.5 (10); HRMS (ESI) calcd for $C_{19}H_{15}NO_5WNa$ [M + Na]$^+$: 544.0355; found: 544.0340.

anti-**21a**



syn-**21a**

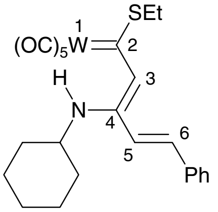
*4.9.4. Data for anti-**21a**{syn-**21a**} (obtained from a 1:1 mixture)*

^{1}H NMR (400 MHz, CDCl$_3$, 300 K) δ 7.47 {7.47} (each m, 1H; *p*-CH Ph), 7.34 {7.34} (each m, 2H; *m*-CH Ph), 7.34 {7.34} (each m, 2H; *o*-CH Ph), 7.22 {7.27} (each d, ^3J(H,H) = 16.2 Hz {15.8 Hz}, 1H; PhC-*H*), 6.99 {6.81} [each d, ^3J(H,H) = 16.2 Hz {15.8 Hz}, 1H; N=CC–H, NOE (+) with NC*H*(CH$_3$)$_2$ {no NOE with NC*H*(CH$_3$)$_2$}], 4.11 {4.03} [each sept., ^3J(H,H) = 6.2 Hz, 1H; NC*H*(CH$_3$)$_2$, NOE (+) with N=CC–H {no NOE with N=CC–H}], 2.93 {2.96} (each q, ^3J(H,H) = 7.4 Hz, 2H; SCH$_2$), 1.29 {1.28} (t, ^3J(H,H) = 7.4 Hz, each 3H; SCH$_2$CH_3), 1.22 {1.17} [each d, ^3J(H,H) = 6.2 Hz, 6 H; NCH(CH_3)$_2$]; ^{13}C NMR (100 MHz, CDCl$_3$, 300 K): δ 158.0 {157.7} (C$_q$; C=N), 136.8 {136.7} (CH; Ph-*C*H), 136.7 {136.0} (C$_q$; *i*-C Ph), 129.0 {128.9} (CH; *p*-CH Ph), 128.6 {128.7} (CH; *m*-CH Ph), 127.3 {127.3} (CH; *o*-CH Ph), 120.0 {126.5} (CH; Ph-CH=*C*H), 53.8 {51.6} [N*C*H(CH$_3$)$_2$], 23.7 {27.0} (SCH$_2$), 24.1 {23.2} [NCH(*C*H$_3$)$_2$], 14.3 {15.7} (SCH$_2$*C*H$_3$). IR (cyclohexane) [cm^{-1} (%)]: $\tilde{\nu}$ =1630.0 (50), 1587 (100) [ν(C=O)]; MS (70 eV): m/z for ^{184}W (%): 233.1 (5) [M]$^+$, 172.1 (35) [M – SEt]$^+$, 130.0 (100) [M – SEt – C_3H_6]$^+$; HRMS (ESI) calcd for $C_{14}H_{19}NS$ [M + H]$^+$: 234.1313; found: 234.1311.

*4.10. (2s-cis, 3Z, 4s-cis,5E)-1,1,1,1,1-Pentacarbonyl-2-ethylsulfanyl-6-phenyl-4-N-cyclohexylamino-1-tungsten-1,3,5-hexatriene (**18b**), pentacarbonyl[(3-ethylsulfanyl-4-phenyl-cyclopent-2-enylidene)- cyclohexyl-amine, N-W]tungsten(0) [(1Z)-**19b** and (1E)-**19b**], pentacarbonyl[3-(cyclohexylamino)-5-phenyl-penta-1,2,4-triene-1-ylidene]tungsten(0) (**20b**)*

(*E*)-*N*-Cyclohexyl-3-phenyl-acrylimidoyl chloride (**5b**), generated from (2*E*)-*N*-cyclohexyl-3-phenyl acrylamide (**4b**, 378 mg, 2.0 mmol) and phosphorous oxychloride (306 mg, 2.0 mmol), was reacted with pentacarbonyl-

[1-(ethylsulfanyl)eth-1-ylidene]tungsten(0) (**1b**, 412 mg, 1.0 mmol). Work-up afforded red crystals of compound **18b** (225 mg, 36%, $R_f = 0.3$ in 10:1 *n*-pentane/diethyl ether). Compound **18b** was transformed into (*Z*)-**19b** ($R_f = 0.7$ in 10:1 *n*-pentane/diethyl ether, yellow oil) in $CDCl_3$, 20 °C, within 3 h. Equilibration of (*Z*)-**19b** and (*E*)-**19b** in solution was accompanied by strong decomposition. A more polar dark red to violet fraction yielded compound **20b** (95 mg, 17%, $R_f = 0.3$ in *n*-pentane/dichloromethane 1:1, violet oil).



18b

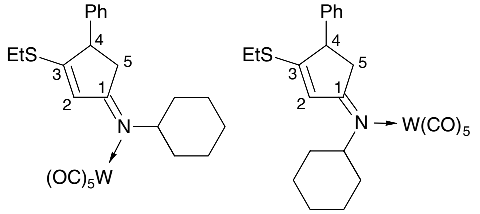
4.10.1. Spectroscopic data of *18b*

^{1}H NMR (600 MHz, $CDCl_3$, 233 K): δ 10.06 (d, br, ^3J(H,H) = 8.1 Hz 1H; NH), 7.63 (m, 2H; *o*-CH Ph), 7.57 (dd, ^3J(H,H) = 15.9 Hz, ^3J(H,H) = 3.1 Hz, 1H; C*H*-Ph), 7.51 (m, 3H; *m*/*p*-CH Ph), 7.00 (d, ^3J(H,H) = 15.9 Hz, 1H; C*H*CHPh), 6.86 (s, 1H; 3-H), 3.75 (m, 1H; NCH), 2.94 (q, 2H; SCH_2CH_3), 2.15, 1.90, 1.73, 1.65, 1.37 (each m, 2:2:1:3:2H; CH_2-cyclohexyl), 1.33 (t, 3H; SCH_2CH_3); ^{13}C NMR (150 MHz, $CDCl_3$, 233 K): δ 225.4 (C_q; W=C), 202.9 and 198.7 [C_q, 1:4, *trans*- and *cis*-CO; $W(CO)_5$], 160.4 (C_q; C4), 143.0 (CH; C6), 134.0 (C_q; *i*-C Ph), 130.8 (CH; *p*-C Ph), 129.1 (CH; *m*-C Ph), 127.9 (CH; *o*-C Ph), 119.9 (CH; C5), 115.1 (CH; C3), 54.9 (CH; NCH), 32.5 (SCH_2CH_3), 32.1 (CH_2; $NCHCH_2$), 24.7 ($NCHCH_2CH_2$), 24.5 ($NCHCH_2CH_2CH_2$), 11.4 (SCH_2CH_3); IR (cyclohexane) [cm^{-1} (%)]: $\tilde{\nu} = 2060.6$ (40), 1934.9 (100), 1918.4 (70), 1907.9 (40) [ν(C≡O)]; IR (diffuse reflexion) [cm^{-1} (%)]: $\tilde{\nu} = 2056.6$ (20), 1882.2 (100), 1627.7 (5), 1578.7 (5), 1505.5 (20), 1452.5 (3), 1387.9 (3), 1363.6 (4), 1325.6 (4), 1310.8 (5), 1288.1 (7), 1257.3 (4), 1233.6 (4); HRMS (ESI) calcd for $C_{24}H_{25}NSO_5WNa$ $[M + Na]^+$: 646.0857; found: 646.0842; elemental analysis (%) calcd for $C_{24}H_{25}NSO_5W$ (623.4): C, 46.24; H, 4.04; N, 2.25; found C, 46.15; H, 3.82; N, 2.18%.

4.10.2. Molecular structure analysis of *18b* (code 3657.AUM)

Formula $C_{24}H_{25}NO_5SW$, $M_r = 623.36$ g mol^{-1}, red crystal, 0.45 × 0.25 × 0.20 mm, $a = 15.684(1)$, $b = 8.513(1)$, $c = 18.472(1)$ Å, $\beta = 97.89(1)°$, $V = 2443.0(4)$ Å^3, $\rho_{calcd} = 1.695$ g cm^{-3}, $\mu = 48.47$ cm^{-1}, empirical absorption correction ($0.219 \leqslant T \leqslant 0.444$), $Z = 4$, monoclinic, space group $P2_1/n$ (no. 14), $\lambda = 0.71073$ Å, $T = 198$ K, ω and φ scans, 15269 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda]_{max} = 0.67$ Å^{-1}, 5861 independent ($R_{int} = 0.029$) and 5106 observed reflections [$I \geqslant 2\sigma(I)$], 295 refined parameters, $R = 0.023$, $wR_2 = 0.051$, max./min. residual electron density 1.22/−0.93 e Å^{-3}, hydrogen atom at N1 from difference fourier map, others calculated and refined as riding atoms [24].

