Thiono, Selenothiono, and Dithiocarboxylic Ester Complexes from Pentacarbonyl(thiobenzaldehyde)tungsten and π-Donor Substituted Alkynes and Decomplexation of the Esters☆

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Received May 4, 1995

Key Words: Thioaldehyde complexes / Dithioester complexes / Selenothiono ester complexes

Pentacarbonyltungsten-coordinated thiobenzaldehyde, $[(CO)_5W\{S=C(Ph)H\}]$ (**1**), reacts with 1-methylthio-1-propyne, 1-ethylseleno-1-propyne, and alkoxyethynes by insertion of the C≡C into the S=C bond to form in a highly regio- and stereoselective manner the α,β-unsaturated dithio, selenothiono, and thionocarboxylic ester complexes (*E*)(C=C)-$[(CO)_5W\{\eta^1\text{-}S=C(XR')C(R)=C(Ph)H\}]$ (**3**) (R = Me: XR' = SMe (**a**), SeEt (**b**); R = H: XR' = OEt (**c**), O*t*Bu (**d**)). The analogous reaction of **1** with bis(alkylthio)ethynes affords mixtures of the (*E*) and (*Z*)(C=C) isomers of $[(CO)_5W\{\eta^1\text{-}S=C(SR)C(SR)=C(Ph)H\}]$ (**6**) [R = Me (**a**), *t*Bu (**b**)]. The *Z* isomers are the initially formed products. Formation of (*Z*)-**6** is followed by $Z \rightarrow E$ isomerization until an equilibrium [*E*/*Z* = 1 (**6a**), 1.5 (**6b**)] is obtained. For R = *t*Bu isomerization is significantly faster than for R = Me. The dithio and thiono ester ligands can be cleaved intact from the metal by treatment with $[NEt_4]Br$ as shown by the examples of **3a**, **3c**, and **6a**. Complex **3c** has been characterized by an X-ray structural analysis.

Simple thioaldehydes such as e.g. thioacetaldehyde and thiobenzaldehyde are unstable compounds and immediately oligomerize[1]. This considerably restricts their potential use in organic synthesis. Thioaldehydes can be stabilized in several ways: by bulky substituents, π-donor groups at the thiocarbonyl carbon or by coordination to a transition metal.

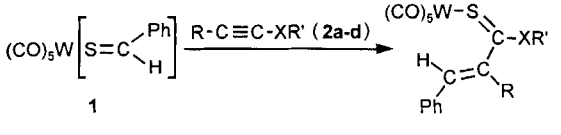
The problems connected with the high reactivity of thioaldehydes can be circumvented by using their complexes. In recent years, pentacarbonylchromium-, -molybdenum-, and -tungsten-coordinated thio- and selenoaldehydes and -ketones turned out to be conveniently accessible C=S and C=Se building blocks for the synthesis of S- and Se-containing heterocycles[2]. Diels-Alder reactions with conjugated dienes gave e.g. 6-membered heterocycles and thia- and selenanorbornene derivatives, respectively[3]. Cycloadditions with vinyl ethers afforded thietane and selenetane complexes[4]. By ring enlargement these 4-membered heterocycles can subsequently be transformed into 5-[5] and 6-membered heterocycles[6] containing two heteroatoms. Thiirane derivatives and their complexes are obtained from pentacarbonyl(thiobenzaldehyde)tungsten and diphenyldiazomethane[7].

We also observed that the C≡C bonds of 1-diethylamino-1-propyne and bis(diethylamino)ethyne insert into the X=C bond of $[(CO)_5M\{X=C(Aryl)R\}]$ (M = Cr, W; X = S, Se, Te; R = H, Aryl) to form transition metal-bound thio-, seleno-, and telluroacrylamide derivatives[8,9]. Decomplexation of these ligands yields the free heterobutadiene derivatives[8]. An extension of this route to other π-donor-substituted alkynes offers – in principle – an easy access to a series of different α,β-unsaturated thione- and selenone derivatives. In this paper we report on the synthesis of thiono, selenothiono, and dithiocarboxylic ester complexes and on the decomplexation of representative examples.

Results and Discussion

Analogously to the reaction of pentacarbonylthio- and -selenobenzaldehyde chromium and tungsten with 1-diethylamino-1-propyne, complex **1** reacts with 1-methylthio-1- (**2a**) and 1-ethylseleno-1-propyne (**2b**) by formal insertion of the C≡C bond into the S=C bond. After chromatography the dithio- and the selenothionocarboxylic ester complexes **3a** and **3b**, respectively, were obtained in moderate yields (Scheme 1).

Scheme 1



1 3a-d

2,3	a	b	c	d
R	Me	Me	H	H
XR'	SMe	SeEt	OEt	OtBu

The reaction very likely proceeds by cycloaddition of the C≡C bond of the alkyne to the S=C bond of **1** to form a thiete complex. Subsequent electrocyclic ringopening gives the final products **3a** and **3b**. Since it has neither been possible to isolate nor to spectroscopically detect the thiete complex, ring opening must be rapid compared to cycloaddition. Thiete formation, however, is plausible on the basis

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of observations made in the system $[(CO)_5W$-{Se=C(Ph)H}] / bis(*tert*-butylthio)ethyne where the corresponding selenete complex was isolated and fully characterized[10].

The reactions of **1** with **2a** and **2b** are much slower than those of **1** with 1-diethylamino-1-propyne[8]. The relative rate of alkyne addition to **1** reflects the decreasing C-nucleophilicity of the alkynes Me−C≡C−XR′ and decreases in the series XR′ = NEt_2, SMe, SeEt. This order of reactivity is in line with the results of kinetic studies of the reactions of diaryl selenoketone complexes with 1-diethylamino-1-propyne[9]. A HOMO(alkyne)−LUMO(complex) control of the reaction and a rate-determining nucleophilic attack of the alkyne at the C=Se carbon atom have been proposed to account for the kinetic data.

