Ethynylthioamide Complexes: Synthesis, Reactivity and an Unusual Coupling Reaction with Diethylaminopropyne

Normen Szesni, Matthias Drexler, Bernhard Weibert, and Helmut Fischer

Fachbereich Chemie, Universität Konstanz, Fach M727, D-78457 Konstanz, Germany

Reprint requests to Prof. Dr. H. Fischer. E-mail: helmut.fischer@uni-konstanz.de

Z. Naturforsch. **2007**, *62b,* 346 – 356; received July 20, 2006

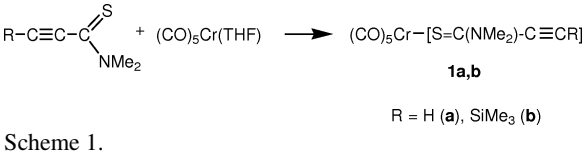
Dedicated to Prof. Helgard G. Raubenheimer on the occasion of his 65 th birthday

The reaction of $[(CO)_5Cr(THF)]$ with propynethioic acid amides, R–C≡C–C(=S)NMe_2 (R = H, $SiMe_3$), yields the thioamide complexes $[(CO)_5Cr–S=C(NMe_2)C≡C–H]$ (**1a**) and $[(CO)_5Cr–S=C(NMe_2)C≡C–SiMe_3]$ (**1b**). Treatment of solutions of **1a** or **1b** with methyllithium generates, *via* deprotonation or desilylation, the lithium salt $Li[(CO)_5Cr–S=C(NMe_2)C≡C]$ (**2**). On filtration over silica, **2** is readily reprotonated. Complex **1a** is inert towards methanol, however, adds diethylamine across the C≡C bond to give the thioacrylamide complex $[(CO)_5Cr–S=C(NMe_2)C(H)=C(H)NMe_2]$ (**3**). Thiourea displaces the thioamide ligand to give $[(CO)_5Cr–S=C(NH_2)_2]$ (**4**). Complex **1a** reacts with half an equivalent of diethylaminopropyne in a three-component coupling to form the homobinuclear complex $[(CO)_5Cr–S=C(NEt_2)–C(CH_3)=C(H)–C(H)=C(NMe_2)–C≡C–C(NMe_2)=S–Cr(CO)_5]$ (**5**) in high yield. The solid state structures of complexes **1a** and **5** were established by X-ray structural analyses.

Key words: Thioamide Complexes, Chromium Complexes, Nucleophilic Addition, Coupling Reaction

Introduction

Thioamides exhibit versatile coordination properties and have been used as ligands in a variety of transition metal complexes. In complexes, thioamides can act as *N*-, *S*-, or *N,S*-donating groups in a terminal or a bridging mode and are capable of generating mononuclear, polynuclear or polymeric complexes [1]. α,β-Unsaturated thioamides (thioacrylamides) carry an additional functional group for potential coordination to transition metals in addition to nitrogen and sulphur. Although a number of complexes have been prepared and structurally characterized the reactivity of coordinated thioacrylamides has only been explored to a minor degree [2]. Non-coordinated thioacrylamides were found to be excellent Michael acceptors. They readily add nucleophiles like organolithium and -magnesium compounds, enolates of ketones, esters and amides or amines across the C=C bond. The scope of the reactivity could be extended to considerably less reactive nucleophiles like sodium malonates by coordination of thioacrylamides to palladium [3]. *Via* coordination to a tricarbonyliron fragment acrylthioamides could be induced to form carbocyclization products in good yields in the reaction with alkynes and carbon monoxide [4].



Scheme 1.

Thioamide complexes containing an α,β carbon-carbon triple bond are unknown until now. In this account we report on the synthesis of the first thioamide complexes derived from propynoic acid, on the coordination mode of these unsaturated thioamide ligands and on the results of some preliminary studies on the reactivity towards simple nucleophiles as well as towards diethylaminopropyne as an example for electron-rich alkynes.

Results and Discussion

The complex $[(CO)_5Cr(THF)]$ reacts readily with propynethioic acid amides by displacement of the weakly coordinating THF ligand to form the propynethioic acid amide complexes **1a** and **1b** (Scheme 1). At ambient temperature the reaction is complete within minutes affording, after chromatography, **1a** and **1b** in 96 % and 93 % yield, respectively. By the same method

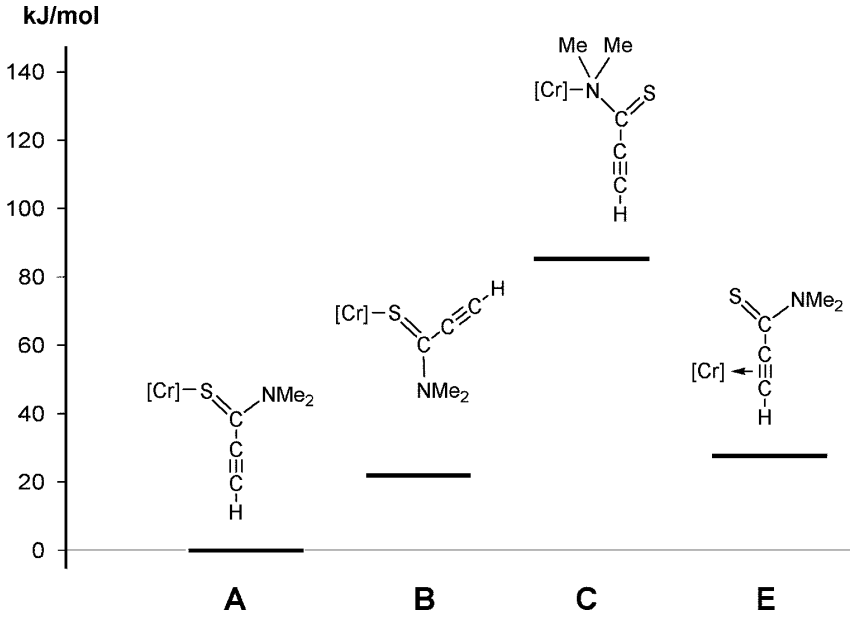
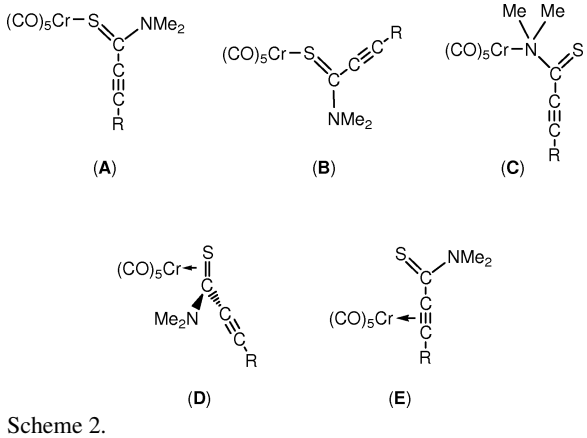


Fig. 1. Relative energies of the various isomers of complex **1a** as calculated on the LACVP*/BP86 level of theory.



Scheme 2.