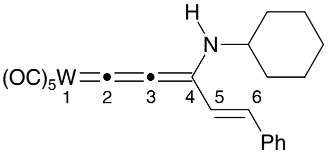
(*Z*)-**19b**



(*E*)-**19b**

4.10.3. Data for *(Z)-19b*

^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ 7.36 (m, 2H; *m*-CH Ph), 7.30 (m, 1H; *p*-CH Ph), 7.13 (m, 2H; *o*-CH Ph), 6.91 (s, 1H; 2-H), 4.07 (m, 1H; Ph-C*H*), 3.34 (dd, ^2J(H,H) = 17.7 Hz, ^3J(H,H) = 7.5 Hz, 1H; *cis*-5-H_2), 2.95 (q, ^3J(H,H) = 7.5 Hz, 2H; SCH_2CH_3), 3.30 (m, 1H; NCH), 2.75 (dd, ^2J(H,H) = 17.7 Hz, ^3J(H,H) = 2.6 Hz, 1H; *trans*-5-H_2), 1.87,1.66 and 1.29 (each m, 4:4:2H; CH_2-cyclohexyl), 1.37 (t, ^3J(H,H) = 7.5 Hz, 3H; SCH_2CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 300 K): δ 201.8 and 199.5 [each C_q, 1:4, *trans*- and *cis*-CO; $W(CO)_5$], 182.6 (C_q; C=N), 172.4 (C_q; C3), 140.9 (C_q; *i*-C Ph), 129.1 (CH; *m*-C Ph), 128.2 (CH; C2), 127.7 (CH; *p*-C Ph), 127.1 (CH; *o*-C Ph), 69.1 (CH; NCH), 52.0 (CH; C4), 41.9 (CH_2; C5), 34.1 (br), 25.8, 25.2, 24.9 (each m, 2:2:1; CH_2-cyclohexyl), 27.0 (SCH_2CH_3), 13.2 (SCH_2CH_3); IR (cyclohexane) [cm^{-1} (%)]: $\tilde{\nu} = 2065.2$ (30), 1961.5 (5), 1927.9 (100), 1918.4 (95), 1915.3 (95), 1907.3 (100) [ν(C≡O)], 1567.6 (10), 1545.7 (15) [ν(C=C) and ν(C=N)]; IR (diffuse reflexion) [cm^{-1} (%)]: $\tilde{\nu} = 2928.0$ (5), 2857.0 (2), 2064.0 (10), 1965.0 (4), 1889.9 (100), 1567.5 (10), 1541.0 (20), 1453.2 (4); HRMS (ESI) calcd for $C_{24}H_{25}NSO_5WNa$ $[M + Na]^+$: 646.0856; found: 646.0859.



20b

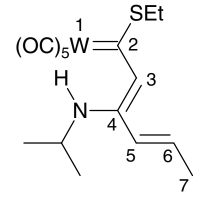
4.10.4. Data for *20b*

^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ 9.24 (br, 1H; NH), 7.99 (d, ^3J(H,H) = 15.4 Hz, 1H; CH=C*H*Ph), 7.45 (m, 2H; *o*-CH Ph), 7.31 (m, 3H; *m*-and *p*-CH Ph), 6.88 (d, ^3J(H,H) = 15.4 Hz, 1H; C*H*=CHPh), 4.32 (m, 1H; NCH), 2.18 and 1.41 (each m, 2H; $NCHCH_2$), 1.82 and 1.42 (each m, 2H; $NCHCH_2CH_2$), 1.63 (m, 2H; $NCHCH_2CH_2CH_2$); ^{13}C NMR (100 MHz, $CDCl_3$, 300 K): δ 203.4 and 197.4 [C_q, 1:4, *trans*- and *cis*-CO; $W(CO)_5$], 193.4 (C_q, small/broad; W=C), 151.2 (C_q; C4), 150.1 (CH; CH=*C*HPh), 134.2 (C_q; *i*-C Ph), 131.3 (CH; *p*-CH Ph), 129.1 (CH; *m*-CH Ph), 128.6 (CH; *o*-CH Ph), 121.7 (CH; *C*H=CHPh), 112.3 (C_q, small/broad; C3), 57.3 (CH; NCH), 32.0 (CH_2; $NCHCH_2$), 25.1 (CH_2;

NCHCH$_2$CH$_2$C*H*$_2$), 24.5 (CH$_2$; NCHCH$_2$C*H*$_2$); IR (dichloromethane) [cm^{-1} (%)]: $\tilde{\nu}$ = 3363.9 (5) [*ν*(N–H)], 2082.8 (2), 1994.2 (30), 1929.1 (100) [*ν*(C≡O)], 1625.7 (10), 1539.1 (10); IR (diffuse reflexion) [cm^{-1} (%)]: $\tilde{\nu}$ = 2082.6 (0.5), 1995.9 (10), 1898.1 (100) [*ν*(C≡O)]; HRMS (ESI) calcd for $C_{22}H_{19}NO_5WNa$ [*M* + Na]$^+$: 584.0668; found: 584.0683.

4.11. (2s-cis,3Z,4s-cis,5E)-1,1,1,1,1-Pentacarbonyl-2-ethylsulfanyl-6-methyl-4-N-isopropylamino-1-tungsten-1,3,5-hexatriene (**18d**), pentacarbonyl[(3-ethylsulfanyl-4-methyl-cyclopent-2-enylidene)-isopropyl-amine, N-W]tungsten(0) [(1Z)-**19d**]

(*E*)-*N*-Isopropyl-but-2-ene-1-carboximidoyl chloride (**5d**), generated as described above from (*E*)-but-2-enonic acid isopropylamide (**4d**, 254 mg, 2.0 mmol) and phosphorous oxychloride (306 mg, 2.0 mmol) was reacted with pentacarbonyl[1-(ethylsulfanyl)eth-1-ylidene]tungsten(0) (**1b**, 412 mg, 1.0 mmol). Addition of triethylamine (808 mg, 8.0 mmol) at −78 °C and direct transfer of the mixture to a precooled column at −78 °C on silica gel (15 × 2 cm, 1:1 *n*-pentane/diethyl ether) afforded a red fraction, from which red crystals of compound **18d** were obtained at −20 °C from *n*-pentane (110 mg, 21%, R_f = 0.5 in 10:1 *n*-pentane/diethyl ether). In solution (CDCl$_3$, 20 °C) **18d** was transformed into (*Z*)-**19d** (R_f = 0.6 in 10:1 *n*-pentane/diethyl ether, yellow oil) within 3 h. Equilibration of (*Z*)-**19d** and (*E*)-**19d** (R_f = 0.5 in 10:1 *n*-pentane/diethyl ether) is accompanied by strong decomposition.