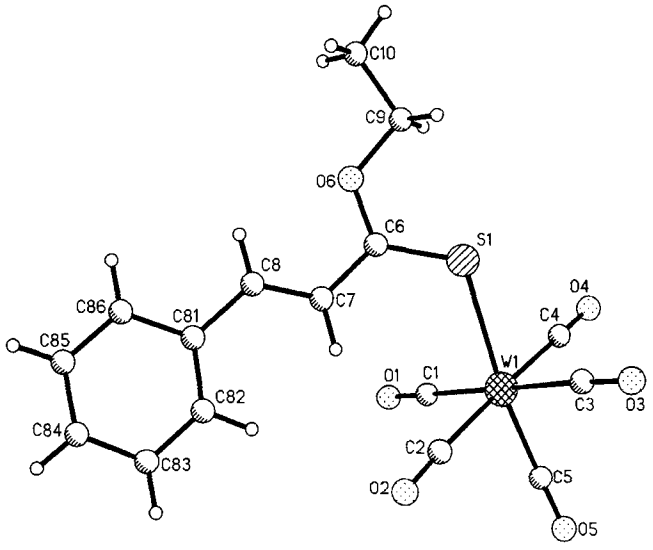
The insertion is not confined to internal electron-rich alkynes. Terminal alkynes such as the alkoxyethynes **2c** and **2d** react with **1** in a similar manner to form the thiono ester complexes **3c** and **3d** (Scheme 1). As expected, the reaction of **2c** with **1** proceeds somewhat faster than the reactions of **1** with **2a** and **2b**, but considerably slower than those of **1** with ynamines. The lower rate for the reaction of **2d** with **1** compared with that of **2c** is probably due to steric factors.

All reactions of **1** with **2a−d** are highly regio- and stereoselective. Only one isomer is formed. From the ν(CO) absorptions in the IR spectra it follows that the heteroester ligand is η^1-bonded to tungsten. In contrast, the starting complex **1** is present in solution as a rapidly equilibrating mixture of the η^2 isomer and the η^1 isomers[11]. The η^1 coordination mode in **3a−d** can also be deduced from the resonance of the thiocarbonyl carbon atom in the ^{13}C-NMR spectra at low field [δ between 239.8 (**3b**) and 207.9 (**3d**)]. A comparison of the C(Ph)*H* resonances of **3a** and **3b** with that of other related thiocarbonyl complexes revealed that C=S and Ph are mutually *trans*-configurated (*E* configuration with respect to the C=C bond). The same arrangement was observed in all kinetically controlled products of the insertion of aminoalkynes into the X=C bond of thio- and selenoaldehyde complexes[8]. In addition, the *E* orientation was confirmed by the ^3J coupling constant of 15.5 Hz in **3c**, **d** which compares well with that observed for the uncoordinated thionocarboxylic ester of **3c** (15.5−16.0 Hz)[12].

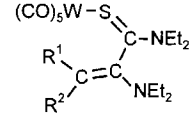
E Orientation and η^1 coordination were also confirmed by the results of an X-ray diffraction study of **3c**. The thionocarboxylic ester framework S(1)−C(6)−C(7)=C(8)−C(81) is planar [torsion angle S(1)−C(6)−C(7)=C(8) 179.4(8)°], i.e. *trans* arrangement on the central C(6)−C(7) bond as shown in Figure 1.

In contrast, in the thioamide complexes (*E*)-**4** and (*Z*)-**4**[8d] and in the selenoamide complexes studied so far[8b,c] the alkene and the X=C−N planes are almost orthogonal [torsion angle 81.4° in (*Z*)-**4** and 82.9° in (*E*)-**4**][8d] due to repulsive steric interactions between both NEt_2 groups. As a consequence of coplanarity and π-interaction of the C=C with the S=C bond the "single bond" distance between both central sp^2-C atoms in **3c** is significantly shorter than in the thioamide complexes **4** [C(6)−C(7): 1.44(1) Å in **3a**, compared to 1.506(8) Å in (*E*)-**4** and 1.52(1) Å in (*Z*)-**4**] and is comparable to that in planar thioacrolein [1.455(27) Å, determined by microwave spectroscopy[13]].

Figure 1. Structure of complex **3c** in the crystal[a]



[a] Selected bond lengths [Å] and angles [°] (standard deviations in brackets) are: W(1)−C(4) 2.04(1), W(1)−C(5) 1.96(1), W(1)−S(1) 2.551(3), S(1)−C(6) 1.66(1), C(6)−O(6) 1.33(1), C(6)−C(7) 1.44(1), C(7)−C(8) 1.32(1), C(8)−C(81), 1.48(1); W(1)−S(1)−C(6) 118.0(3), S(1)−C(6)−O(6) 121.2(7), S(1)−C(6)−C(7) 125.3(7), C(6)−C(7)−C(8) 123.7(9), C(7)−C(8)−C(81) 126.5(9); C(1)−W(1)−S(1)−C(6) 47.6(5), W(1)−S(1)−C(6)−C(7) 10.4(10), S(1)−C(6)−C(7)−C(8) 179.4(8), S(1)−C(6)−O(6)−C(9) 3.8(12), C(6)−C(7)−C(8)−C(81) −176.6(9).



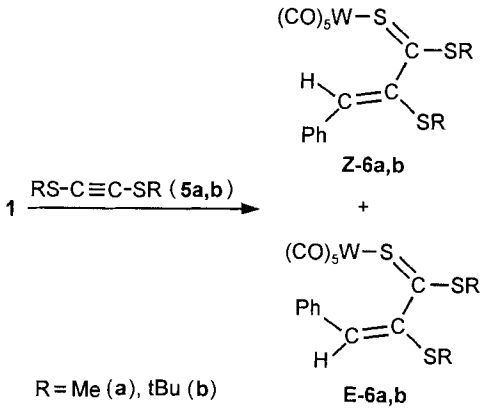
Z-4: R^1=H, R^2=Ph
E-4: R^1=Ph, R^2=H

Compounds **3c** and **3d** are configurationally stable. Compounds **3a** and **3b** slowly isomerize in solution. When a solution of e.g. **3a** in $CDCl_3$ was kept for several days at −30°C, the ^1H spectrum exhibited an additional set of signals. A resonance at δ = 6.50 for the C(Ph)*H* atom indicated a *Z* arrangement of S=C and Ph at the C=C bond. Compound **3b** isomerized similarly [δ = 6.42 for C(Ph)*H*]. After one day at −30°C the initial *E*/*Z* ratio (100:0) of **3b** had changed to 72:28 as determined by integration of the C(Ph)*H* resonance. Isomerization was accompanied by decomposition of the complexes. Therefore, (*Z*)-**3c**, **d** were not obtained in a pure form.

