Ring Expansion of Spirocyclic Cyclobutenylidene Ligands in Pentacarbonylchromium Complexes to Tetrahydroindene Derivatives

Helmut Fischer*, Christoph C. Karl, and Gerhard Roth

Fakultät für Chemie, Universität Konstanz,
Postfach 5560 M727, D-78434 Konstanz, Germany

Received January 15, 1996

Key Words: Vinylidene complexes / Cyclobutenylidene complexes / Tetrahydroindenes / Thioether complexes

Pentacarbonyl(pentamethylenevinylidene)chromium, $[(CO)_5Cr{=}C{=}C(CH_2)_5]$ (**1**), reacts with 1-methylthio-1-propyne (**2a**) and *N*-(1-propynyl)phenothiazine (**2b**) by regiospecific addition of the C≡C bond of the alkyne to the C=C bond of the vinylidene ligand of **1**. Initially, complexes with a spirocyclic cyclobutenylidene ligand are formed, $[(CO)_5Cr{=}CC(Me){=}C(SMe)C(CH_2)_5]$ (**3**) and $[(CO)_5Cr{=}C{-}C(Me){=}C\{N(C_6H_4)_2S\}C(CH_2)_5]$ (**10**). Subsequent thermally initiated ring expansion affords the 2-methyl-4,5,6,7-tetrahydroindenyl(methyl)thioether complex $[(CO)_5Cr{-}S(Me)(Me\text{-}C_9H_{10})]$ (**4**) and the *N*-(2-methyl-4,5,6,7-tetrahydroindenyl)phenothiazine complex $[(CO)_5Cr{-}S(C_6H_4)_2{-}N{-}(Me\text{-}C_9H_{10})]$ (**11**), respectively. In both complexes, **4** and **11**, the ligand is coordinated to the metal via the sulfur atom. The constitutions were established by (H,H)-, (H,C)- and NOE-correlated NMR spectroscopy. In the reaction of **1** with **2a**, in addition to **3** and **4**, the methyl(propynyl)thioether complex $[(CO)_5Cr{-}S(Me)C{\equiv}CMe]$ (**5**) was formed. An isolable 3-methylthio-substituted cyclobutenylidene complex, $[(CO)_5Cr{=}C{-}C(Me){=}C(SMe)CPh_2]$ (**9**) was obtained from $[(CO)_5Cr{=}C{=}CPh_2]$ (**8**) and **2a**. The 4,5,6,7-tetrahydroindenylthioether ligand of **11** was cleaved from the metal by exposure of **11** adsorbed on silica gel to air or by treatment of **11** with $[NEt_4]Br$ in dichloromethane.

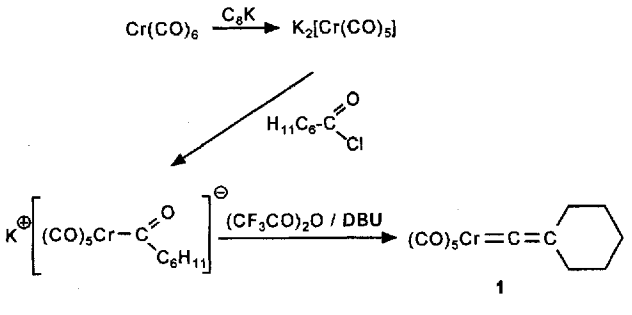
Recently, 4,5,6,7-tetrahydroindenes have attracted considerable interest. They have been employed as precursors for ligands in zirconocene and titanocene complexes used in olefin polymerization[1–3] and as precursors of vitamin-A analogs[4–6] and steroid components[7–9]. However, the number of synthetic routes to 4,5,6,7-tetrahydroindenes is rather restricted. 4,5,6,7-Tetrahydroindenes are not accessible by hydrogenation of indenes. An exception is the hydrogenation of metal-coordinated η^5-indenyl ligands[1,2,10]. Routes to 4,5,6,7-tetrahydroindenes include condensation[11–13] and electrocyclic ring closure reactions[14–16], thermal rearrangements of geminal cyclohexane-annulated dibromovinylcyclopropanes[17,18] (vinylcyclopropylidene-cyclopentenylidene rearrangement) and 1,5-alkyl shift in partially unsaturated spirocycles[19–22].

Previously, we described the synthesis of π-donor-substituted cyclobutenylidene complexes and cyclobutenones from pentacarbonyl(vinylidene) complexes of chromium and tungsten and electron-rich alkynes such as 1-diethylamino- and 1-ethoxy-1-propyne[23]. We now report on the preparation of pentacarbonylchromium complexes with a spirocyclic cyclobutenylidene ligand, the thermal rearrangement of the cyclobutenylidene ligands to substituted 4,5,6,7-tetrahydroindenes and the decomplexation of *N*-(2-methyl-4,5,6,7-tetrahydroindenyl)phenothiazine.