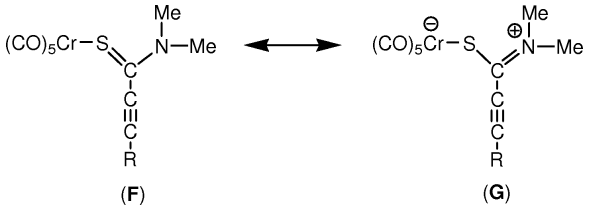
pentacarbonyl thiourea and thiocarbonato complexes of chromium, molybdenum, and tungsten have previously been synthesized [5].

The new complexes **1a** and **1b** are stable in an inert gas atmosphere and are soluble in common organic solvents. These complexes were fully characterized by spectroscopic means and elemental analysis. The IR spectra of **1a** and **1b** show the typical pattern of a *pseudo*-octahedral [$(CO)_5$M–L] complex. Several isomers for **1a, b** are conceivable (**A** – **E**, Scheme 2) due to the multifunctionality of the propynethioic acid amide ligand.

The coordination mode of thioketones and thioaldehydes to transition metals strongly depends on the substitution pattern and the co-ligand sphere. In pentacarbonyl transition metal complexes thioketones and thioaldehydes usually coordinate *via* one of the two lone electron pairs at the sulphur atom (η^1 coordination modes **A** and **B**) [6]. An equilibrium between η^1 and η^2 isomers in solution (corresponding to isomers **A/B** and **D**) was observed for some thiobenzaldehyde complexes of tungsten [7] and of ruthenium [8]. The isomers were found to rapidly interconvert. Exclusively the η^2 coordination mode, comparable to **D**, was found in thioaldehyde complexes of titanium, zirconium, tantalum, iron, rhenium, rhodium, osmium, and some cyclopentadienyl molybdenum complexes [6]. Some thioketone ligands in vanadium, cobalt, rhodium, palladium, and platinum complexes also exhibit η^2 coordination [6]. The rapid interconversion of two η^1 thioaldehyde isomers (corresponding to an interconversion of **A** and **B**) was also observed [9].

In addition to η^1(S) and η^2(C=S) coordination, bonding *via* the lone electron pair at the nitrogen atom (**C**) and *via* the CC triple bond (**E**) is likewise conceivable.

The position of the ν(CO) absorptions at rather low energy indicates that the thioamide ligand is a strong donor. In the ^{1}H and the ^{13}C NMR spectra, complexes **1a** and **1b** show two sets of methyl resonances, however, only one set of signals for the remaining hydrogen and carbon atoms. Therefore, the coordination modes



Scheme 3.

C – **E** can be excluded. In **C** both methyl groups are equivalent and should give rise to only one methyl resonance. In the η^2 bonding modes **D** and **E** the thioamide ligand is expected to exhibit pronounced π-acceptor properties and the ν(CO) absorptions should appear at considerably higher energy. The observation of only one set of ^{13}C resonances for the C_3 fragment indicates the presence of only structures **A** *or* **B**, or of a rapidly interconverting equilibrium of **A** and **B** in solution. In the solid state (see below) **1a** adopts conformation **A** (*E* isomer with respect to the C=S bond). Very likely, the same isomer is present in solution. An η^1 coordination mode comparable to **A** has also been reported for related thioacrylamide complexes [2a, 2b, 10]. The assumption is in accord with the results of DFT calculations on **1a**. Isomer **B** was calculated to be 29 kJ/mol higher in energy than isomer **A**. Isomer **E** is higher in energy than **B** only by about 5 kJ/mol (34 kJ/mol with respect to **A**) whereas the "amine" isomer **C** is considerably higher in energy (by 99 kJ/mol) (Fig. 1). For isomer **D** no local minimum on the energy surface could be located.

The inequivalence of the methyl resonances in the NMR spectra indicates hindered rotation around the C–NMe bond and some double-bond character of this bond. From the temperature-dependence of the ^{1}H NMR spectra in $C_6D_5CD_3$ the energy barrier to rotation around the C–NMe bond in **1b** is calculated to be $\Delta G^{\#}$ = 79.6 kJ/mol (coalescence at 92 °C; compound **1a** rapidly decomposed under similar conditions). This emphasizes that the zwitterionic resonance form **G** (Scheme 3) significantly contributes to the stabilization of the complexes [11].

The structure of complex **1a** was additionally confirmed by an X-ray structural analysis (Fig. 2, Table 1). As deduced from the spectroscopic data the thioamide ligand is η^1-bound to the chromium atom and is staggered with respect to the *cis*-CO ligands [C(2)–Cr(1)–S(1)–C(8) = 43.98(2)°]. The Cr(1)–S(1) bond length (2.417(2) Å) agrees well with that in known thioamide chromium complexes [$(CO)_5$Cr–S=C(NMe$_2$)–S–C(=O)NMe$_2$] (2.449(1) Å) [2a] and [$(CO)_5$Cr–S=C(NMe$_2$)Me] (2.454(1) Å) [12]. The trigonal-planar environment of the atoms C(8) and N(1) (sum of angles = 360° in both cases) together with the rather short C(8)–N(1) distance indicates a partial double bond character of C(8)–N(1) comparable to that of aminocarbene complexes [13]. The signifi-

Table 1. Crystal data and refinement details for the complexes **1a** and **5**.

	1a	**5**
Formula	$C_{10}H_7CrNO_5S$	$C_{27}H_{27}Cr_2N_3O_{10}S_2$
M_r	305.23	721.64
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$
a [Å]	8.6484(13)	10.240(2)
b [Å]	8.237(5)	28.907(6)
c [Å]	9.095(6)	11.683(2)
β [deg]	93.68(7)	110.12(3)
V [Å^3]	646.6(6)	3247.2(11)
Z	2	4
Crystal size [mm^3]	$0.5 \times 0.4 \times 0.3$	$0.5 \times 0.5 \times 0.5$
ρ_{calc} [g cm^{-3}]	1.568	1.476
μ, [mm^{-1}	1.056	0.854
F(000)	308	1480
T [K]	188(2)	188(2)
2θ range (°)	4.48 – 53.98	4.46 – 54.18
Index range	$-10 \le h \le 11$	$-12 \le h \le 13$
	$-10 \le k \le 10$	$-36 \le k \le 0$
	$-11 \le l \le 11$	$-14 \le l \le 0$
Number of data	2240	7417
Number of unique data	1521	7076
Parameters	99	397
$R(F)$ for $I \ge 2\sigma(I)$	0.0490	0.0492
$wR_2(F^2)$ for all data	0.1107	0.1185
Goodness-of-fit on F^2	1.061	1.047