The reaction of **1** with the bis-alkylthio-substituted alkynes **5a**, **b** afforded, after chromatography, the α,β-unsaturated α-alkylthio dithionocarboxylic ester complexes **6a**, **b** in 77% (R = Me) and 58% (R = *t*Bu) yield (Scheme 2). Although the HOMO in **5a**, **b** is higher in energy than that of **2a**[14] the reaction of **1** with **5a**, **b** proceeds slower than with **2a**. The same applies to the reactions of **1** with 1-diethylamino-1-propyne and bis(diethylamino)ethyne. This

indicates that the polarity of the triple bond of the alkyne enhances the reaction rate.

Scheme 2



In contrast to the complexes **3** the compounds **6a**, **b** were obtained as mixtures of the *E* and *Z* isomers with respect to the C=C bond. The configurational assignment was based on a comparison of the resonance of the =C*H* atom in **6a**, **b** with that in related thiono- and dithiocarboxylic esters. Due to the anisotropic effect of the thiocarbonyl group the ^{1}H-NMR signal of the *trans*-H atom (*E* isomer) appears at higher field compared to that of the *cis*-H atom[15].

It was not possible to separate the isomers by column chromatography. From ^{1}H-NMR spectroscopical monitoring of the reaction of **1** with **5a** at ca. −40 °C it followed that the *Z*/*E* ratio of **6a** in the initial phase of the reaction was >9:1. After several days at −30 °C the *Z*/*E* ratio was 1:1. It did not change any more even at room temperature. Therefore, we can safely conclude that the *Z* isomer [Ph and C(=S)SR *trans*] is the kinetically controlled reaction product. Formation of the *Z* isomer of **6a** is then followed by a slower isomerization until the equilibrium ratio of 1:1 is obtained.

The reaction of **1** with **5b** is significantly slower than that with **5a**, probably due to unfavorable steric interactions in the transition state between the bulky S*t*Bu substituent and the C(Ph)H moiety of the thioaldehyde ligand. Very likely, again the *Z* isomer is initially formed. However, since the reaction of **1** with **5b** to form **6b** is slow and requires approximately three days at −30 °C for complete consumption of **1**, the *E*/*Z* ratio of 1.5:1 of the crude reaction mixture is already that occurring at the equilibrium. Obviously, the rate for $Z \rightarrow E$ isomerization is comparable to or even faster than the rate of formation of (*Z*)-**6b**. The 1.5:1 ratio did not change in $CDCl_3$ at room temperature within 7 days, only slow decomposition of **6b** was observed. The higher *E*/*Z* equilibrium ratio of 1.5:1 for **6b** compared to 1:1 for **6a** reflects the increased steric interaction of the *t*Bu with the Ph group (in **6b**) versus that of the Me with the Ph group (**6a**) in the *E* isomer.

Position and intensity ratios of the ν(CO) absorptions of **6a**, **b** and the position of the ^{13}C-NMR resonance of the thiocarbonyl carbon are similar to those of **3a–d**, $[(CO)_5W\{S=C(SR)C(Ph)=C(OEt)Ph\}]$[16] (R = Me, Et) and $[(CO)_5W\{S=C(SMe)Me\}]$[17] which indicates that the ligand in **6a**, **b** is also η^1-bonded.

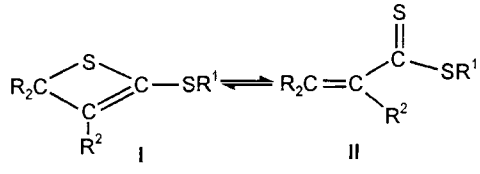
In contrast to the ^{1}H-NMR spectra of **3a–c**, those of **6a** are temperature-dependent. At room temperature **6a** shows a single set of resonances for each isomer. When solutions of **6a** in [D_6]acetone were cooled the signals broadened until at −70 °C a double set of resonances for the *E* and the *Z* isomer each (intensity ratio ca. 1:1 for *E*-**6a** and 1.6:1 for *Z*-**6a**) was observed. The ^{13}C-NMR spectrum of **6a** at −35 °C also exhibited two sets of signals. Therefore, (*E*)- and (*Z*)-**6a** are both present as two isomers which rapidly interconvert at room temperature. From the coalescence of the C(Ph)*H* and the C(=S)SCH_3 resonances of (*E*)-**6a** at −8 ± 5 °C the free energy of activation for the interconversion of the isomers of (*E*)-**6a** was calculated to be $\Delta G^{\neq}$ = 55 ± 1 kJ mol^{-1}. The coalescence temperature for the corresponding signal of (*Z*)-**6a** was −59 ± 5 °C, the estimated value of $\Delta G^{\neq}$ 44 ± 3 kJ mol^{-1}.

In contrast to **6a** there was no splitting of ^{1}H-NMR signals when solutions of **6b** were cooled from 5 °C to −70 °C and only one set of ^{13}C-NMR resonances for (*E*)- and (*Z*)-**6b** each was observed at −35 °C. On warming to room temperature, the ^{1}H resonance of the C(=S)SCH_3 group broadened. Compound **6b** rapidly decomposed in $CDCl_3$ above room temperature. Therefore, it was not possible to obtain NMR spectra at elevated temperatures.

Several processes could account for the appearance of two sets of signals in the NMR spectra of **6a** at low temperature:

(a) Reversible electrocyclic ring closure to 2*H*-thiete complexes. A rapid interconversion of 2*H*-thietes (**I**) and α,β-unsaturated dithioesters (**II**) was already observed by Bos et al. (Scheme 3; R_2C = xanthenylidene, thioxanthenylidene; R^1 = Me, *t*Bu; R^2 = SMe, S*t*Bu, Ph, 2-thienyl)[18].

Scheme 3



However, a comparison of the low-temperature NMR spectra of **6a**, especially the ^{1}H resonances of the C(Ph)*H* hydrogen atom, contradicts such an interpretation.

(b) "*E*/*Z* isomerization" with respect to the S=C bond. ^{1}H-NMR studies of $[(CO)_5M\{S=CMe_2\}]$ (M = Cr, W)[19] show that the activation energy for equilibration of both Me groups in these complexes is smaller than 35 kJ mol^{-1}. Very likely the activation energy for this type of isomerization in (*E*)- and (*Z*)-**6a** is similarly small and therefore cannot account for the splitting of signals in **6a**.