Results and Discussion

The starting pentamethylenevinylidene complex (**1**)[24] was generated by the reaction sequence shown in Scheme 1. Reduction of $Cr(CO)_6$ with C_8K gave $K_2[Cr(CO)_5]$[25]. Reaction of $K_2[Cr(CO)_5]$ with cyclohexylcarbonyl chloride afforded potassium pentacarbonyl(cyclohexylcarbonyl)chromate by a method described by M. F. Semmelhack et al.[26]. Reaction of the pentacarbonyl(cyclohexylcarbonyl)chromate with trifluoroacetic anhydride/DBU finally yielded the vinylidene complex **1**. By an analogous procedure, cationic vinylidene complexes of iron were prepared from acyl complexes by Hughes et al.[27].

Scheme 1

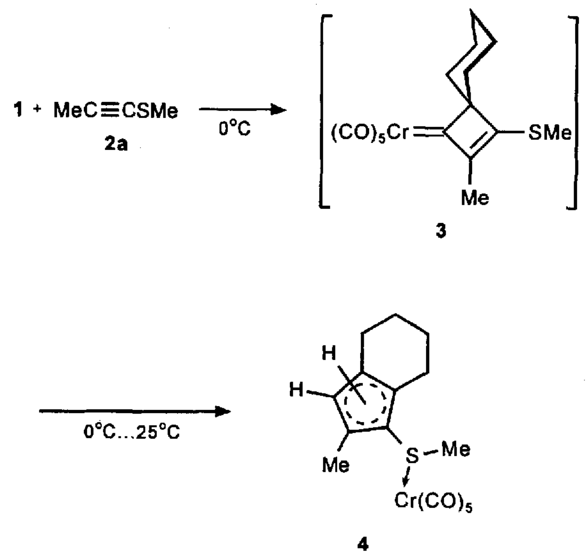


At 0 °C, complex **1** rapidly reacts with 1-methylthio-1-propyne (**2a**) in *n*-pentane/dichloromethane to give the 2-methyl-4,5,6,7-tetrahydroindenyl(methyl)thioether complex **4**. Complex **4** is presumably formed by an initial regiospecific cycloaddition of the C≡C bond of **2a** to the C=C bond of **1** and subsequent ring expansion of the resulting 3-methylthio-substituted cyclobutenylidene complex **3** (vide infra) (Scheme 2). [2 + 2] cycloaddition of alkynes to the C=C bond of pentacarbonyl(vinylidene) complexes was also observed in the reactions of ynamines and alkoxypropynes with $(CO)_5M{=}C{=}CR_2$ (M = Cr, W; R = alkyl,

0009–2940/96/0606–0615 $ 15.00+.25/0

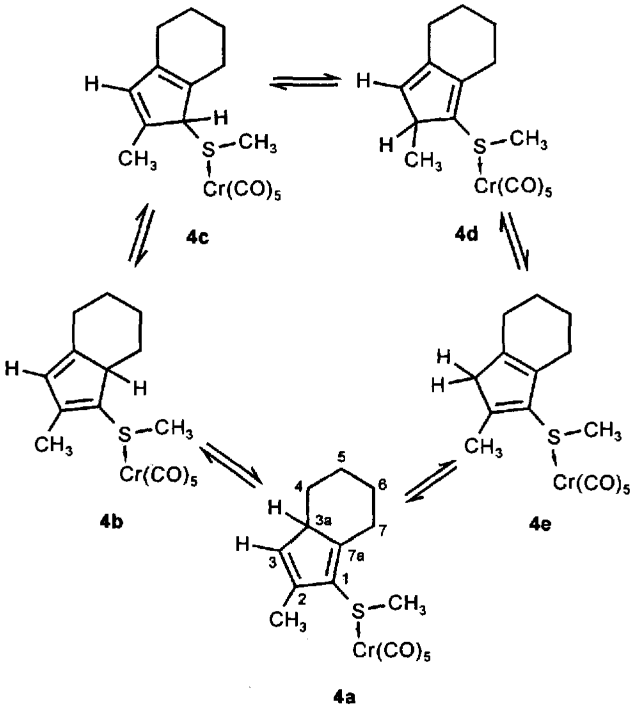
aryl)[23,24,28] leading to 3-amino- and 3-alkoxycyclobutenylidene complexes, respectively.

Scheme 2



Complex **4** was obtained as a chromatographically inseparable mixture of the five tautomers **4a**–**e** shown in Scheme 3. The sulfur atom in **4** is a stereogenic center. However, diastereomers of **4a**–**d** could not be detected due to rapid pyramidal inversion at sulfur. The barrier to pyramidal inversion in pentacarbonyl(thioether) complexes is usually very low[29], e.g. for $[(CO)_5Cr\{S(Me)[CH(Me)Ph]\}]$ $\Delta G^{\neq}$ is 40.2 kJ/mol[30].