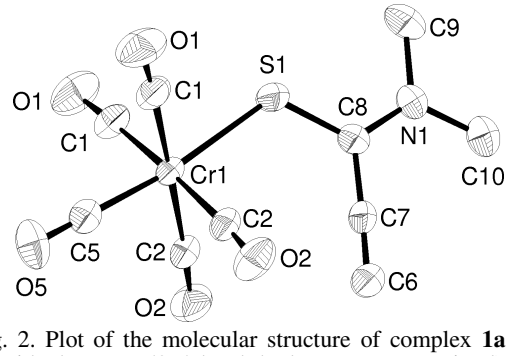
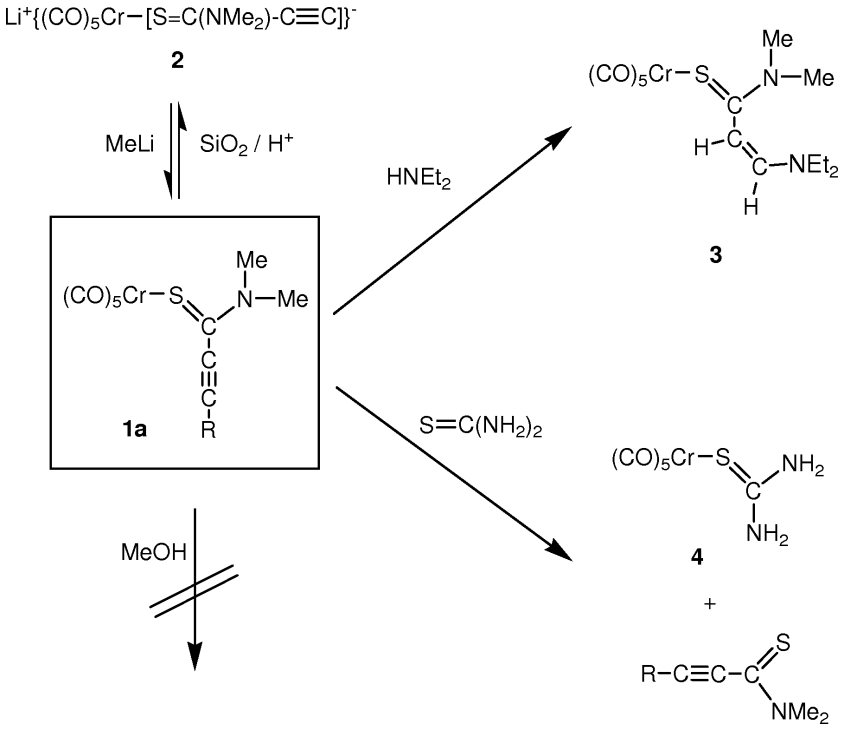


Fig. 2. Plot of the molecular structure of complex **1a** (ellipsoids drawn at 50 % level, hydrogen atoms omitted). Selected bond lengths (Å) and angles (°) are: Cr(1)–C(1) 1.893(3), Cr(1)–C(2) 1.883(3), Cr(1)–C(5) 1.830(5), Cr(1)–S(1) 2.417(2), S(1)–C(8) 1.667(4), C(8)–N(1) 1.326(5), C(8)–C(7) 1.431(5), C(7)–C(6) 1.157(6); Cr(1)–S(1)–C(8) 118.46(14), S(1)–C(8)–N(1) 121.3(3), S(1)–C(8)–C7(1) 121.0(3), N(1)–C(8)–C(7) 117.7(4), C(6)–C(7)–C(8) 178.3(4).



Scheme 4.

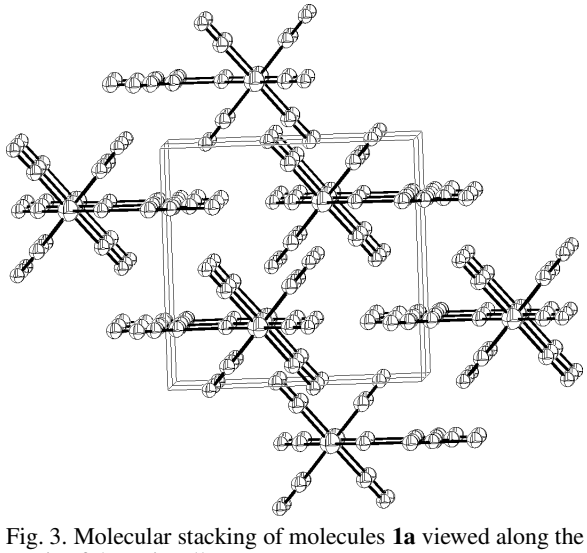


Fig. 3. Molecular stacking of molecules **1a** viewed along the *c* axis of the unit cell.

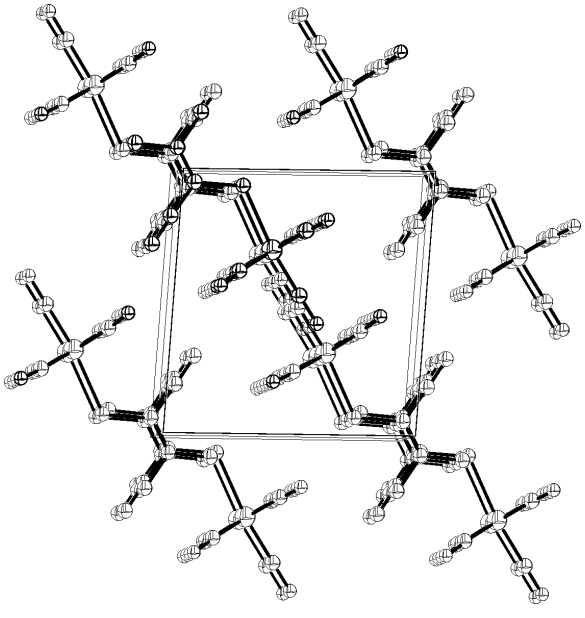


Fig. 4. Molecular stacking of molecules **1a** viewed along the *b* axis of the unit cell.

cant shortening of the Cr–CO_{trans} bond (1.830(5) Å) when compared to the *cis*-Cr–CO bonds (average: 1.888 Å) emphasizes the pronounced *trans* influence of the thioamide ligand deduced from the IR spectra. In the crystal the molecules of **1a** are arranged in two double-stacks without significant intermolecular interactions between the stacks: a head-to-tail double-stack along the crystallographic *c* axis (Fig. 3) and a tail-to-tail double-stack along the *b* axis (Fig. 4).

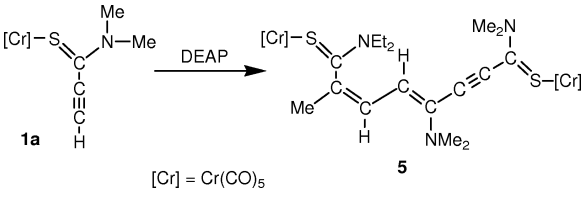
Complex **1a** is readily deprotonated by methyllithium to form the metalate Li[$(CO)_5$Cr–S=C(NMe_2)C≡C)] (**2**) identified by its IR spectrum. The reaction is highly selective. Neither products derived from addition of the carbanion to the triple bond of the thioamide nor a thiolate complex formed by addition of $[CH_3]^-$ to the sp^2 carbon atom of the S=C fragment could be detected. Compound **2** is also formed by desilylation of **1b** with methyllithium. On filtration over silica, **2** is reprotonated by the protons at the silica surface and **1a** is formed in almost quantitative yield (Scheme 4).