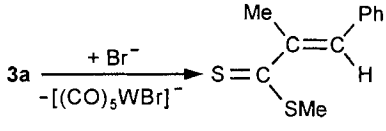
(c) Restricted rotation around the SC–SMe bond as observed in thiocarbene complexes. The barrier to rotation of SMe around the C(carbene)–S bond in $[(CO)_5Cr=C(SMe)Me]$ is 63–71 kJ mol^{-1}[20]. Since both sp^2-C atoms in **6a** are significantly less electrophilic than the C(carbene) atom in this thiocarbene complex the barrier to rotation

around the SC–SMe bond in **6a** is expected to be much lower and could be in the range observed for (*E*)- and (*Z*)-**6a**.

(d) Restricted "rotation" around the S=C–C=C single bond. An equilibrium between a coplanar (fully conjugated, see the solid-state structure of **3c**, Figure 1) and a twisted (non-conjugated, see the solid-state structures of e.g. **4**[8d]) conformer has already been suggested for **II** (Scheme 3: R_2C = 2-norbornanylidene[21]) and [$(CO)_5W${S=C(SEt)-C(Ph)=C(OEt)Ph}] ($\Delta G^{\neq}$ ca. 66 kJ mol^{-1})[16]. A similar equilibrium most plausibly explains the temperature dependence of the ^{1}H-NMR spectra of (*E*)- and (*Z*)-**6a** and the appearance of two sets of ^{13}C-NMR signals. Both conformers differ in the torsion angle S=C–C=C (presumably ca. 0° versus ≈80–90°). On the basis of molecular modelling, a higher barrier to interconversion of the coplanar and the twisted conformer of (*E*)-**6a** than of (*Z*)-**6a** is to be expected. This prediction agrees well with the observed difference in the free energy of activation. Such an interpretation (equilibrium between coplanar and twisted conformer) is also supported by the failure to detect a splitting of resonances when solutions of **6b** are cooled to −70 °C. Steric interactions between the two bulky S*t*Bu substituents render a coplanar conformation energetically very unfavorable.

The decomplexation of the thiocarbonyl ligands was studied with some representative examples. Complex **3a** reacts with tetraethylammonium bromide in dichloromethane to form the dithiocarboxylic ester derivative **7**. Orange crystalline **7** was obtained after column chromatography and recrystallization in 53% yield (Scheme 4). At room temperature **7** dimerized in solution within several hours.

Scheme 4

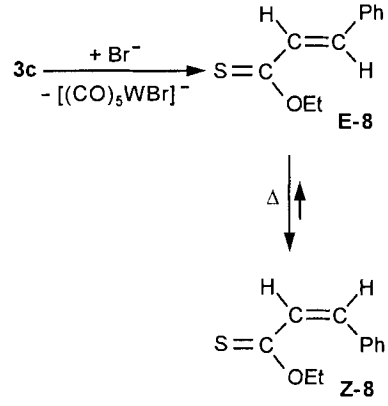


7

The analogous reaction of **3c** with tetraethylammonium bromide in dichloromethane gave a mixture of (*E*)-**8** and (*Z*)-**8** (Scheme 5). Compound **8** (*E*/*Z* = 2.6:1, total yield: 71%) was obtained after purification as a yellow oil. The *E*/*Z* ratio of the crude reaction products (before chromatography) as determined by ^{1}H-NMR spectroscopy was 19:1. Obviously, decomplexation of the thiocarboxylic *O*-ethyl ester is followed by slower isomerization. The *E*/*Z* ratio of 2.6 did not change when a solution of **8** in $CDCl_3$ was kept for 8 hours at room temperature. Addition of trifluoroacetic acid did not influence the ratio either.

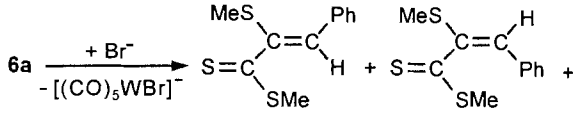
Treatment of a solution of (*E*)-**6a**/(*Z*)-**6a** (1:1) in dichloromethane with tetraethylammonium bromide and chromatography afforded a mixture of (*E*)-**9**, (*Z*)-**9**, and **10** (Scheme 6). It was not possible to completely separate these compounds. The identification of these compounds was based on their NMR spectra. In contrast to (*E*)- and (*Z*)-**6a** the ^{1}H-NMR spectra of (*E*)-/(*Z*)-**9** are not temperature-dependent. Obviously, abstraction of the bulky pentacarbonyltungsten fragment strongly reduces the activation barrier to interconversion of the coplanar and the twisted conformer. The ^{1}H resonances of the coordinated and the free dithiocarboxylic esters differ only slightly ($\Delta\delta < 0.15$). An exception is the C(Ph)*H* signal: decomplexation ((*Z*)-**6a** → (*Z*)-**9**) gives rise to a low-field shift of $\Delta\delta = 0.8$.

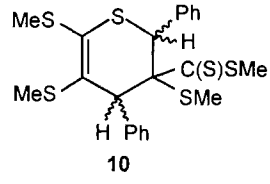
Scheme 5



Dimer **10** is the [4 + 2] cycloadduct of the S=C–C=C unit to the C=C bond in **9**. The connectivity in **10** was derived from ^{1}H- and ^{13}C-NMR spectra. A similar cycloadduct was obtained from sequential reaction of MeCH=CHMgBr with CS_2 and MeI[12a]. A dithiocarboxylic ester, (*E*)-S=C(SMe)CH=C(Me)H, was proposed as an intermediate. In addition to **10** another dimer was formed whose structure could not unambiguously be established.

Scheme 6





10

When a solution of a mixture of **9** and **10** in $CDCl_3$ was kept for 45 days at −30 °C, (*E*)-**9** partially isomerized to (*Z*)-**9**. Dimerization to form **10** was not observed. Since there also occured no dimerization of the coordinated dithiocarboxylic ester in **6a**, dimer **10** was presumably formed by reaction of **6a** with **9** and subsequent decomplexation.

Support of this work by the *Deutsche Forschungsgemeinschaft* and the *Fonds der Chemischen Industrie* is gratefully acknowledged.