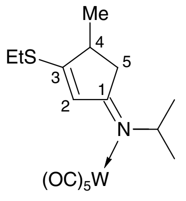


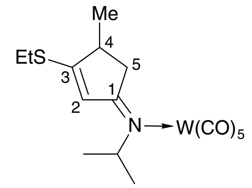
18d

4.11.1. Data for 18d

^{1}H NMR (600 MHz, CDCl$_3$, 233 K): *δ* 10.00 (s, br, ^3J(H,H) = 8.3 Hz, 1H; NH), 6.89 (dq, ^3J(H,H) = 15.3 Hz, ^3J(H,H) = 6.9 Hz, 1H; 6-H), 6.72 (s, 1H; 3-H), 6.40 (dq, ^3J(H,H) = 15.3 Hz, ^4J(H,H) = 1.2 Hz, 1H; 5-H), 4.10 [d{sept}, ^3J(H,H) = 8.3 Hz, ^3J(H,H) = 6.9 Hz, 1H; C*H*(CH$_3$)$_2$], 2.90 (q, ^3J(H,H) = 7.5 Hz, 2H; SC*H*$_2$CH$_3$), 2.07 (dd, ^3J(H,H) = 6.9 Hz, ^4J(H,H) = 1.2 Hz, 3H; 7-CH$_3$), 1.47 [d, ^3J(H,H) = 6.6 Hz, 6 H; CH(C*H*$_3$)$_2$], 1.32 (t, 3H; SCH$_2$C*H*$_3$); ^{13}C NMR (150 MHz, CDCl$_3$, 233 K): *δ* 224.2 (C$_q$; W=C), 202.9 and 198.7 [C$_q$, 1:4, *trans*- and *cis*-CO; W(CO)$_5$], 160.8 (C$_q$; C4), 143.7 (CH; C6), 124.0 (CH; C5), 115.1 (CH; C3), 47.3 (CH; NCH), 32.3 (SCH$_2$CH$_3$), 22.0 (CH$_3$; NCH(*C*H$_3$)$_2$]), 19.9 (CH$_3$; C7), 11.4 (SCH$_2$*C*H$_3$); IR (cyclohexane) [cm^{-1} (%)]: $\tilde{\nu}$ = 3201.1 (1) [*ν*(N–H)], 2061.0 (30), 1935.1 (100), 1918.9 (70), 1906.8 (50) [*ν*(C≡O)], 1556.0 (5), 1508.4 (5); HRMS (ESI) calcd for $C_{16}H_{19}NSO_5W$ [*M* – H]$^-$: 520.0410; found: 520.0415; elemental analysis (%) calcd for $C_{16}H_{19}NSO_5W$ (521.2): C, 36.87; H, 3.67; N, 2.69; found C, 36.79; H, 3.69; N, 2.61%.

(*Z*)-**19d**





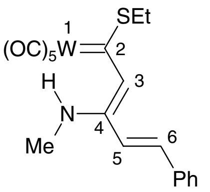
(*E*)-**19d**

4.11.2. Data for (Z)-19d

^{1}H NMR (400 MHz, CDCl$_3$, 300 K): *δ* 6.66 (d, ^3J(H,H) = 1.2 Hz, 1 H; 2-H), 3.83 (sept., ^3J(H,H) = 6.6 Hz, 1H; NCH), 3.08 (dd, ^2J(H,H) = 17.1 Hz, ^3J(H,H) = 7.0 Hz, 1H; *cis*-5-H$_2$), 3.02 (m, 1H; C*H*CH$_3$), 2.98 (q, ^3J(H,H) = 7.4 Hz, 2H; SC*H*$_2$CH$_3$), 2.38 (dd, ^2J(H,H) = 17.1 Hz, ^3J(H,H) = 2.0 Hz, 1H; *trans*-5-H$_2$), 1.43 (t, ^3J(H,H) = 7.4 Hz, 3H; SCH$_2$C*H*$_3$), 1.28 and 1.27 [each d, ^3J(H,H) = 6.6 Hz, 3H; NCH(C*H*$_3$)$_2$], 1.24 (d, ^3J(H,H) = 7.0 Hz, 3H; CHC*H*$_3$); ^{13}C NMR (100 MHz, CDCl$_3$, 300 K): *δ* 201.7 and 199.4 [each C$_q$, 1:4, *trans*- and *cis*-CO; W(CO)$_5$], 182.5 (C$_q$; C=N), 174.6 (C$_q$; C3), 126.7 (CH; C2), 60.1 (CH; NCH), 40.9 (CH; C4), 40.2 (CH$_2$; C5), 26.9 (S*C*H$_2$CH$_3$), 23.8 and 23.7 (each CH$_3$; NCH(*C*H$_3$)$_2$]), 20.6 (CH$_3$; CH*C*H$_3$), 13.4 (SCH$_2$*C*H$_3$); IR (cyclohexane) [cm^{-1} (%)]: $\tilde{\nu}$ = 2065.2 (25), 1928.9 (70), 1922.5 (60), 1915.4 (55), 1908.3 (100) [*ν*(C≡O)], 1569.7 (5), 1545.5 (5) [*ν*(C=N) and *ν*(C=C)]; HRMS (ESI) calcd for $C_{16}H_{18}NSO_5W$ [*M* – H]$^-$: 520.0410; found: 520.0429.

4.12. (2s-cis,3Z,4s-cis,5E)-1,1,1,1,1-Pentacarbonyl-2-ethylsulfanyl-6-phenyl-4-N-methylamino-1-tungsten-1,3,5-hexatriene (**18f**), pentacarbonyl[(3-ethylsulfanyl-4-phenyl-cyclopent-2-enylidene)-methyl- amine, N-W]tungsten(0) [(1Z)-**19f** and (1E)-**19f**], pentacarbonyl[3-(methylamino)-5-phenyl-penta-1,2,4-triene-1-ylidene]tungsten(0) (**20f**)

(*E*)-*N*-Methyl-3-phenyl-acrylimidoyl chloride (**5f**), generated *in situ* from (2*E*)-*N*-methyl-3-phenyl acrylamide (**4f**, 332 mg, 2.0 mmol) and phosphorous oxychloride (306 mg, 2.0 mmol), was reacted with pentacarbonyl[1-(ethylsulfanyl)eth-1-ylidene]tungsten(0) (**1b**, 412 mg, 1.0 mmol) as described above at −78 °C to give compound **18f** (250 mg, 49%, R_f = 0.6 in 1:2 *n*-pentane/diethyl ether, red oil). Compound **18f** in CDCl$_3$, 20 °C was transformed into the yellow compound (*Z*)-**19f** (195 mg, 35%, R_f = 0.6 in 10:1 *n*-pentane/diethyl ether, yellow oil) after short time. An equilibrium between (*Z*)-**19f** and (*E*)-**19f** (R_f = 0.4 in 10:1 *n*-pentane/diethyl ether) with a *E*/*Z*-ratio of 2:3 was established after 14 d, 20 °C. A more polar dark red to violet fraction yielded compound **20f** (109 mg, 22%, R_f = 0.6 in 1:1 dichloromethane/diethyl ether, violet oil).

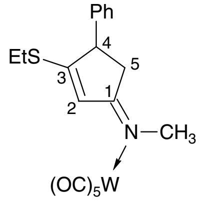


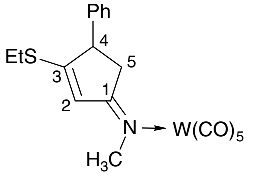
18f

4.12.1. Data for ***18f***

^{1}H NMR (600 MHz, CDCl$_3$, 233 K): δ 0.02 (q, br, ^3J(H,H) = 5.6 Hz, 1H; NH), 7.65 (m, 2 H; *o*-CH Ph), 7.65 (d, ^3J(H,H) = 16.1 Hz, 1H; C*H*-Ph), 7.51 (m, 3H; *m/p*-CH Ph), 6.96 (d, ^3J(H,H) = 16.1 Hz, 1H; C*H*CHPh), 6.86 (s, 1H; 3-H), 3.32 (d, ^3J(H,H) = 5.6 Hz, 3 H; NCH$_3$), 2.95 (q, br, 2H; SCH_2CH$_3$), 1.34 (t, 3H; SCH$_2$CH_3); ^{13}C NMR (150 MHz, CDCl$_3$, 233 K): δ 225.4 (C$_q$; W=C), 202.9 and 198.5 [each C$_q$, 1:4, *trans*- and *cis*-CO; W(CO)$_5$], 163.3 (C$_q$; C4), 144.6 (CH; C6), 133.8 (C$_q$; *i*-C Ph), 131.2 (CH; *p*-C Ph), 129.1 and 128.2 (CH; *o*- and *m*-C Ph), 118.7 (CH; C5), 114.9 (CH; C3), 32.7 (SCH$_2$CH$_3$), 31.1 (CH$_2$; NCH$_3$), 11.4 (SCH$_2$CH$_3$); IR (cyclohexane) [cm^{-1} (%)]: $\tilde{\nu}$ = 2060.9 (40), 1936.3 (100), 1911.8 (60) [ν(C≡O)]; HRMS (ESI) calcd for C$_{19}$H$_{17}$NSO$_5$WNa [*M* + Na]$^+$: 578.0229; found: 578.0231.