Complex **1a** is inert towards methanol. In contrast, diethylamine rapidly adds to the triple bond to give the corresponding thioacrylamide **3** in 98 % yield (Scheme 4). From the shift of the *trans*-ν(CO) absorption to longer wavelengths by about 17 cm^{-1} it follows that the aminothioacrylamide ligand in **3** is a considerably better donor than the propynethioic acid amide ligand in **1a**. The formation of only one isomer (with respect to the C=C bond) could be detected. From the coupling constant of ^3J = 12.1 Hz for the olefinic hydrogen atoms a *cis* arrangement can be deduced. Similarly to **1a**, two signals are found for the *N*-methyl groups in the NMR spectra of **3**. The inequivalence of the two N-Et groups shows that the C_β-bound NEt_2 substituent likewise acts as a π donor and contributes to the resonance stabilization of the compound. This is in accordance with the shift of the ν(CO) absoptions in the IR spectra towards lower energy. In general the spectroscopic data agree well with those of known thioacrylamide complexes [10, 14].

Addition of thiourea to solutions of **1a** led to displacement of the propynethioic acid amide ligand and to the formation of the thiourea complex **4** (95 %) and free thioamide (Scheme 4).

The reaction of **1a** with diethylaminopropyne provided an unusual result. Chromium- and tungsten-coordinated thioaldehydes and thioketones react with diethylaminopropyne by regioselective [2+2]-cycloaddition of the C≡C bond to the S=C bond and subsequent stereoselective electrocylic ring opening to give thioacrylamide complexes [15]. When diethylaminopropyne (DEAP) was added to a solution of **1a** in CH_2Cl_2 the starting complex **1a** was completely consumed already after the addition of half an equivalent of DEAP. After subsequent chromatography of the reaction mixture the dinuclear complex **5** was isolated as the only product in 85 % yield (Scheme 5).

In the IR spectrum, complex **5** shows only one set of pentacarbonyl ν(CO) absorptions. However, the



Scheme 5.

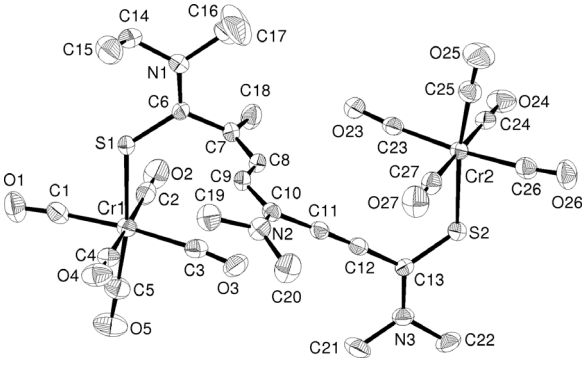
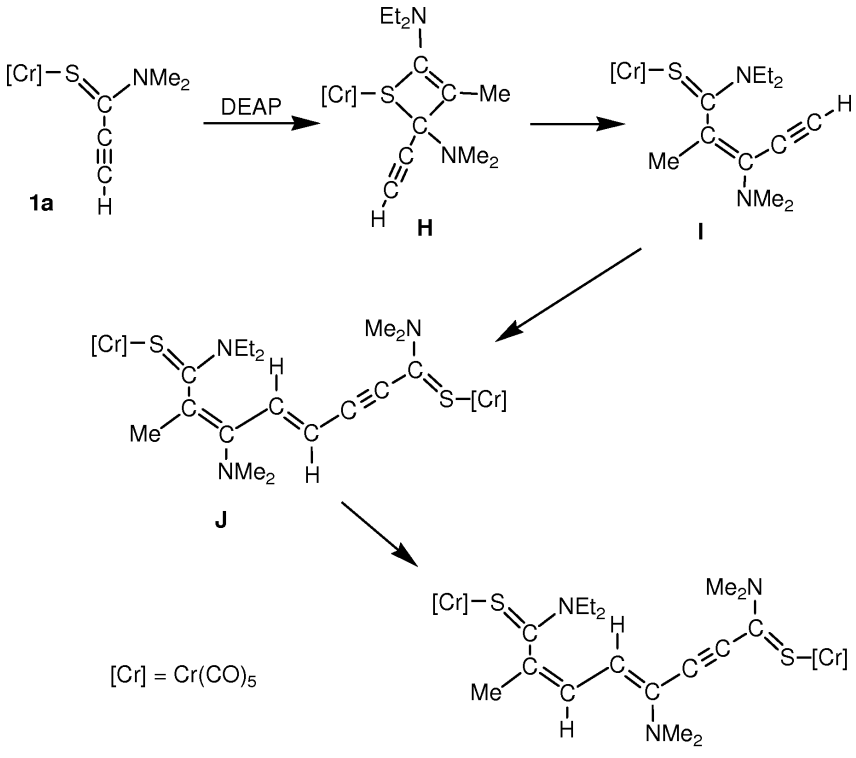


Fig. 5. Plot of the molecular structure of complex **5** in the crystal (ellipsoids drawn at 50 % level, hydrogen atoms omitted). Selected bond lengths (Å): Cr(1)–C(1) 1.880(4), Cr(1)–C(2) 1.909(4), Cr(1)–C(3) 1.927(4), Cr(1)–C(4) 1.892(4), Cr(1)–C(5) 1.849(4), Cr(1)–S(1) 2.449(1), Cr(2)–C(23) 1.908(3), Cr(2)–C(24) 1.906(3), Cr(2)–C(25) 1.838(3), Cr(2)–C(26) 1.892(3), Cr(2)–C(27) 1.897(3), Cr(2)–S(2) 2.441(1), S(1)–C(6) 1.690(3), C(6)–N(1) 1.324(4), C(6)–C(7) 1.483(4), C(7)–C(8) 1.336(4), C(8)–C(9) 1.432(4), C(9)–C(10) 1.364(4), C(10)–C(11) 1.446(4), C(11)–C(12) 1.187(4), C(12)–C(13) 1.432(4), C(13)–S(2) 1.687(3), C(13)–N(3) 1.334(4).

^{13}C NMR spectrum exhibits two sets of resonances for *cis* and *trans* carbonyl carbon atoms thus indicating the existence of two different pentacarbonylmetal moieties. In addition, two signals are found at rather low field assigned to two inequivalent thiocarbonyl carbon atoms. From the observation of two sets of resonances for the substituents at both amino groups (Me/Me and Et/Et) attached to the thiocarbonyl functionalities again a high barrier to rotation around the (S)C–N bonds can be deduced. Unfortunately, the rotational barrier could not be determined due to the rather low thermal stability of **5**.

The solid state structure of **5** was also established by an X-ray structural analysis (Fig. 5, Table 1). Each of the two thioamide groups is η^1-bound to a chromium atom. The Cr(1)–S(1) (2.449(1) Å) and Cr(2)–S(2) (2.441(1) Å) bond lengths differ slightly and are only marginally longer than in complex **1a**. The N(1)–C(6) (1.324(4) Å) and N(3)–C(13) bonds (1.334(4) Å) are



Scheme 6.