Experimental

All manipulations were carried out under either nitrogen or argon by using conventional Schlenk techniques. Solvents were dried by refluxing over sodium/benzophenone ketyl, CaH_2, or $LiAlH_4$ and were freshly distilled prior to use. The silica gel used for chromatography (Baker, silica gel for flash chromatography) was nitro-

gen saturated. Flash chromatography was performed at an N_2 pressure of 1.3 bar. The yields refer to analytically pure compounds and were not optimized. The complex **1**[12] and the alkynes **2a**[22], **2b**[22], **2d**[23], **5a**[22], and **5b**[24] were prepared according to literature procedures, alkyne **2c** was purchased from Merck and was used without further purification. – IR: FT-IR-spectrophotometer, Fa. Bio-Rad and Perkin-Elmer IR spectrophotometer 983 G. – ^{1}H NMR and ^{13}C NMR: Bruker WM 250, Bruker AC 250, Jeol 400. If not specifically mentioned $CDCl_3$ was used as the solvent. Chemical shifts are reported relative to TMS (^{1}H NMR) or relative to the solvent signal (^{13}C NMR). – UV-Vis: Hewlett-Packard diode array spectrophotometer 8452A. – MS: Finnigan MAT 312, modified for EI (70 eV) or FAB-MS (matrix: NBOH).

Pentacarbonyl[S-methyl (E)-2-methyl-3-phenyldithio-2-propenoate]tungsten (**3a**): A solution of 0.39 g (0.87 mmol) of **1** and 0.30 ml (3.5 mmol) of **2a** in 4 ml of dichloromethane is stirred for 3 h at −20 °C and then chromatographed. The red main fraction is eluted with *n*-pentane/dichloromethane (ratio decreasing from 10:1 to 5:1). The solvent is removed in vacuo at −10 °C. Crystallization of the resulting red oil from pentane at −30 °C gives **3a** as red crystals which melt at room temp. Yield 0.23 g (0.43 mmol; 49%, based on **1**), m.p. ca. 25 °C. – IR (*n*-pentane): ν(CO) = 2073 cm^{-1} w, 1983 vw, 1950 vs, 1934 m. – ^{1}H NMR (223 K): δ = 2.37 (br s, 3H, Me), 2.80 (s, 3H, SMe), 6.77 [br s, 1H, C(Ph)*H*], 7.47–7.49 (m, 5H, Ph). – ^{13}C NMR (260 K): δ = 19.6 (Me), 21.9 (SMe), 128.4, 128.5, 129.4, 132.9, 134.8, 142.1 (Ph, C_α, C_β), 196.8 (*cis*-CO), 201.7 (*trans*-CO), 235.2 (*C*S(SMe)). – UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 468 nm (3.978). – MS (EI), *m/z* (%): 208 (77) [M − $W(CO)_5$]$^+$, 161 (100) [M − $W(CO)_5$ − SMe]$^+$, 115 (77) $[C_9H_7]^+$, 91 (57) $[C_7H_7]^+$, 77 (34) $[C_6H_5]^+$, 47 (26) [SMe]$^+$. – $C_{16}H_{12}O_5S_2W$ (532.3): calcd. C 36.11, H 2.27; found C 36.05, H 2.48.

Pentacarbonyl(Se-ethyl (E)-2-methyl-3-phenylselenothiono-2-propenoate)tungsten (**3b**): 0.35 ml (4.8 mmol) of **2b** is added at −30 °C to a blue solution of 0.24 g (0.54 mmol) of **1** in 3 ml of dichloromethane. After 2 h 45 min another 0.35 ml (4.76 mmol) of **2b** is added. The solution is stirred for 50 min at −20 °C and then for 30 min at room temp. Flash chromatography at −75 °C with *n*-pentane/dichloromethane (ratio decreasing from 20:1 to 5:1) gives a red band which contains **3b**. The solvent of the red fraction is removed in vacuo at −30 °C and the oily residue crystallized from *n*-pentane at −78 °C; red crystals. Yield 0.10 g (0.17 mmol; 32% based on **1**), m.p. 35 °C. – IR (*n*-pentane): ν(CO) = 2072 cm^{-1} w, 1985 vw, 1951 vs, 1937 m. – ^{1}H NMR (238 K): δ = 1.57 (t, *J* = 7.6 Hz, 3H, $SeCH_2CH_3$), 2.38 (d, *J* = 1.2 Hz, 3H, Me), 3.35 (q, *J* = 7.6 Hz, 2H, $SeCH_2$), 6.78 [q, *J* = 1.2 Hz, 1H, C(Ph)*H*], 7.39–7.48 (m, 5H, Ph). – ^{13}C NMR (238 K): δ = 14.0 ($SeCH_2CH_3$), 19.8 (Me), 30.2 ($SeCH_2$), 128.5, 128.6, 129.5, 131.6, 134.9, 144.9 (Ph, C_α, C_β), 196.8 (*cis*-CO, J_{WC} = 128.5 Hz), 202.4 (*trans*-CO, J_{WC} = 153.9 Hz), 239.8 (CS). – UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 486 nm (3.934). – MS (FAB, based on ^{184}W), *m/z* (%): 594 (1) [M]$^+$, 538 (2) [M − 2 CO]$^+$, 481 (3) [M − 3 CO − Et]$^+$, 454 (2) [M − 5 CO]$^+$, 453 (2) [M − 4 CO − Et]$^+$, 425 (6) [M − 5 CO − Et]$^+$, 161 (100) [M − $W(CO)_5$ − SeEt]$^+$, 129 (15) [M − $W(CO)_5$ − SeEt − S]$^+$. – $C_{17}H_{14}O_5SSeW$ (593.2): calcd. C 34.42, H 2.38; found C 34.38, H 2.39. – Mol. mass 594 (FAB-MS, ^{184}W).