(*Z*)-**19f**

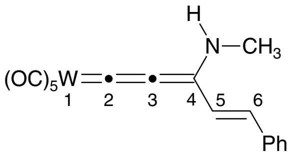




(*E*)-**19f**

*4.12.2. Data for (Z)-**19f** {(E)-**19f**} (obtained from a 10:6.5 Z/E mixture)*

^{1}H NMR (600 MHz, CDCl$_3$, 298 K): δ 7.36 {7.36} (m, 2H; *m*-CH Ph), 7.31 {7.31} (m, 1H; *p*-CH Ph), 7.15 {7.15} (m, 2H; *o*-CH Ph), 6.58 {6.26} (d, ^4J(H,H) = 1.4 Hz {1.4 Hz}, 1H; 2-H, NOE (+) with SCH_2 {NOE (+) with NCH_3 and SCH_2}), 4.12 {4.05} (m, 1H; 4-H), 3.54 {3.68} (s, 3H; NCH$_3$, NOE (+) with 5-H$_2$ {NOE (+) with 2-H}), 3.24 {3.40} (ddd,^2J(H,H) = 18.0 Hz {18.0 Hz}, ^3J(H,H) = 7.6 Hz {7.6 Hz}, ^5J(H,H) = 0.7 Hz {1.4 Hz}, 1H; *cis*-5-H$_2$, NOE (+) with 4-H, NCH_3 and *trans*-5-H$_2$ {NOE (+) with 4-H and *trans*-5-H$_2$}), 2.95 {2.87} (q, 2H; SCH_2CH$_3$), 2.64 {2.90} (ddd, ^2J(H,H) = 18.0 Hz {18.0 Hz}, ^3J(H,H) = 2.6 Hz {2.6 Hz}, ^5J(H,H) = 0.7 Hz {1.4 Hz}, 1H; *trans*-5-H$_2$), 1.38 {1.32} (t, 3H; SCH$_2$CH_3); ^{13}C NMR (150 MHz, CDCl$_3$, 298 K): δ 202.5 and 199.0 {202.4 and 198.7} [each C$_q$, 1:4, *trans*- and *cis*-CO; W(CO)$_5$], 184.4 {184.0} (C$_q$; C=N), 173.1 {175.4} (C$_q$; C3), 140.7 {140.5} (C$_q$; *i*-C Ph), 129.1 {129.0} (CH; *m*-C Ph), 127.9 {127.8} (CH; *p*-C Ph), 127.2 {127.2} (CH; *o*-C Ph), 126.2 {115.1} (CH; C2), 53.4 {53.9} (NCH$_3$), 52.5 {51.3} (CH; C4), 40.8 {49.0} (CH$_2$; C5), 27.2 {26.9} (SCH$_2$CH$_3$), 13.2 {13.0} (SCH$_2$CH$_3$); IR (cyclohexane) [cm^{-1} (%)]: $\tilde{\nu}$ = 2066.4 (20), 1965.0 (5), 1925.3 (100), 1910.9 (50) [ν(C≡O)], 1606.1 (5), 1544.1 (5) [ν(C=C) and ν(C=N)]; IR (diffuse reflexion) [cm^{-1} (%)]: $\tilde{\nu}$ = 2065.6 (5), 1971.0 (3), 1897.1 (100), 1602.4 (4), 1541.7 (10); MS (70 eV): *m/z* for ^{184}W (%): 555 (30) [*M*]$^+$, 471 (75) [*M* – 3CO]$^+$, 442 (50) [*M* – 3CO – Et]$^+$, 415 (40) [*M* – 5CO]$^+$, 231 (100) [*M* – W(CO)$_5$]$^+$, 170 (70) [*M* – W(CO)$_5$ – SEt]$^+$; HRMS (ESI) calcd for C$_{19}$H$_{17}$NSO$_5$WNa [*M* + Na]$^+$: 578.0253; found: 578.0237.



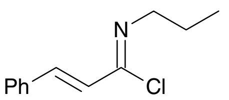
20f

4.12.3. Data for ***20f***

^{1}H NMR (400 MHz, CDCl$_3$, 300 K): δ 10.36 (s, br, 1H; NH), 7.98 (d, ^3J(H,H) = 15.4 Hz, 1H; PhC*H*), 7.51 (m, 2H; *o*-CH Ph), 7.28 (m, 3H; *m*- and *p*-CH Ph), 6.98 (d, ^3J(H,H) = 15.4 Hz, 1H; PhCH=C*H*), 3.38 (s, 3H; NCH$_3$); ^{13}C NMR (100 MHz, CDCl$_3$, 300 K): δ 203.3 and 197.4 [each C$_q$, 1:4, *trans*- and *cis*-CO; W(CO)$_5$], 193.9 (C$_q$, dynamically broadened; W=C), 154.1 (C$_q$; C4), 149.8 (CH; C6), 134.2 (C$_q$; *i*-C Ph), 131.2 (CH; *p*-CH Ph), 129.0 and 128.6 (each CH; *o*- and *m*-CH Ph), 121.9 (CH; C5), 112.3 (C$_q$; C3), 34.1 (NCH$_3$); IR (dichloromethane) [cm^{-1} (%)]: $\tilde{\nu}$ = 3386.7 (4) [ν(N–H)], 2083.0 (1), 1992.9 (35), 1929.8 (100) [ν(C≡O)], 1625.5 (7), 1565.3 (6), 1473.1 (10), 1451.4 (3); MS-ES (ES$^-$/NaBF$_4$-addition): *m/z* (%) = 580 (100) [*M* + BF$_4$]$^-$, 1073 (10) [2*M* + BF$_4$]$^-$.

*4.13. (E)-N-Propyl-3-phenyl-acrylimidoyl chloride (**5g**), (2s-cis,3Z,4s-cis,5E)-1,1,1,1,1-Pentacarbonyl-2-ethylsulfanyl-6-phenyl-4-N-propylamino-1-tungsten-1,3,5-hexatriene (**18g**), pentacarbonyl[(3-ethylsulfanyl-4-phenyl-cyclopent-2-enylidene)-propyl-amine, N-W]tungsten(0) [(1Z)-**19g** and (1E)-**19g**], pentacarbonyl[3-(propylamino)-5-phenyl-penta-1,2,4-triene-1-ylidene]tungsten(0) (**20g**)*

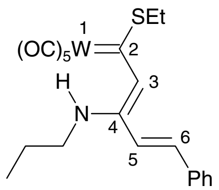
(*E*)-*N*-Propyl-3-phenyl-acrylimidoyl chloride (**5g**), generated *in situ* as described above from (2*E*)-*N*-propyl-3-phenyl acrylamide (**4g**, 378 mg, 2.0 mmol) and phosphorous oxychloride (306 mg, 2.0 mmol) and pentacarbonyl-[1-(ethylsulfanyl)eth-1-ylidene]tungsten(0) (**1b**, 412 mg, 1.0 mmol). Work-up gave red crystals of compound **18g** (328 mg, 56%, R_f = 0.3 in 7:3 *n*-pentane/diethyl ether). In solution (CDCl$_3$, 20 °C) **18g** was transformed into (*Z*)-**19g** (R_f = 0.7 in 10:1 *n*-pentane/diethyl ether, yellow oil) within 4 h. In CDCl$_3$ (*Z*)-**19g** and (*E*)-**19g** (R_f = 0.5 in 10:1 *n*-pentane/diethyl ether, yellow oil) had an equilibrium with a *E*/*Z*-ratio of 3:4 after 11 d at 20 °C. A more polar dark red to violet fraction yielded **20g** (160 mg, 31%, R_f = 0.7 in dichloromethane, violet oil).



5g

*4.13.1. Data for **5g** (obtained from a 1:1 mixture of the amide and phosphorous oxychloride in $CDCl_3$ after 48 h, 20 °C; yield estimated according to NMR ca. 85%)*

^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ 8.02 (d, ^3J(H,H) = 15.3 Hz, 1 H; PhC*H*), 7.82 (d, ^3J(H,H) = 15.3 Hz, 1H; PhCH=C*H*), 7.76 (m, 2H; *o*-CH Ph), 7.55 (m, 1H; *p*-CH Ph), 7.46 (m, 2H; *m*-CH Ph), 3.87 (t, ^3J(H,H) = 7.3 Hz; 2 H; NCH$_2$), 1.95 (m, 2H; NCH$_2$CH_2), 1.08 (t, ^3J(H,H) = 7.4 Hz, 3H; NCH$_2$CH$_2$CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 300 K): δ 167.8 (C$_q$; C=N), 154.5 (CH; Ph*C*H), 133.3 (CH; *p*-C Ph), 132.2 (C$_q$; *i*-C Ph), 130.0 (CH; *o*-C Ph), 129.1 (CH; *m*-C Ph), 117.1 (CH; *C*H=CH-Ph), 51.1 (CH$_2$; NCH$_2$), 20.9 (NCH$_2$*C*H$_2$CH$_3$), 10.9 (NCH$_2$CH$_2$*C*H$_3$).