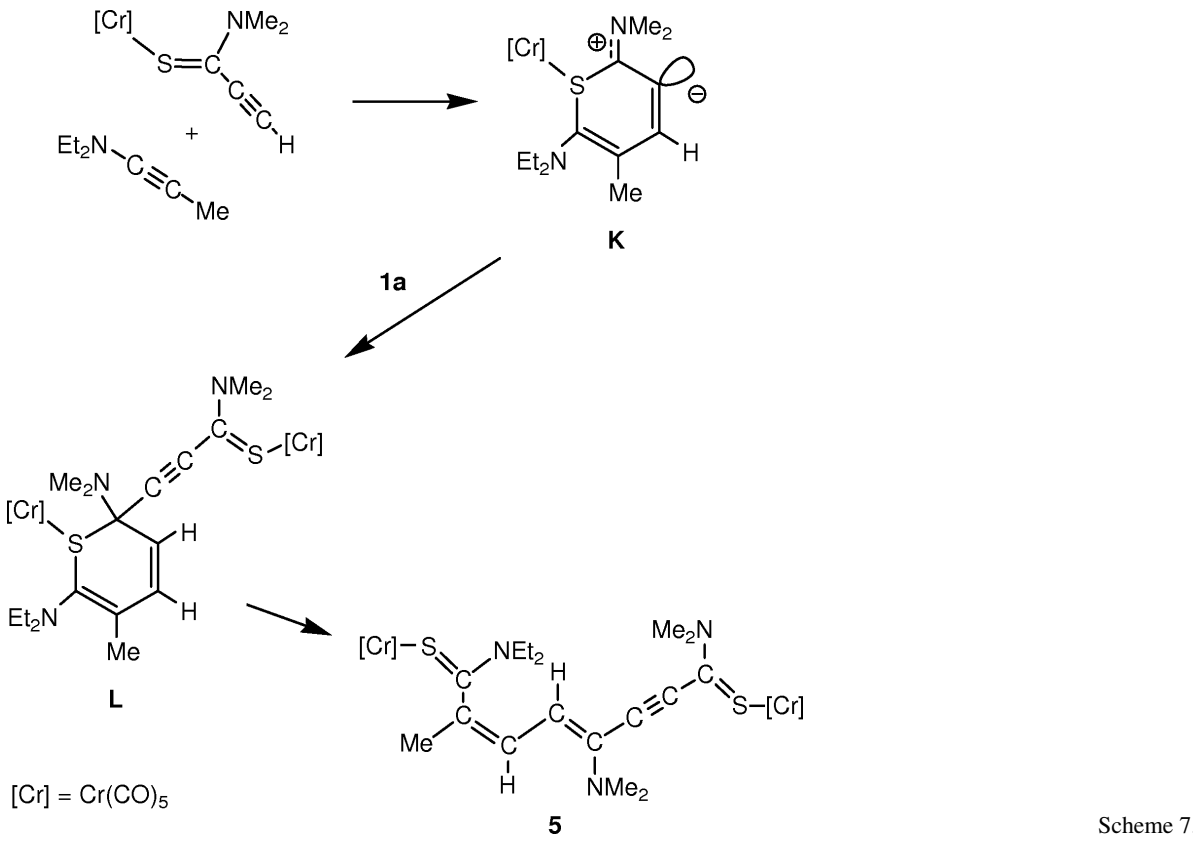
rather short, indicative of partial double bonds. Both thioamide moieties are arranged almost orthogonally to the plane formed by the carbon atoms of the π chain [C(6)–C(13)] thus excluding electronic communication between the thioamide moieties. The C(7)–C(8) and C(9)–C(10) bonds of the unsaturated carbon array are in good agreement with common [C(sp^2)-C(sp^2)] double bond lengths, and the C(6)–C(7) and C(8)–C(9) bonds match with an average C(sp^2)-C(sp^2) single bond.

Several mechanisms for the formation of compound **5** are conceivable. The most likely ones are depicted in Schemes 6 and 7. The reaction of **1a** with diethylaminopropyne could be initiated by a nucleophilic addition of the β carbon atom of the ynamine to the thiocarbonyl carbon atom of **1a** analogously to the reactions of electron-rich alkynes like Et_2N–C≡C–Me (a) with thioaldehyde complexes to give thioacrylamide complexes or (b) with carbonyl compounds like esters or amides to give acrylamides [16]. Such an initial step could be followed by cyclization and regioselective electrocyclic ring opening (**H** → **I**, Scheme 6). Nucleophilic addition of a second molecule of **1a** to the triple bond of **I** gives **J**. Subsequent 3,1-H and 1,3-NMe_2 shifts, which presumably contribute to the stabilization of the π system, finally afford compound **5** (Scheme 6).

An alternative mechanism involves initial 1,4-cycloaddition of the CC triple bond of the ynamine to the S=C–C≡C unit to give **K**. The 1,4-cycloaddition of various olefins such as vinyl ethers, styrenes, norbornene, acrolein, and ethyl propiolate to ruthenium-coordinated thiocinnamalaldehydes has recently been reported [17]. Nucleophilic addition of another molecule of **1a** and electrocyclic ring opening likewise yield, *via* **L**, compound **5** (Scheme 7).

The latter mechanism seems more likely, however, neither one of the presumed intermediates of the reaction could be isolated or spectroscopically detected. It is worth mentioning that a similar coupling with a second different alkyne, like for instance 1-hexyne or phenylacetylene, could not be observed, even when the second alkyne was used as the solvent.

Mono-decomplexation could be achieved by treating solutions of **5** with a 5-fold excess of acetonitrile. Stirring the solutions for several hours at ambient temperature afforded a mononuclear thioamide complex and acetonitrile pentacarbonyl chromium, [$(CO)_5$Cr–



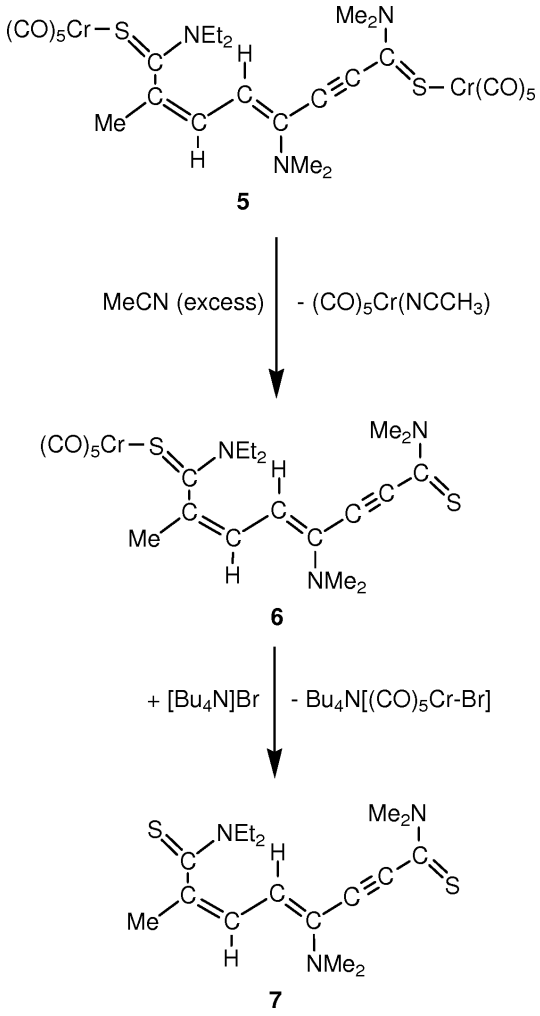
Scheme 7.