Pentacarbonyl(O-ethyl (E)-3-phenylthio-2-propenoate)tungsten (**3c**): 0.4 ml (2.5 mmol) of **2c** is added at −25 °C to a solution of 0.27 g (0.61 mmol) of **1** in 3 ml of dichloromethane. In the course of 1 h at −25 °C the color of the solution changes from violet to red. The solution is chromatographed at −35 °C. With *n*-pentane/dichloromethane (10:1) a red band is eluted which contains **3c**. Removal of the solvent in vacuo at room temp. and crystallization of the residue from dichloromethane/*n*-pentane at −30 °C give **3c** in the form of red crystals. Yield 0.12 g (0.23 mmol; 38% based on **1**), m.p. 85 °C (dec.). – IR (*n*-pentane): ν(CO) = 2074 cm^{-1} w, 1985 vw, 1945 vs, 1929 s. – ^{1}H NMR (238 K): δ = 1.61 (t, *J* = 7.0 Hz, 3H, OCH_2CH_3), 4.63 (q, *J* = 7.0 Hz, 2H, OCH_2), 7.54 (d, *J* = 15.4 Hz, 1H, C_α-H), 7.44–7.57 (m, 3H, Ph), 7.66–7.68 (m, 2H, Ph), 7.71 [d, *J* = 15.5 Hz, 1H, C(Ph)*H*]. – ^{13}C NMR (238 K): δ = 14.0 (OCH_2CH_3), 70.6 (OCH_2), 125.4, 129.0, 129.3, 131.7, 133.4, 141.3 (Ph, C_α, C_β), 196.9 (*cis*-CO, J_{WC} = 129.4 Hz), 201.6 (*trans*-CO), 209.0 (CS). – UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 489 nm (3.876). – MS (FAB, based on ^{184}W), *m/z* (%): 516 (100) [M]$^+$, 460 (81) [M − 2 CO]$^+$, 432 (82) [M − 3 CO]$^+$, 376 (49) [M − 5 CO]$^+$, 347 (18) [M − 5 CO − Et]$^+$, 193 (15) [M − $W(CO)_5$ + H]$^+$, 147 (23) [M − $W(CO)_5$ − OEt]$^+$, 131 (64) [M − $W(CO)_5$ − SEt]$^+$, 115 (26) $[C_9H_7]^+$. – $C_{16}H_{12}O_6SW$ (516.2): calcd. C 37.23, H 2.34; found C 37.02, H 2.23. – Mol. mass 516 (FAB-MS, ^{184}W).

Pentacarbonyl(O-tert-butyl (E)-3-phenylthio-2-propenoate)tungsten (**3d**): A solution of 0.44 g (0.99 mmol) of **1** and 0.40 ml (3.4 mmol) of **2d** in 3 ml of dichloromethane is stirred for 3 h 30 min. The reaction temperature is allowed to gradually increase from −50 °C to −21 °C. Then additional 0.10 ml (0.86 mmol) of **2d** is added. After stirring for 110 min another 0.10 ml (0.86 mmol) of **2d** are added. After 5 h 10 min the reaction is complete. During this period the temperature of the solution has increased to −10 °C. The red-violet solution is chromatographed at −40 °C. With *n*-pentane/dichloromethane (ratio decreasing from 10:1 to 2:1) a red band is eluted. The solvent is removed in vacuo at room temp. and the residue crystallized at −30 °C from *n*-pentane, red needles. Yield 0.10 g (0.18 mmol; 18% based on **1**), m.p. 75 °C (dec.). – IR (*n*-pentane): ν(CO) = 2073 cm^{-1} w, 1983 vw, 1942 vs, 1927 s. – ^{1}H NMR ([D$_6$]acetone, 238 K): δ = 1.84 [s, 9H, $OC(CH_3)_3$], 7.61 (d, *J* = 15.5 Hz, 1H, C_α-H), 7.58–7.64 (m, 3H, Ph), 7.85–7.93 (m, 2H, Ph), 7.90 [d, *J* = 15.6 Hz, 1H, C(Ph)*H*]. – ^{13}C NMR (238 K): δ = 27.9 [$OC(CH_3)_3$], 90.7 [$OC(CH_3)_3$], 128.2, 128.9, 129.3, 131.4, 133.5, 140.5 (Ph, C_α, C_β), 197.1 (*cis*-CO, J_{WC} = 129.5 Hz), 201.9 (*trans*-CO), 207.9 (CS). – UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 490 nm (3.787). – MS (FAB, based on ^{184}W), *m/z* (%): 544 (5) [M]$^+$, 488 (32) [M − 2 CO]$^+$, 460 (3) [M − 3 CO]$^+$, 432 (10) [M − 4 CO]$^+$, 404 (7) [M − 5 CO]$^+$, 348 (5) [M − 5 CO − C_4H_8]$^+$, 147 (11) [M − $W(CO)_5$ − OC_4H_9]$^+$, 131 (100) [M − $W(CO)_5$ − SC_4H_9]$^+$, 115 (8) $[C_9H_7]^+$. – $C_{18}H_{16}O_6SW$ (544.2): calcd. C 39.73, H 2.96; found C 39.46, H 2.80. – Mol. mass 544 (FAB-MS, ^{184}W).

Pentacarbonyl(S-methyl 2-methylthio-3-phenylthio-2-propenoate)-tungsten (**6a**): A solution of 0.29 g (0.65 mmol) of **1** and 0.40 ml (4.0 mmol) of **5a** in 3 ml of dichloromethane is stirred for 2 h. The temperature of the solution gradually increases from −30 °C to −11 °C and the color changes from violet to red. Flash chromatography with *n*-pentane/dichloromethane (10:1) at −40 °C gives first a yellow band (containing **5a**) and then a red band. The red fraction is collected and the solvent removed in vacuo. Compound **6a** is obtained as a mixture of the configurational isomers (*Z*)-**6a**/(*E*)-**6a** varying from 7.5/1 to 1/1. It has not been possible to separate the isomers. Yield 0.28 g (0.50 mmol; 77% based on **1**). – IR (*n*-pentane): ν(CO) = 2072 cm^{-1} w, 1985 vw, 1953 vs, 1939 sh. – ^{1}H NMR (298 K): (*Z*)-**6a**: δ = 2.27 (s, 3H; SMe); 2.85 [s, 3H, C(S)SMe], 6.84 [s, 1H, C(Ph)*H*], 7.28–7.44 (m, 3H, Ph), 7.70–7.73 (m, 2H, Ph); (*E*)-**6a**: δ = 2.39 (s, 3H, SMe), 2.71 [s, 3H, C(S)SMe], 6.63 [s, 1H, C(Ph)*H*], 7.28–7.44 (m, 5H, Ph). – ^{13}C NMR (238 K): δ = 15.90, 15.63 (SMe), 22.17, 22.09, 21.61 [C(S)S*C*H$_3$], 126.2–139.5 (Ph, C_a, C_b), 196.21 (J_{WC} = 129.0 Hz), 196.54 (J_{WC} = 129.4 Hz), 196.59 (J_{WC} = 129.2 Hz, *cis*-CO), 202.46, 202.24, 202.22 (*trans*-CO), 228.42, 225.18 (C(S)S). (For (*Z*)-**6a**/(*E*)-

6a = 1/1; In addition to the signal of the configurational isomers signals originating from rotamers are observed. It was not possible to unambiguously assign these resonances). – UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 494 nm (4.077). – MS (FAB, based on ^{184}W), *m/z* (%): 564 (6) $[M]^+$, 536 (100) $[M - CO]^+$, 480 (80) $[M - 3\ CO]^+$, 424 (41) $[M - 5\ CO]^+$, 409 (36) $[M - 5\ CO - Me]^+$, 193 (50) $[M - W(CO)_5 - SMe]^+$, 161 (77) $[M - W(CO)_5 - SMe - S]^+$. – $C_{16}H_{12}O_5S_3W$ (564.3): calcd. C 34.06, H 2.14; found C 33.95, H 2.42. – Mol. mass 564 (FAB-MS, ^{184}W).