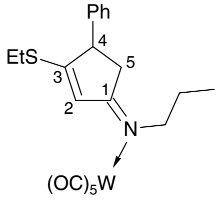


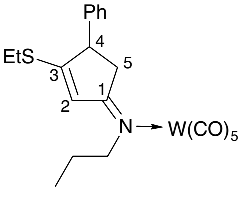
18g

*4.13.2. Data for **18g***

^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ 9.92 (s, br, 1H; NH), 7.56 (m, 2H; *o*-CH Ph), 7.50 (d, br, 1H; C*H*-Ph), 7.45 (m, 3H; *m*/*p*-CH Ph), 6.94 (d, br, 1H; C*H*CHPh), 6.85 (s, 1H; 3-H), 3.52 (m, 2H; NCH$_2$), 2.94 (q, 2 H; SCH_2CH$_3$), 1.91 (m, 2H; NCH$_2$CH_2), 1.34 (t, 3H; SCH$_2$CH_3), 1.08 (t, 3H; NCH$_2$CH$_2$CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 300 K): δ 229.6 (C$_q$; W=C), 202.8 and 199.0 [each C$_q$, 1:4, *trans*- and *cis*-CO; W(CO)$_5$], 162.5 (C$_q$; C4), 143.4 (CH; C6), 134.5 (C$_q$; *i*-C Ph), 130.9 (CH; *p*-C Ph), 129.2 and 128.0 (CH; *o*- and *m*-C Ph), 120.2 (CH, br; C5), 115.6 (CH, br; C3), 47.0 (CH$_2$; NCH$_2$), 33.0 (S*C*H$_2$CH$_3$), 22.5 (NCH$_2$*C*H$_2$CH$_3$), 11.8 (SCH$_2$*C*H$_3$), 11.4 (NCH$_2$CH$_2$*C*H$_3$); IR (cyclohexane) [cm^{-1} (%)]: $\tilde{\nu}$ = 2060.7 (40), 1935.1 (100), 1917.7 (60) [ν(C≡O)]; HRMS (ESI) calcd for $C_{21}H_{20}NSO_5W$ [$M-$H]$^-$: 582.0567; found: 582.0593.

(*Z*)-19g

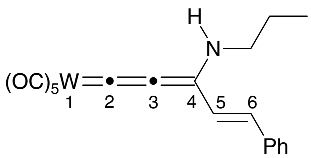




(*E*)-19g

*4.13.3. Data for (Z)-**19g** {(E)-**19g**} (obtained from a 10:3 Z/E mixture)*

^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ 7.35 {7.35} (m, 2H; *m*-CH Ph), 7.29 {7.29} (m, 1H; *p*-CH Ph), 7.12 {7.12} (m, 2H; *o*-CH Ph), 6.60 {6.16} (d, ^4J(H,H) = 1.4 Hz {1.4 Hz}, 1H; 2-H), 4.10 {4.02} (m, 1H; 4-H), 3.61 {3.80} (t {m}, ^3J(H,H) = 8.4 Hz, 2H; NCH$_2$), 3.25 {3.37} (dd, ^2J(H,H) = 17.9 Hz {17.9 Hz}, ^3J(H,H) = 7.7 Hz {7.7 Hz}, 1H; *cis*-5-H$_2$), 2.93 {2.85} (q, ^3J(H,H) = 7.4 Hz {7.4 Hz}, 2H; SCH_2CH$_3$), 2.67 {2.87} (dd, ^2J(H,H) = 17.9 Hz {17.9 Hz}, ^3J(H,H) = 2.6 Hz {2.6 Hz}, 1H; *trans*-5-H$_2$), 1.68 {1.76} (m, 2H; NCH$_2$CH_2CH$_3$), 1.36 {1.31} (t, ^3J(H,H) = 7.4 Hz {7.4 Hz}, 3H; SCH$_2$CH_3), 0.94 {1.02} (t, ^3J(H,H) = 7.4 Hz {7.4 Hz}, 3H; NCH$_2$CH$_2$CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 300 K): δ 202.0 and 199.1 {202.0 and 198.8} [C$_q$, 1:4, *trans*- and *cis*-CO; W(CO)$_5$], 183.7 {185.5} (C$_q$; C=N), 172.9 {174.8} (C$_q$; C3), 140.8 {140.6} (C$_q$; *i*-C Ph), 129.1 {129.0} (CH; *m*-C Ph), 127.8 {127.7} (CH; *p*-C Ph), 127.1 {127.1} (CH; *o*-C Ph), 126.8 {115.5} (CH; C2), 67.4 {67.9} (CH$_2$; NCH$_2$), 52.5 {51.2} (CH; C4), 40.0 {49.5} (CH$_2$; C5), 27.1 {26.8} (S*C*H$_2$CH$_3$), 22.8 {23.3} (NCH$_2$*C*H$_2$CH$_3$), 13.2 {13.0} (SCH$_2$*C*H$_3$), 11.1 {11.1} (NCH$_2$CH$_2$*C*H$_3$); IR (cyclohexane) [cm^{-1} (%)]: $\tilde{\nu}$ = 2065.8 (20), 1963.5 (5), 1923.1 (100), 1909.3 (70) [ν(C≡O)], 1595.5 (5), 1545.2 (5) [ν(C=C) and ν(C=N)]; IR (diffuse reflexion) [cm^{-1} (%)]: $\tilde{\nu}$ = 2064.8 (10), 1967.4 (3), 1865.0 (100), 1591.3 (20), 1535.7 (30), 1493.5 (7), 1474.8 (5), 1453.9 (10), 1319.9 (8), 1073.3 (4); HRMS (ESI) calcd for $C_{21}H_{21}NSO_5WNa$ [M + Na]$^+$: 606.0543; found: 606.0534.



20g

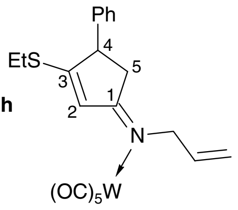
4.13.4. Data for 20g

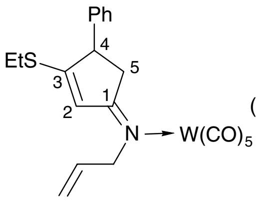
^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ 10.45 (s, br, 1H; NH), 8.00 (d, ^3J(H,H) = 15.4 Hz, 1H; PhC*H*), 7.52 (m, 2H; *o*-CH Ph), 7.34 (m, 1H; *p*-CH Ph), 7.28 (m, 2H; *m*-CH Ph), 7.02 (m, ^3J(H,H) = 15.4 Hz, 1H; PhCH=C*H*), 3.79 (m, 2H; NCH$_2$), 1.81 (m, 2H; NCH$_2$CH_2), 1.03 (t, 3H; NCH$_2$CH$_2$CH_3); ^{13}C NMR (125 MHz, $CDCl_3$, 298 K): δ 203.3 and 197.4 [each C$_q$, 1:4, *trans*- and *cis*-CO; W(CO)$_5$], 190.8 (C$_q$, br; W=C); [compare: 191.0; W(CO)$_6$], 153.3 (C$_q$; C4), 149.9 (CH; C6), 134.2 (C$_q$; *i*-C Ph), 131.1 (CH; *p*-CH Ph), 129.0 (CH; *m*-CH Ph), 128.7 (CH; *o*-CH Ph), 121.7 (CH; C5), 111.4 (C$_q$; C3), 49.5 (NCH$_2$), 22.2 (NCH$_2$CH_2), 11.4 (NCH$_2$CH$_2$CH_3); IR (dichloromethane) [cm^{-1} (%)]: $\tilde{\nu}$ = 3377.3 (5) [ν(N-H)], 2083.0 (2), 1993.2 (25), 1929.5 (100) [ν(C≡O)], 1625.6 (10), 1550.1 (10), 1470.4 (10), 1450.1 (10); IR (diffuse reflexion) [cm^{-1} (%)]: $\tilde{\nu}$ = 3358.1 (10) [ν(N-H)], 2083.5 (1), 2002.5 (40), 1968.8 (20), 1899.0 (100), 1870.7 (75), 1845.7 (40) [ν(C≡O)], 1622.9 (10), 1555.3 (30); HRMS (ESI) calcd for $C_{19}H_{15}NO_5WNa$ [$M+$Na]$^+$: 544.0355; found: 544.0346.