N≡C–CH_3]. Only one isomer of the thioamide complex was detected and was isolated after chromatographic workup as a red oil in 68 % yield. Based on the shift of the ^{13}C NMR resonances of the S=C–NMe_2 carbon atoms on decomplexation, the thioamide complex was assigned the structure **6** (Scheme 8). Full decomplexation could not be accomplished, neither by extending the reaction time considerably nor by using acetonitrile in large excess. Substituting pyridine for acetonitrile only led to decomposition of **6**. The pentacarbonyl chromium moiety could be recovered in the form of the pyridine complex [$(CO)_5$Cr–NC_5H_5] (92 % yield). The bridging bis(thioamide) ligand was obviously unstable under the reaction conditions employed and gave only unidentified decomposition products. However, when compound **6** was treated with [NBu_4]Br, decomplexation without decomposition could be achieved and the bisthioamide **7** (Scheme 8) could be isolated in 87 % yield.

In summary, complexes derived from propynoic acid thioamide are readily accessible from [$(CO)_5$Cr–THF] and the free thioamides. The propynoic acid thioamide ligands are moderate Michael acceptors as demonstrated by the addition of diethylamine to the CC triple bond of [$(CO)_5$Cr–S=C(NMe_2)–C≡C–H] and the failure of any reaction with the weaker nucleophile methanol. An unprecedented coupling of two thioamide ligands with one equivalent of diethylaminopropyne is observed in the reaction of **1a** with diethylaminoprop-1-yne. The bridging bis(thioamide) ligand in the resulting homodinuclear complex [$(CO)_5$Cr–S=C(NEt_2)–C(CH_3)=C(H)–C(H)=C(NMe_2)–C≡C–C(NMe_2)=S–Cr$(CO)_5$] can be mono-decomplexed with acetonitrile and liberated completely with [NBu_4]Br.

Experimental Section

All operations were performed in an inert gas atmosphere using standard Schlenk techniques. Solvents were dried by distillation from CaH_2 (CH_2Cl_2), $LiAlH_4$ (pentane) or sodium (THF). The silica gel used for chromatography (Baker, silica for flash chromatography) was argon-saturated and otherwise used as supplied. The yields refer to analytically pure substances and are not optimized. Instrumenta-



Scheme 8.

tion: ^{1}H NMR and ^{13}C NMR spectra were recorded with a Jeol JNX 400 and a Varian Inova 400 spectrometer at ambient temperature. Chemical shifts are relative to the residual solvent or tetramethyl silane peaks. IR: Biorad FTS 60. MS: Finnigan MAT 312. Elemental analysis: Heraeus CHN-O-Rapid. The following compounds were prepared according to literature procedures: *N,N*-dimethyl propyne thioic acid amide [18], *N,N*-dimethyl-3-trimethylsilyl propyne thioic acid amide [18], *N,N*-diethylaminoprop-1-yne [19]. All other chemicals were used as purchased from commercial suppliers.

*[(CO)$_5$Cr–S=C(NMe$_2$)–C≡C–H] (**1a**) and*
*[(CO)$_5$Cr–S=C(NMe$_2$)–C≡C–Si(CH$_3$)$_3$] (**1b**)*

At r. t. 0.57 g (5 mmol) of *N,N*-dimethyl propyne thioic acid amide {0.93 g (5 mmol) of *N,N*-dimethyl-3-trimethylsilyl propyne thioic acid amide} was added to 50 mL of a solution of [(CO)$_5$Cr(THF)] (0.1 M in THF). The reaction mixture was stirred at ambient temperature. The progress of the reaction was monitored by IR spectroscopy. When all of the starting material was consumed (after *ca.* 5 min) the solvent was removed *in vacuo* and the deep red residue was chromatographed on silica gel at −20 °C using mixtures of pentane/CH_2Cl_2 (polarity increasing from 3:1 to 1:1) as eluent. The first yellow fraction contained [Cr(CO)$_6$]. The second intensely red fraction was collected and the solvent removed *in vacuo* yielding 1.47 g (4.80 mmol; 96 %) of complex **1a** {1.75 g (4.63 mmol; 93 %) of complex **1b**} as an orange solid.

1a: M. p. 111 – 113 °C (dec.). – IR (THF): ν(CO) = 2062 m, 1979 w, 1937 vs, 1900 m cm^{-1}; ν(C≡C) = 2100 w cm^{-1}. – ^{1}H NMR (400 MHz, [D$_6$]acetone): δ = 3.01 (s, 3H, NCH$_3$), 3.19 (s, 3H, NCH$_3$), 4.80 (s, 1H, CCH). – ^{13}C NMR (100 MHz, [D$_6$]acetone): δ = 42.9 (NCH$_3$), 46.7 (NCH$_3$), 78.9 (*C*CH), 96.8 (C*C*H), 178.6 (C=S), 216.5 (*cis*-CO), 223.8 (*trans*-CO). – MS (FAB): *m/z* (%) = 305 (43) [M$^+$], 248 (58) [(M – 2CO)$^+$], 221 (100) [(M – 3CO)$^+$], 193 (71) [(M – 4CO)$^+$], 165 (69) [(M – 5CO)$^+$]. – $C_{10}H_7CrNO_5S$ (305.23): calcd. C 39.35, H 2.31, N 4.59; found C 39.00, H 2.56, N 4.64.

1b: M. p. 89 – 91 °C. – IR (THF): ν(CO) = 2061 m, 1980 w, 1937 vs, 1901 m cm^{-1}; ν(C≡C) not found. – ^{1}H NMR (400 MHz, [D$_6$]acetone): δ = 0.08 (s, 9H, Si(CH$_3$)$_3$), 3.18 (s, 3H, NCH$_3$), 3.36 (s, 3H, NCH$_3$). – ^{13}C NMR (100 MHz, [D$_6$]acetone): δ = −0.30 (Si(CH$_3$)$_3$), 43.6 (NCH$_3$), 47.4 (NCH$_3$), 99.6 (*C*CSi(CH$_3$)$_3$), 114.6 (C*C*Si(CH$_3$)$_3$), 179.1 (C=S), 217.4 (*cis*-CO), 224.6 (*trans*-CO). – MS (FAB): *m/z* (%) = 377 (23) [M$^+$], 321 (19) [(M – 2CO)$^+$], 293 (78) [(M – 3CO)$^+$], 265 (100) [(M – 4CO)$^+$], 237 (98) [(M – 5CO)$^+$]. – $C_{13}H_{15}CrNO_5S$ (377.41): calcd. C 41.37, H 4.01, N 3.71; found C 41.52, H 4.11, N 3.78.

*Li[(CO)$_5$Cr–S=C(NMe$_2$)–C≡C] (**2**)*

At −78 °C a solution of 0.67 mL (1.0 mmol) of methyllithium (1.5 M in Et$_2$O) was added to a solution of 0.305 g (1 mmol) of **1a** in 20 mL of THF. The colour of the solution gradually changed from deep-red to orange. The completion of the reaction was indicated by IR-spectroscopy. IR (THF, cm^{-1}): ν(CO): 2035 m, 1910 vs, 1874 m.