Pentacarbonyl(S-tert-butyl 3-phenyl-2-tert-butylthiodithio-2-propenoate)tungsten (**6b**): A solution of 0.40 g (0.90 mmol) of **1** and 0.32 g (1.6 mmol) of **5b** in 3 ml of dichloromethane is kept at −30°C for 3 d. The solution is warmed to room temp., stirred for 10 min and then chromatographed with *n*-pentane/dichloromethane (ratio decreasing from 1:0 to 5:1) at −40°C. The red-violet band containing **6b** as a mixture of configurational isomers (*E*/*Z* = ca. 1.5:1) is eluted. Removal of the solvent in vacuo and crystallization of the residue from *n*-pentane gives dark red crystals. The *E*/*Z* ratio can be increased to 3.5/1 by repetitive crystallization. However, it has not been possible to completely separate the isomers. Yield 0.32 g (0.50 mmol; 56% based on **1**), m.p. [of (*E*)-**6b**/(*Z*)-**6b** 3.3/1] 85°C (dec.). – IR (*n*-pentane): ν(CO) = 2071 cm^{-1} w, 1987 vw, 1951 vs, 1946 vs, 1931 s. – ^1H NMR ([D$_6$]acetone, 238 K): (*Z*)-**6b**: δ = 1.43 (s, 3H, SMe), 1.77 [s, 3H, C(S)SMe], 7.81 [s, 1H, C(Ph)*H*], 7.46–7.51 (m, 3H, Ph), 8.24–8.25 (m, 2H, Ph); (*E*)-**6b**: δ = 1.49 (s, 3H, SMe), 1.67 [s, 3H, C(S)SMe], 7.46–7.51 (m, 3H, Ph), 7.54 [s, 1H, C(Ph)*H*], 7.57–7.81 (m, 2H, Ph). The assignment of the signals in the Ph area is based on the relative intensities. – ^{13}C NMR (223 K): (*Z*)-**6b**: δ = 28.0 [SC(CH_3)$_3$], 31.3 [C(S)SC(CH_3)$_3$], 51.6 (S*C*Me$_3$), 54.6 [C(S)S*C*Me$_3$], 197.5 (*cis*-CO), 203.4 (*trans*-CO), 230.5 [*C*(S)SCMe$_3$]; (*E*)-**6b**: δ = 27.5 [SC(CH_3)$_3$], 31.2 [C(S)SC(CH_3)$_3$], 49.9 (S*C*Me), 54.4 [C(S)S*C*Me], 197.1 (*cis*-CO, J_{WC} = 129.6 Hz), 203.0 (*trans*-CO), 229.9 [*C*(S)S]; (*Z*)-**6b**/(*E*)-**6b**: δ = 128.2, 128.4, 128.8, 129.3, 130.0, 131.2, 134.1, 138.6, 144.9, 145.2 (Ph, C_β, C_β). – UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 500 nm (3.989). – MS (FAB, based on ^{184}W), *m/z* (%): 649 (4) $[M + H]^+$, 620 (94) $[M - CO]^+$, 564 (33) $[M - 3\ CO]^+$, 563 (39) $[M - CO - C_4H_9]^+$, 536 (27) $[M - 4\ CO]^+$, 508 (34) $[M - 5\ CO]^+$, 507 (36) $[M - 3\ CO - C_4H_9]^+$, 480 (43) $[M - 4\ CO - C_4H_8]^+$, 451 (37) $[M - 5\ CO - C_4H_9]^+$, 424 (18) $[M - 4\ CO - 2\ C_4H_8]^+$, 395 (61) $[M - 5\ CO - C_4H_8 - C_4H_9]^+$, 179 (66) $[M - W(CO)_5 - SC_4H_9 - C_4H_8]^+$, 147 (71) $[M - W(CO)_5 - SC_4H_9 - SC_4H_8]^+$, 115 (100) $[M - W(CO)_5 - 3\ S - C_4H_9 - C_4H_8]^+$. – $C_{22}H_{24}O_5S_3W$ (648.5): calcd. C 40.75, H 3.73; found C 40.77, H 3.80.

S-Methyl (E)-2-Methyl-3-phenylthio-2-propenoate (**7**): A solution of 290 mg (0.55 mmol) of **3a** and 300 mg (1.4 mmol) of [NEt$_4$]Br in 5 ml of dichloromethane is stirred for 16 h at 4°C and then for 2 h at room temp. The color of the solution changes from red to yellow-brown. The solution is chromatographed with *n*-pentane/dichloromethane (ratio decreasing from 10:1 to 5:1) at −40°C. The yellow band is collected. Removal of the solvent in vacuo and crystallization of the residue from *n*-pentane/dichloromethane at −30°C gives **7** as orange crystals. Yield 60 mg (0.29 mmol; 53% based on **3a**), m.p. 34°C. – ^1H NMR: δ = 2.44 (d, *J* = 0.7 Hz, 3H, Me), 2.70 (s, 3H, SMe), 7.26–7.45 (m, 5H, Ph), 7.60 (br s, 1H, C(Ph)*H*). – ^{13}C NMR (238 K): δ = 19.0 (Me), 20.4 (SMe), 232.8 [C(S)S], 128.1, 128.3, 129.8, 135.9, 143.7 (Ph, C_α, C_β). – UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 476 nm (2.637). – MS (EI), *m/z* (%): 208 (94) $[M]^+$, 193 (8) $[M - Me]^+$, 161 (100) $[M - SMe]^+$, 128 (68) $[M - SMe - S - H]^+$, 115 (36) $[M - 2\ S - 2\ Me + H]^+$, 91 (19) $[C_7H_7]^+$. – $C_{11}H_{12}S_2$ (208.4): calcd. C 63.42, H 5.81; found C 63.27, H 5.87. – Mol. mass 208 (EI-MS).