*4.14. Pentacarbonyl[allyl-(3-ethylsulfanyl-4-phenyl-cyclopent-2-enylidene)- amine, N-W]tungsten(0) [(1Z)-**19h** and (1E)-**19h**], pentacarbonyl[3-(allylamino)-5-phenyl-penta-1,2,4-triene-1- ylidene]tungsten(0) (**20h**)*

(*E*)-*N*-Allyl-3-phenyl-acrylimidoyl chloride (**5h**), generated from (2*E*)-*N*-allyl-3-phenyl acrylamide (**4h**, 372 mg, 2.0 mmol) and phosphorous oxychloride (306 mg, 2.0 mmol) was reacted with pentacarbonyl[1-(ethylsulfanyl)eth-1-ylidene]tungsten(0) (**1b**, 412 mg, 1.0 mmol). Reaction with triethylamine (808 mg, 8.0 mmol) at −78 °C and work-up by flash chromatography at 20 °C on silica gel (40 × 1 cm, 1:1 *n*-pentane/diethyl ether) afforded a red compound ($R_f = 0.2$ in 10:1 *n*-pentane/diethyl ether) which was thermolabil and was transformed into compound (*Z*)-**19h** (128 mg, 22%, $R_f = 0.6$ in 10:1 *n*-pentane/diethyl ether, yellow oil) within short time. Compounds (*Z*)-**19h** and (*E*)-**19h** ($R_f = 0.5$ in 10:1 *n*-pentane/diethyl ether, yellow oil) were in equilibrium in 7:10 *E*/*Z*-ratio after 14 d, 20 °C in $CDCl_3$. A more polar dark red to violet fraction yielded compound **20h** (55 mg, 11%, $R_f = 0.5$ in 1:1:1 *n*-pentane/diethyl ether/dichloromethane, violet oil).

(*Z*)-**19h**

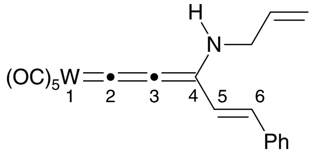




(*E*)-**19h**

*4.14.1. Data for(Z)-**19h**{(E)-**19h**} (obtained from a 10:4 mixture)*

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ 7.35 {7.35} (m, 2H; *m*-CH Ph), 7.30 {7.30} (m, 1H; *p*-CH Ph), 7.11 {7.13} (m, 2H; *o*-CH Ph), 6.66 {6.11} (d, ^4J(H,H) = 1.4 Hz {1.4 Hz}, 1H; 2-H), 5.83 {5.89} (ddt, ^3J(H,H) = 17.3 Hz {17.3 Hz}, ^3J(H,H) = 10.5 Hz {10.5 Hz}, ^3J(H,H) = 4.7 Hz {4.7 Hz}, 1H; $CH_2CH{=}CH_2$), 5.28 {5.34} (ddt, ^2J(H,H) = 1.1 Hz {1.1 Hz}, ^3J(H,H) = 10.5 Hz {10.5 Hz}, ^4J(H,H) = 1.9 Hz {1.9 Hz}, 1H; *cis*-$CH_2CH{=}CH_2$), 5.11 {5.14} (ddt, ^2J(H,H) = 1.1 Hz {1.1 Hz}, ^3J(H,H) = 17.3 Hz {17.3 Hz}, ^4J(H,H) = 1.9 Hz {1.9 Hz}, 1H; *trans*- $CH_2CH{=}CH_2$), 4.38 {4.55} (m, 2H; NCH_2), 4.10 {4.06} (m, 1H; 4-H), 3.25 {3.46} (dd, ^2J(H,H) = 18.2 Hz {18.2 Hz}, ^3J(H,H) = 7.6 Hz {7.6 Hz}, 1H; *cis*-5-H_2), 2.96 {2.82} (q, 2H; SCH_2CH_3), 2.67 {2.96} (dd, ^2J(H,H) = 18.2 Hz {18.2 Hz}, ^3J(H,H) = 2.6 Hz {2.6 Hz}, 1H; *trans*-5-H_2), 1.38 {1.30} (t, ^3J(H,H) = 7.4 Hz {7.4 Hz}, 3H; SCH_2CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 300 K): δ 202.2 and 199.0 {202.1 and 198.7} [each C_q, 1:4, *trans*- and *cis*-CO; $W(CO)_5$], 185.6 {185.2} (C_q; C=N), 174.2 {175.7} (C_q; C3), 140.5 {140.4} (C_q; *i*-C Ph), 132.3 {133.0} (CH; $CH_2CH{=}CH_2$), 129.1 {129.1} (CH; *m*-C Ph), 127.8 {127.8} (CH; *p*-C Ph), 127.2 {127.2} (CH; *o*-C Ph), 126.3 {116.2} (CH; C2), 116.6 {116.9} (CH_2; $CH_2CH{=}CH_2$), 67.3 {67.8} (CH_2; NCH_2), 52.6 {51.3} (CH; C4), 40.2 {49.2} (CH_2; C5), 27.3 {26.9} (SCH_2CH_3), 13.2 {12.9} (SCH_2CH_3); IR (cyclohexane) [cm^{-1} (%)]: $\tilde{\nu} = 2066.4$ (25), 1966.1 (5), 1925.1 (100), 1909.3 (50) [ν(C≡O)], 1594.7 (10), 1543.8 (10) [ν(C=C) and ν(C=N)]; IR (diffuse reflexion) [cm^{-1} (%)]: $\tilde{\nu} = 2065.2$ (10), 1968.4 (4), 1881.5 (100), 1591.5 (13), 1537.8 (15), 1493.9 (3), 1454.4 (4); HRMS (ESI) calcd for $C_{21}H_{19}NSO_5WNa$ $[M + Na]^+$: 604.0386; found: 604.0379.



20h

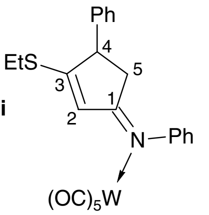
*4.14.2. Data for **20h***

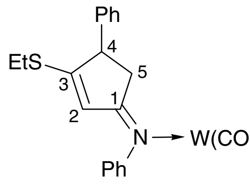
^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ 10.30 (s, br; 1H; NH), 7.99 (d, ^3J(H,H) = 15.4 Hz, 1H; PhC*H*), 7.53 (m, 2H; *o*-CH Ph), 7.34 (m, 1H; *p*-CH Ph), 7.29 (m, 2H; *m*-CH Ph), 7.04 (m, ^3J(H,H) = 15.4 Hz, 1H; PhCH=C*H*), 5.90 (m, 1H; NCH_2CH), 5.38 (d, br, ^3J(H,H) = 15.4 Hz, 1H; *trans*-NCH_2CHCH_2), 5.28 (d, br, ^3J(H,H) = 10.2 Hz, 1H; *cis*-NCH_2CHCH_2), 4.40 (m, 2H; NCH_2).; ^{13}C NMR (100 MHz, $CDCl_3$, 300 K): δ 203.3 and 197.4 [each C_q, 1:4, *trans*- and *cis*-CO; $W(CO)_5$], (C_q; W=C), [25] 152.8 (C_q; C4), 150.3 (CH; C6), 134.3 (C_q; *i*-C Ph), 131.2 (CH; *p*-CH Ph), 130.7 (NCH_2CH), 129.0 (CH; *m*-CH Ph), 128.7 (CH; *o*-CH Ph), 121.8 (CH; C5), 119.8 (NCH_2CHCH_2), (C_q; C3), [25] 50.0 (NCH_2); IR (dichloromethane) [cm^{-1} (%)]: $\tilde{\nu} = 2083.0$ (1), 1993.5 (30), 1929.0 (100) [ν(C≡O)]; HRMS (ESI) calcd for $C_{19}H_{13}NO_5WNa$ $[M + Na]^+$: 542.0198; found: 542.0181.