*[(CO)$_5$Cr–S=C(NMe$_2$)–C(H)=C(H)NEt$_2$] (**3**)*

At r. t. 0.11 mL (1.1 mmol) of diethylamine was added to a solution of 0.305 g (1 mmol) of **1a** in 5 mL of THF. The colour of the solution instantaneously changed from deep-red to orange. After 5 min at this temperature the solvent was removed *in vacuo*. The residue was chromatographed on silica gel at −20 °C using mixtures of pentane/CH_2Cl_2

(polarity increasing from 2:1 to 1:2) as eluent. The orange fraction was collected and the solvent was removed *in vacuo* to yield 0.37 g (0.98 mmol; 98 %) of **3** as an orange solid.

M. p. 89 – 91 °C (dec.). – IR THF): ν(CO) = 2053 m, 1924 vs, 1883 m cm^{-1}. – ^{1}H NMR (400 MHz, [D$_6$]acetone): δ = 0.77 (t, $^3J_{HH}$ = 7.0 Hz, 6H, 2NCH$_2$C*H*$_3$), 2.97 (br, 10H, 2NCH$_3$; 2NC*H*$_2$CH$_3$), 5.10 (d, $^3J_{HH}$ = 12.1 Hz, 1H, HC=C), 7.70 (d, $^3J_{HH}$ = 12.1 Hz, 1H, C=CH). – ^{13}C NMR (100 MHz, [D$_6$]acetone): δ = 11.7 (NCH$_2$*C*H$_3$), 14.7 (NCH$_2$*C*H$_3$), 42.9 (br, 2, 44.1 (NCH$_3$), 44.1 (N*C*H$_2$CH$_3$), 52.0 (N*C*H$_2$CH$_3$), 94.6 (*C*=C–NEt$_2$), 160.1 (C=*C*–NEt$_2$), 192.8 (C=S), 218.2 (*cis*-CO), 225.0 (*trans*-CO). – MS (EI): *m/z* (%) = 378 (10) [M$^+$], 322 (29) [(M – 2CO)$^+$], 294 (22) [(M – 3CO)$^+$], 266 (100) [(M – 4CO)$^+$], 238 (37) [(M – 5CO)$^+$]. – C$_{14}$H$_{18}$CrN$_2$O$_5$S (378.36): calcd. C 44.44, H 4.80, N 7.40; found C 44.58, H 4.61, N 7.14.

*[(CO)$_5$Cr–S=C(NH$_2$)$_2$] (**4**)*

At r. t. 0.15 g (2.0 mmol) of thiourea was added to a solution of 0.305 g (1 mmol) of **1a** in 5 mL of THF. The progress of the reaction was followed by IR-spectroscopy. When all of the starting material was consumed, the solvent was removed *in vacuo* and the residue chromatographed on silica gel at −20 °C using mixtures of pentane/CH$_2$Cl$_2$ (polarity increasing from 1:1 to 0:1) as eluent. The yellow fraction was collected and the solvent removed *in vacuo* yielding 0.25 g (0.95 mmol; 95 %) of **4** as a yellow solid. Compound **4** was identified by comparison of the spectroscopic data with those published [20].

*[(CO)$_5$Cr–S=C(NEt$_2$)–C(CH$_3$)=CH–CH=C(NMe$_2$)–C≡C–C(NMe$_2$)=S–Cr(CO)$_5$] (**5**)*

At r. t. 0.06 g (0.5 mmol) of *N,N*-diethylaminoprop-1-yne was added to a solution of 0.305 g (1 mmol) of **1a** in 5 mL of THF. The reaction mixture was stirred at ambient temperature and the progress of the reaction was monitored by IR-spectroscopy. After 30 min the solvent was removed *in vacuo* and the residue chromatographed on silica gel at −20 °C using mixtures of pentane/CH$_2$Cl$_2$ (polarity increasing from 1:1 to 1:3) as eluent. The red fraction was collected. The solvent was removed *in vacuo* yielding 0.31 g (0.85 mmol; 85 %) of **5** as a red solid.

M. p. 68 – 70 °C (dec.). – IR (THF): ν(CO) = 2060 m, 1977 vw, 1938 vs, 1929 s, 1897 m cm^{-1}. – ^{1}H NMR (400 MHz, CDCl$_3$): δ = 1.16 (t, $^3J_{HH}$ = 7.1 Hz, 3H, NCH$_2$C*H*$_3$), 1.29 (t, $^3J_{HH}$ = 7.1 Hz, 3H, NCH$_2$C*H*$_3$), 1.93 (s, 3H, C=CC*H*$_3$), 2.77 (s, 6H, N(CH$_3$)$_2$), 3.46 –,3.53 (br, 8H, N(CH$_3$)$_2$; NC*H*$_2$CH$_3$), 3.88 (m, 1H, NC*H*$_2$CH$_3$), 4.00 (m, 1H, NC*H*$_2$CH$_3$), 5.10 (d, $^3J_{HH}$ = 11.8 Hz, 1H, CH$_3$C=C(H)–(*H*)C=C), 7.70 (d, $^3J_{HH}$ = 11.8 Hz, 1H, CH$_3$C=C(*H*)–(H)C=C). – ^{13}C NMR (100 MHz, CDCl$_3$): δ = 10.9, 13.7 (NCH$_2$*C*H$_3$), 22.2 (C=C*C*H$_3$), 40.2 (2NCH$_3$), 42.7 (NCH$_3$), 46.0 (NCH$_3$), 46.1, 49.4 (N*C*H$_2$CH$_3$), 90.1 (C≡*C*–CSNMe$_2$), 97.0 (*C*≡C–CSNMe$_2$), 106.1 (CH$_3$*C*=C–C=C), 128.0 (CH$_3$C=*C*–C=C), 128.5 (CH$_3$C=C–*C*=C), 131.8 (CH$_3$C=C–C=*C*), 178.7 (NMe$_2$–C=S), 200.9 (NEt$_2$–C=S), 215.4, 216.3 (*cis*-CO), 223.2, 223.6 (*trans*-CO). – MS (EI): *m/z* (%) = 721 (8) [M$^+$], 665 (21) [(M – 2CO)$^+$], 609 (22) [(M – 4CO)$^+$], 581 (30) [(M – 5CO)$^+$], 497 (25) [(M – 8CO)$^+$], 473 (92) [(M – 9CO)$^+$], 441 (73) [(M – 10CO)$^+$], 497 (25) [(M – 10CO – Cr)$^+$]. – C$_{27}$H$_{27}$Cr$_2$N$_3$O$_{10}$S$_2$ (721.64): calcd. C 44.94, H 3.77, N 5.82; found C 44.96, H 3.78, N 5.82.