O-Ethyl 3-Phenylthio-2-propenoate (**8**): A solution of 70 mg (0.14 mmol) of **3c** and 120 mg (0.57 mmol) of [NEt$_4$]Br in 3 ml of dichloromethane is stirred for 23 h at 4°C. The color of the solution changes from red to yellow-brown. The solvent is removed in vacuo and the residue is extracted with *n*-pentane [(*E*)-**8**/(*Z*)-**8** ≈ 19/1]. The solvent is removed in vacuo from the extract. The residue is dissolved in 3 ml of dichloromethane and the solution chromatographed at −35°C. With *n*-pentane/dichloromethane (ratio decreasing from 10:1 to 5:1) a yellow band is eluted. Removal of the solvent gives **8** [(*E*)-**8**/(*Z*)-**8** = 2.6/1) as a yellow oil. Yield 20 mg (0.10 mmol; 71% based on **3c**). The compound **8** is identified by comparison of its MS and NMR spectra with those of published **8**[12].

S-Methyl 2-Methylthio-3-phenyldithio-2-propenoate (**9**) *and Thiacyclopentene* **10**: A solution of 0.49 g (0.87 mmol) of a mixture of (*Z*)-**6a** and (*E*)-**6a** (*E*/*Z* ≈ 1/1) and 0.63 g (3.0 mmol) of [NEt$_4$]Br in 4 ml of dichloromethane is stirred at 4°C for 22 h. The red-violet solution turns yellow-brown. The solution is chromatographed with *n*-pentane/dichloromethane (ratio decreasing from 10:1 to 5:1) at −35°C (eluant: *n*-pentane/CH_2Cl_2, ratio decreasing from 10:1 to 3:1). The first (red) band contains (*E*)-**6a**/(*Z*)-**6a**/(*E*)-**9**/(*Z*)-**9** and another unidentified compound. The second (yellow) band gives a mixture of (*E*)-**9**/(*Z*)-**9** and **10** (ratio 79:15:6), which cannot be separated by chromatography. Therefore, the spectroscopic data refer to this mixture. Yield 0.10 g (0.42 mmol; 48% based on **6a**). – ^1H NMR: (*E*)-**9a**: δ = 2.38 (s, 3H, SMe), 2.65 (s, 3H, C(S)SCH$_3$), 6.59 [s, 1H, C(Ph)*H*], 7.16–7.44 (m, 5H, Ph); (*Z*)-**9a**: δ = 2.27 (s, 3H, SCH$_3$), 2.72 [s, 3H, C(S)SCH$_3$], 7.20–7.47 (m, 3H, Ph), 7.64 [s, 1H, C(Ph)*H*], 7.77–7.82 (m, 2H, Ph); **10**: δ = 2.09 (s, 3H, SMe), 2.25 (s, 3H, SMe), 2.42 (s, 3H, SMe), 2.55 (s, 3H, SMe), 4.28 [s, 1H, C(Ph)*H*], 5.72 [s, 1H, C(Ph)*H*], 7.16–7.44 (m, 10H, Ph). – ^{13}C NMR (238 K): (*E*)-**9a**: δ = 15.9 (SCH$_3$), 20.5 [C(S)S*C*H$_3$], 124.4, 127.4, 128.2, 128.4, 134.9, 142.2 (Ph, C_α, C_β), 229.9 [C(S)S]; (*Z*)-**9a**: δ = 17.1 (SCH$_3$), 21.3 [C(S)S*C*H$_3$], 128.2, 128.4, 129.0, 130.5, 136.3, 141.9 (Ph, C_α, C_β), 229.4 [C(S)S]; **10**: δ = 15.9, 17.7, 18.6, 21.0 (SCH$_3$), 52.0, 62.3, 70.2 (2-C, 3-C, 4-C), 120.4–138.8 (Ph, 5-C, 6-C), 233.3 [C(S)S]. – MS (EI), *m/z* (%): 240 (91) $[M]^+$, 193 (23) $[M - SMe]^+$, 178 (14) $[M - S - 2\ Me]^+$, 161 (100) $[M - 2\ S - Me]^+$, 146 (26) $[M - 2\ SMe]^+$, 134 (27) $[M - Me - C(S)SMe]^+$, 102 (23) $[M - SMe - C(S)SMe]^+$, 91 (20) $[C_7H_7]^+$. – $C_{11}H_{12}S_3$ (240.4): calcd.C 54.96, H 5.03; found C 54.69, H 5.11. – Mol. mass 240 (EI-MS).

X-ray Structural Analysis of **3c**: $C_{10}H_{12}O_6SW$, molecular mass 516.2, crystal size 0.2 × 0.2 × 0.2 mm^3 (obtained from *n*-pentane/CH_2Cl_2, 10/1); orthorhombic, space group *Pbca*, *a* = 13.615(4), *b* = 13.716(4), *c* = 19.031(7) Å, *V* = 3554(2) $Å^3$, *Z* = 8, d_{calcd} = 1.929 g cm^{-1}; μ(Mo-K_α) = 6.778 mm^{-1}, *F*(000) = 1968; ω-scan, 2Θ range 4.0–52.0°, scan rate 1.5–29.3° min^{-1} in ω; Δω = 0.60°, 3930 reflections collected, 3502 independent reflections, 2359 reflections with $I > 4.0\sigma(I)$; 217 refined parameters; R = 0.045, R_w = 0.050. Largest difference peak (hole): +1.18 e$Å^{-3}$ (−0.71 e$Å^{-3}$). – The measurements were made at −45°C with a crystal of **3c** mounted in a glass capillary on a Siemens R3m/V diffractometer (graphite monochromator, Mo-K_α radiation, λ = 0.71073 Å). A semi-empirical absorption correction (based on 10 reflections) was carried out. The structure was solved by Patterson methods using the SHELXTL PLUS (VMS) program package [transmission (max./min.): 0.022/0.009]. The positions of the hydrogen atoms were calculated by assuming ideal geometry (d_{C-H} = 0.96 Å) and their coordinates were refined together with the attached C atoms as "riding model". The positions of all other atoms were refined anisotropically by the full-matrix least-squares method. Complete

lists of atom coordinates and thermal parameters have been deposited[25].

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* Dedicated to Prof. *R. R. Schmidt* on the occasion of his 60th birthday.

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[25] Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-401736, the authors and the journal citation.

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