*4.15. Pentacarbonyl[(3-ethylsulfanyl-4-phenyl-cyclopent-2-enylidene)-phenyl-amine, N-W]tungsten(0) [(1 Z)-**19i** and (1E)-**19i**], pentacarbonyl[3-(phenylamino)-5-phenyl-penta-1,2,4-triene-1-ylidene]tungsten(0) (**20i**), (E)-3,N-diphenyl-thioacrylimidic acid ethyl ester (**21i**)*

(*E*)-*N*-Phenyl-3-phenyl-acrylimidoyl chloride (**5i**), generated *in situ* from (2*E*)-*N*-phenyl-3-phenyl acrylamide (**4i**, 446 mg, 2.0 mmol) and phosphorous oxychloride (306 mg, 2.0 mmol) at 20 °C, 5 d, was reacted with pentacarbonyl[1-(ethylsulfanyl)eth-1-ylidene]tungsten(0) (**1b**, 412 mg, 1.0 mmol) and triethylamine (808 mg, 8.0 mmol) at −78 °C. Work-up at 20 °C with silica gel (40 × 1 cm, 1:1 *n*-pentane/diethyl ether) gave colorless compound **21i** (82 mg, 37%, $R_f = 0.8$ in 10:1 *n*-pentane/diethyl ether) and a yellow compound (*Z*)-**19i** (13 mg, 2%, $R_f = 0.5$ in 10:1 *n*-pentane/diethyl ether, yellow oil). Equilibration of (*Z*)-**19i** and (*E*)-**19i** ($R_f = 0.4$ in 10:1 *n*-pentane/diethyl ether) is accompanied by strong decomposition. ^{1}H NMR data of (*E*)-**19i** were obtained from a sample freshly collected by chromatography. A polar deep blue fraction (30 mg, $R_f = 0.3$ in 1:1:1 *n*-pentane/diethyl ether/dichloromethane) was not characterized completely. A structure **20i** is proposed on the basis of an exact mass determination.

(Z)-**19i**

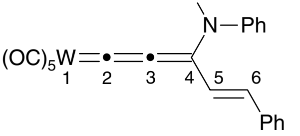




(E)-**19i**

4.15.1. Data for (Z)-**19i**{(E)-**19i**} (^{1}H NMR data could be collected only partially from a 20:1 mixture due to facile decomposition)

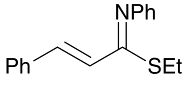
^{1}H NMR (500 MHz, CDCl$_3$, 298 K): δ 7.36 (m, 2H; *m*-CH N-Ph), 7.33 (m, 2H; *m*-CH Ph), 7.27 (m, 1H; *p*-CH Ph), 7.13 (m, 1H; *p*-CH N-Ph), 7.08 (m, 2H; *o*-CH Ph), 6.88 (m, 2H; *o*-CH Ph), 6.77 {5.47} (d, ^4J(H,H) = 1.4 Hz {1.4 Hz}, 1H; 2-H), 4.03 {4.16} (m, 1H; 4-H), 2.84 {3.59} (dd, ^2J(H,H) = 18.9 Hz {18.3 Hz}, ^3J(H,H) = 7.4 Hz {7.5 Hz}, 1H; *cis*-5-H$_2$), 3.02 {2.58} (q, ^3J(H,H) = 7.4 Hz {7.6 Hz}, 2H; SC*H*$_2$CH$_3$), 2.28 {3.06} (dd,^2J(H,H) = 18.9 Hz {18.3 Hz}, ^3J(H,H) = 2.8 Hz {2.6 Hz}, 1H; *trans*-5-H$_2$), 1.42 {1.13} (t, ^3J(H,H) = 7.4 Hz {7.6 Hz}, 3H; SCH$_2$C*H*$_3$); ^{13}C NMR (125 MHz, CDCl$_3$, 298 K): δ 203.2 and 198.9 [C$_q$, 1:4, *trans*- and *cis*-CO; W(CO)$_5$], 185.5 (C$_q$; C=N), 177.0 (C$_q$; C3), 155.7 (C$_q$; *i*-C N-Ph), 140.3 (C$_q$; *i*-C CH-Ph), 129.5 and 129.4 (CH; *m*-C N-Ph), 129.1 (CH; *m*-C CH-Ph), 127.8 (CH; *p*-C CH-Ph), 127.1 (CH; *o*-C CH-Ph), 125.9 (CH; *p*-C N-Ph), 125.0 (CH; C2), 120.6 and 120.5 (each CH; *o*-C N-Ph), 52.7 (CH; C4), 42.1 (CH$_2$; C5), 27.4 (S*C*H$_2$CH$_3$), 13;2 (SCH$_2$*C*H$_3$); IR (cyclohexane) [cm^{-1} (%)]: $\tilde{\nu}$ = 2067.0 (25), 1970.6 (10), 1941.1 (50), 1929.1 (100), 1923.4 (80), 1907.7 (50) [ν(C≡O)], 1585.5 (10), 1538.7 (10) [ν(C=C) and ν(C=N)]; HRMS (ESI) calcd for C$_{24}$H$_{19}$NSO$_5$WNa [*M* + Na]$^+$: 640.0378; found: 640.0378.



20i

4.15.2. Data for **20i**

HRMS (ESI) calcd for C$_{22}$H$_{12}$NO$_5$W [*M* − H]$^-$: 554.0223; found: 554.0242.



21i

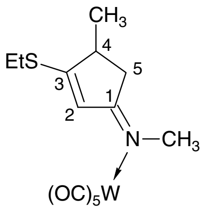
4.15.3. Data for **21i**

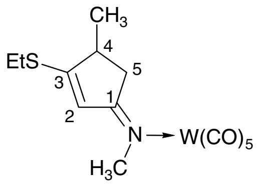
^{1}H NMR (400 MHz, CDCl$_3$, 300 K): δ 7.43 (d, ^3J(H,H) = 16.3 Hz, 1H; PhC*H*), 7.30 (m, 7 H; *m*-CH N-Ph and *o*-, *m*-, *p*-CH Ph), 7.08 (m, 1H; *p*-CH N-Ph), 6.83 (m, 2H; *o*-CH N-Ph), 6.69 (d, ^3J(H,H) = 16.3 Hz, 1H; PhCHC*H*), 3.12 (q, ^3J(H,H) = 7.4 Hz, 2H; SCH$_2$), 1.38 (t, ^3J(H,H) = 7.4 Hz; SCH$_2$C*H*$_3$); ^{13}C NMR (100 MHz, CDCl$_3$, 300 K): δ 163.4 (C$_q$; C=N), 150.5 (C$_q$; *i*-C N-Ph), 137.8 (CH; Ph-*C*H), 135.4 (C$_q$; *i*-C Ph), 129.3, 128.8, 128.7, 127.5 (each CH, 1:2:2:2; *m*-C N-Ph and *o*-, *m*-, *p*-C Ph), 123.5 (CH; p-C N-Ph), 121.4 (CH; PhCH*C*H), 120.9 (CH; *o*-C N-Ph), 24.1 (SCH$_2$), 14.2 (SCH$_2$*C*H$_3$); IR (cyclohexane) [cm^{-1} (%)]: $\tilde{\nu}$ = 1627.3 (30), 1580.5 (100) [ν(C=N)]; HRMS (ESI) calcd for C$_{17}$H$_{18}$NS [*M* + H]$^+$: 268.1154; found: 268.1144.

4.16. Pentacarbonyl[(3-ethylsulfanyl-4-methyl-cyclopent-2-enylidene)-methyl- amine, N-W]tungsten(0) [(1Z)-**19j** and (1E)-**19j**]

(*E*)-*N*-Methyl-but-2-ene-1-carboximidoyl chloride (**5j**), generated *in situ* from (*E*)-but-2-enonic acid methylamide (**4j**, 198 mg, 2.0 mmol) and phosphorous oxychloride (306 mg, 2.0 mmol), was reacted with pentacarbonyl[1-(ethylsulfanyl)eth-1-ylidene]tungsten(0) (**1b**, 412 mg, 1.0 mmol) and triethylamine (808 mg, 8.0 mmol) at −78 °C. Work-up at 20 °C on silica gel (40 × 1 cm, 1:1 *n*-pentane/diethyl ether) afforded a red thermolabile compound (R_f = 0.3 in 1:1 *n*-pentane/diethyl ether) which was transformed into yellow compound (*Z*)-**19j** (130 mg, 26%, R_f = 0.7 in 10:1 *n*-pentane/diethyl ether, yellow oil) after a short time. A 2:3 equilibrium (*Z*)-**19j** and (*E*)-**19j** was achieved at 20 °C, 14 d in CDCl$_3$ (R_f = 0.6 in 10:1 *n*-pentane/diethyl ether).