*[(CO)$_5$Cr–S=C(NEt$_2$)–C(CH$_3$)=C(H)–C(H)=C(NMe$_2$)–C≡C–C(=S)NMe$_2$] (**6**)*

At r. t. 2 mL of acetonitrile was added to a solution of 0.34 g (0.47 mmol) of **5** in 2 mL of CH$_2$Cl$_2$. The reaction mixture was stirred at ambient temperature and the progress of the reaction was monitored by TLC. After *ca.* 6 h the solvent was removed *in vacuo* and the residue chromatographed on silica at −20 °C using mixtures of pentane/CH$_2$Cl$_2$ (polarity increasing from 1:2 to 1:4) as the eluent. The red fraction was collected and the solvent was removed *in vacuo* yielding 0.17 g (0.32 mmol; 68 %) of **6** as a red oil.

IR (THF): ν(CO) = 2059 m, 1971 vw, 1935 vs, 1931 s, 1895 m cm^{-1}. – ^{1}H NMR (400 MHz, CDCl$_3$): δ = 1.15 (t, $^3J_{HH}$ = 7.1 Hz, 3H, NCH$_2$C*H*$_3$), 1.25 (t, $^3J_{HH}$ = 7.1 Hz, 3H, NCH$_2$C*H*$_3$), 1.91 (s, 3H, C=CC*H*$_3$), 2.73 (s, 6H, N(CH$_3$)$_2$), 3.36, 3.52 (s, 2 × 3H, NCH$_3$), 3.66 (m, 2H, NC*H*$_2$CH$_3$), 3.94, 4.01 (m, 2 × 1H, NC*H*$_2$CH$_3$), 5.11 (d, $^3J_{HH}$ = 11.7 Hz, 1H, CH$_3$C=C(H)–(*H*)C=C), 6.43 (d, $^3J_{HH}$ = 11.7 Hz, 1H, CH$_3$C=C(*H*)–(H)C=C). – ^{13}C NMR (100 MHz, CDCl$_3$): δ = 11.2 (NCH$_2$*C*H$_3$), 14.0 (NCH$_2$*C*H$_3$), 22.8 (C=C*C*H$_3$), 40.3 (NCH$_3$), 40.9 (NCH$_3$), 44.0 (NCH$_3$), 47.0, 50.7 (N*C*H$_2$CH$_3$), 91.3 (C≡*C*–CSNMe$_2$), 94.1 (*C*≡C–CSNMe$_2$), 107.0 (CH$_3$*C*=C–C=C), 128.0 (CH$_3$C=*C*–C=C), 129.9 (CH$_3$C=C–*C*=C), 134.0 (CH$_3$C=C–C=*C*), 176.9 (NMe$_2$–C=S), 201.2 (NEt$_2$–C=S), 217.3 (*cis*-CO), 224.3 (*trans*-CO). – MS (EI): *m/z* (%) = 529 (16) [M$^+$], 473 (51) [(M – 2CO)$^+$], 441 (46) [(M – C$_3$H$_6$NS)$^+$], 389 (100) [(M – 5CO)$^+$]. – C$_{22}$H$_{27}$CrN$_3$O$_{10}$S$_2$ (529.59): calcd. C 49.90, H 5.14, N 7.93; found C 50.33, H 5.50, N 7.34.

*Et$_2$N(S=)C–C(CH$_3$)=C(H)–C(H)=C(NMe$_2$)–C≡C–C(=S)NMe$_2$ (**7**)*

At r. t. 1.0 g (3.1 mmol) of [Bu$_4$N]Br was added to a solution of 0.25 g (0.47 mmol) of **6** in 10 mL of THF. The reaction mixture was stirred and the progress of the reaction monitored by IR-spectroscopy. After 24 h at room temperature the solvent was removed *in vacuo*. The residue was dissolved in acetone and filtered over a short (*ca.* 3 cm) column of silica at *ca.* −100 °C. The orange-red fraction was collected and

the solvent was removed *in vacuo*. The residue was washed twice with 5 mL of pentane and twice with 10 mL of ether each yielding 0.14 g (0.41 mmol; 87 %) of **2** as an orange oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.15 (t, $^3J_{HH}$ = 7.1 Hz, 3H, NCH_2CH_3), 1.25 (t, $^3J_{HH}$ = 7.1 Hz, 3H, NCH_2CH_3), 2.11 (s, 3H, $C{=}CCH_3$), 2.72 (s, 6H, NCH_3), 3.41 (s, 3H, NCH_3), 3.46 (s, 3H, NCH_3), 3.61 (m, 2H, NCH_2), 3.66 (m, 1H, NCH_2), 4.24 (m, 1H, NCH_2), 5.24 (d, $^3J_{HH}$ = 12.1 Hz, 1H, $CH_3C{=}C(H){-}(H)C{=}C$), 6.06 (d, $^3J_{HH}$ = 12.1 Hz, 1H, $CH_3C{=}C(H){-}(H)C{=}C$). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.6 (NCH_2CH_3), 19.6 (NCH_2CH_3), 24.0 ($C{=}CCH_3$), 40.3 (NCH_3), 40.9 (NCH_3), 43.8 (NCH_3), 44.7 (NCH_2), 46.9 (NCH_2), 92.5 ($C{\equiv}C{-}CSNMe_2$), 92.8 ($C{\equiv}C{-}CSNMe_2$), 108.3 ($CH_3C{=}C{-}C{=}C$), 122.2 ($CH_3C{=}C{-}C{=}C$), 131.6 ($CH_3C{=}C{-}C{=}C$), 133.7 ($CH_3C{=}C{-}C{=}C$), 176.8 ($NMe_2{-}C{=}S$), 200.9 ($NEt_2{-}C{=}S$). – MS (EI): *m*/*z* (%) = 337 (41) [M^+], 322 (70) [$(M - CH_3)^+$], 322 (100) [$(M - 2CH_3)^+$]. – $C_{17}H_{27}N_3S_2$ (337.54): calcd. C 60.48, H 8.06, N 12.45; found C 60.81, H 8.41, N 12.01.

Computational details

All *ab initio* calculations were performed using Jaguar [21] (version 5.5.016) running on Linux- 2.4.20-28.7smp on six Athlon MP 2400+ dual-processor workstations (Beowulf-cluster) parallelized with MPICH 1.2.4. Initial structures were obtained by MM+ optimization using Hyperchem [22]. Geometries were optimized using the LACVP* basis set (ECP for Cr, N31G6* for all other atoms) and the BP86 density functional. The second derivatives at 298.15 K were calculated to ensure that true minima were found, by showing no large negative frequencies. All reported energies are Gibbs free energies at 298.15 K.

*X-Ray structural analyses of **1a** and **5***

Single crystals suitable for X-ray structural analyses were obtained by slow diffusion of *n*-hexane at 4 °C into a solution of **1a** and **5** in CH_2Cl_2. The measurements were performed with a crystal mounted on a glass fibre on a Siemens P4 diffractometer (graphite monochromator, MoK_α, radiation, λ = 0.71073 Å). For the data collection the Wyckoff technique was used. A semiempirical absorption correction (ω scan with 12 reflections) was performed. The structures were solved by Direct Methods using the SHELXTL-97 program package [23]. The position of the hydrogen atoms were calculated by assuming ideal geometry, and their coordinates were refined together with those of the attached carbon atoms as riding-model. All other atoms were refined anisotropically.

CCDC 617198 (**1a**) and and CCDC 617199 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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