(Z)-**19j**





(E)-**19j**

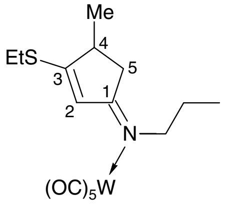
4.16.1. Data for (Z)-**19j**{(E)-**19j**} (obtained from a 10:4 mixture)

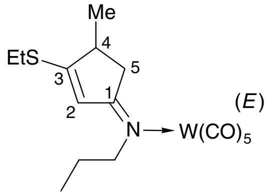
^{1}H NMR (500 MHz, CDCl$_3$, 298 K) δ 6.35 {6.07} (d, ^4J(H,H) = 1.3 Hz {1.3 Hz}, 1H; 2-H, NOE (+) with SC*H*$_2$ {NOE (+) with NC*H*$_3$ and SC*H*$_2$}), 3.52 {3.58} (s, 3H; NCH$_3$, NOE (+) with 5-H$_2$ {NOE (+) with 2-H}), 3.06 {3.04} ("t", ^3J(H,H) = 7.1 Hz, 1H; *cis*-5-H$_2$), 2.95 {3.11} (m, 1H; C*H*CH$_3$), 2.97 {2.92} (q, 2H; SC*H*$_2$CH$_3$), 2.25 {2.45} ("d", ^2J(H,H) = 17.7 Hz {17.7 Hz}, 1H; *trans*-5-H$_2$, NOE (+) with NC*H*$_3$, *cis*-5-H$_2$ and 4-H NOE (+) with 4-H and *cis*-5-H$_2$), 1.43 {1.40} (t, ^3J(H,H) = 7.4 Hz, 3H; SCH$_2$C*H*$_3$), 1.24 {1.26} (d, ^3J(H,H) = 7.1 Hz, 3 H; CHC*H*$_3$); ^{13}C NMR (125 MHz, CDCl$_3$, 298 K): δ 202.6 and 199.0 {202.5 and 198.9} [each C$_q$, 1:4, *trans*- and *cis*-CO; W(CO)$_5$], 184.5 {184.0} (C$_q$; C=N), 175.2 {177.3} (C$_q$; C3), 124.7 {114.0} (CH; C2), 53.2 {53.5} (NCH$_3$), 41.4 {40.2} (CH; C4), 39.1 {47.8} (CH$_2$; C5), 26.9 {26.7} (S*C*H$_2$CH$_3$), 20.6 {20.5} (*C*HCH$_3$), 13.3 {13.1} (SCH$_2$*C*H$_3$); IR (cyclohexane) [cm^{-1} (%)]: $\tilde{\nu}$ = 2066.3 (15), 1964.6 (5), 1924.7 (100), 1909.7 (40) [ν(C≡O)], 1606.7 (5), 1545.5 (5) [ν(C=C) and ν(C=N)]; HRMS (ESI) calcd for C$_{14}$H$_{15}$NSO$_5$WNa [*M* + Na]$^+$: 516.0072; found: 516.0057.

*4.17. Pentacarbonyl[(3-ethylsulfanyl-4-methyl-cyclopent-2-enylidene)-propyl-amine, N-W]tungsten(0) [(1Z)-**19k** and (1E)-**19k**]*

(*E*)-*N*-Propyl-but-2-ene-1-carboximidoyl chloride (**5k**), generated *in situ* from (*E*)-but-2-enonic acid propylamide (**4k**, 254 mg, 2.0 mmol) and phosphorous oxychloride (306 mg, 2.0 mmol) was reacted with pentacarbonyl[1-(ethylsulfanyl)eth-1-ylidene]tungsten(0) (**1b**, 412 mg, 1.0 mmol) and triethylamine (808 mg, 8.0 mmol) at −78 °C. Work-up at 20 °C on silica gel (40 × 1 cm, 1:1 *n*-pentane/diethyl ether) afforded yellow compound (*Z*)-**19k** (55 mg, 11%, $R_f = 0.6$ in 10:1 *n*-pentane/diethyl ether, yellow oil), which in $CDCl_3$ achieved a 9:10 equilibrium of (*Z*)-**19k** and (*E*)-**19k** ($R_f = 0.5$ in 10:1 *n*-pentane/diethyl ether) after 14 d, 20 °C.

(*Z*)-**19k**





(*E*)-**19k**

*4.17.1. Data for (Z)-**19k**{(E)-**19k**}*

^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ 6.37 {5.96} (d, $^3J(H,H) = 1.2$ Hz {1.2 Hz}, 1H; 2-H), 3.60 {3.71} (m, 1H; NCH_2), 3.03 {3.14} (m, 1H; C*H*CH_3), 2.98 {3.09} (dd, $^2J(H,H) = 17.2$ Hz {17.6 Hz}, $^3J(H,H) = 7.0$ Hz {7.1 Hz}, 1H; *cis*-5-H_2), 2.96 {2.91} (q, $^3J(H,H) = 7.3$ Hz {7.4 Hz}, 2H; SCH_2CH_3), 2.28 {2.43} (dd, $^2J(H,H) = 17.2$ Hz {17.6 Hz}, $^3J(H,H) = 2.0$ Hz {2.4 Hz}, 1H; *trans*-5-H_2), 1.66 {1.66} (m, 2H; $NCH_2CH_2CH_3$); 1.42 {1.40} (t, $^3J(H,H) = 7.3$ Hz {7.4 Hz}, 3H; SCH_2CH_3), 1.24 {1.26} (d, $^3J(H,H) = 7.0$ Hz, 3H; $CHCH_3$); 0.97 {0.97} (t, 3H; $NCH_2CH_2CH_3$); ^{13}C NMR (150 MHz, $CDCl_3$, 300 K): δ 202.2 and 199.1 {202.3 and 198.9} [each C_q, 1:4, *trans*- and *cis*-CO; $W(CO)_5$], 183.7 {183.4} (C_q; C=N), 174.9 {176.7} (C_q; C3), 125.4 {114.2} (CH; C2), 67.3 {67.6} (CH; NCH_2), 41.4 {40.0} (CH; C4), 38.2 {48.3} (CH_2; C5), 26.9 {26.6} (SCH_2CH_3), 22.8 {23.2} (CH_2; $NCH_2CH_2CH_3$]), 20.6 {20.5} (CH_3; $CHCH_3$), 13.3 {13.1} (SCH_2CH_3), 11.3 {11.2} (CH_3; $NCH_2CH_2CH_3$); IR (cyclohexane) [cm^{-1} (%)]: $\tilde{\nu} = 2065.6$ (25), 1963.2 (5),1924.2 (100), 1909.3 (70) [ν(C≡O)], 1597.4 (5), 1547.1 (5) [ν(C=N) and ν(C=C)]; HRMS (ESI) calcd for $C_{16}H_{19}NSO_5WNa$ $[M + Na]^+$: 544.0386; found: 544.3384.

5. Supplementary material

CCDC 622534 and 622535 contain the supplementary crystallographic data for **13a** and **18b**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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[23] Not observed or equal to the signal of the major isomer.

[24] Data sets were collected with a Nonius KappaCCD diffractometer, equipped with a Nonius FR591 rotating-anode generator. Programs used: data collection: COLLECT (Nonius B.V., 1998); data reduction: Denzo-SMN (Z. Otwinowski, W. Minor, Methods Enzymol. 276 (1997) 307–326); absorption correction: SORTAV (R.H. Blessing, Acta Crystallogr. Sect. A 51 (1995) 33–37; R.H. Blessing, J. Appl. Cryst. 30 (1997) 421–426); structure solution: SHELXS-97 (G.M. Sheldrick, Acta Crystallogr. Sect. A 46 (1990) 467–473); structure refinement: (SHELXL-97, G.M. Sheldrick, Universität Göttingen, 1997); graphics: SCHAKAL (E. Keller, Universität Freiburg, 1997).

[25] Not detected at ambient temperature due to dynamic line broadening.