Scheme 3



The ^{1}H- and ^{13}C-NMR spectra of **4** show five sets of signals. The five well-separated resonances in the ranges δ = 2.16–2.97 and δ = 36.7–55.3 of the (H,C)-correlated NMR spectrum (HMQC) were assigned to the tautomeric hydrogen and carbon atoms of the five-membered ring. The signals for the 3-H and C-3 atoms (four signals each) of the tautomers **4a**–**d** are observed in the olefinic region at δ = 5.58–5.99 and δ = 116.8–132.5. It was possible to assign most of the resonances of the various tautomeric forms through a combination of (H,H)-correlated (DQFCOSY), H-relayed-(H,H)-correlated (TOCSY) and two-dimensional NOE exchange spectra (ROESY)[31]. ROE exchange is e.g. observed between the alkenyl proton (3-H) in **4a** and the bridgehead proton (3a-H), the protons of the adjacent CH_3 group and that methylene C-4 proton which is shifted to lower field. Analogously, in **4d** a ROE exchange also occurs between 3-H and 2-H and the corresponding methyl protons and the lower-field-shifted methylene proton (4-H). Whereas in **4b** only a ROE exchange signal between 3-H and the alkenyl CH_3 group is observed, in **4c** there is an additional exchange signal between 3-H and 1-H. Since no ROE cross signal for an exchange between 3-CH_2 (at δ = 2.84/46.8) and an olefinic proton was found, these signals were assigned to tautomer **4e**. This conclusion is confirmed by the fact that the resonance at δ = 46.8 is the only positive signal of the five-membered ring in the *J*-modulated ^{13}C-NMR spin-echo experiment. Based on the ^{1}H-NMR spectrum the tautomeric ratio of **4a**–**e** in dichloromethane is 2.5:1.0:2.0:5.9.

The connectivity of the carbon framework in **4** was additionally established by a single-crystal X-ray diffraction study. Due to the poor quality of the crystal and a data set insufficient for complete refinement a detailed discussion of the bond lengths and angles in **4** is, however, not feasible.

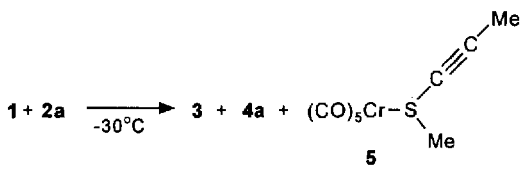
When the reaction of **1** with **2a** was performed at −30°C, only the tautomer **4a** was formed in addition to **3** and the methyl(propynyl)thioether complex **5** (Scheme 4). Very likely, compound **5** was formed by replacement of the vinylidene ligand in **1** by **2a**. A similar substitution of nitrogen nucleophiles for the vinylidene ligand was reported recently[23].

When a solution containing **3**, **4a**, and **5** (ratio 45:5:50) in dichloromethane was slowly warmed from −45°C to 25°C, the intensity of the ^{1}H-NMR resonances of **3** decreased and those of **4a** simultaneously increased. At room temperature the signals of **3** had completely disappeared. Throughout the reaction the intensity of the signals of **5** remained constant. When the solution was kept at room temperature for several hours, **4a** tautomerized to form a mixture of all isomers **4a**–**e**. From these observations it follows that the cyclobutenylidene complex **3** selectively rearranges to **4a**. In the final equilibrium, tautomer **4e** dominated. This agrees with earlier observations that the 1*H*-tautomer of 4,5,6,7-tetrahydroindenes is the thermodynamically most stable tautomer[17,18]. The energy difference between **4a** and **4e** at 0°C is 1.9 ± 0.2 kJ/mol [determined by integration of the 3-H (δ = 6.03) and 3-CH_2 (δ = 2.86) signals of **4a** and **4e**, respectively].

The equilibrium ratio remained approximately constant when the solution was again cooled to −45°C. These observations confirm the conclusion that ring expansion (**3** → **4a**) precedes tautomerization.

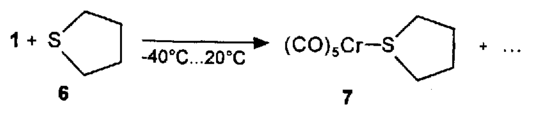
During the reaction of **1** with **2a** the IR spectrum of the reaction mixture shows two ν(CO) absorption of low intensity at 2059 cm^{-1} and 1910 cm^{-1} in addition to those of the starting compound and the isolated products. Very likely, these bands are due to an ylide complex formed by nucleophilic addition of the alkyne to the electrophilic vinylidene α-carbon via the sulfur atom. Addition of nucleophiles to the metal-bound carbon atom of electrophilic carbene and vinylidene complexes is well-known[32,33] and has repeatedly been used to trap labile carbene and vinylidene complexes. Since the ylide complex was formed in only a small amount it was not possible to isolate the compound by crystallization. On chromatographic workup of the reaction mixture the ylide complex quickly decomposed. At temperatures above −30 °C **2a** dissociated from the ylide complex and **1** was regenerated. The thermolability and the positions of the ν(CO) absorptions of the ylide complex are comparable to those of the corresponding thioether adducts of pentacarbonyl(benzylidene)tungsten[33].

Scheme 4



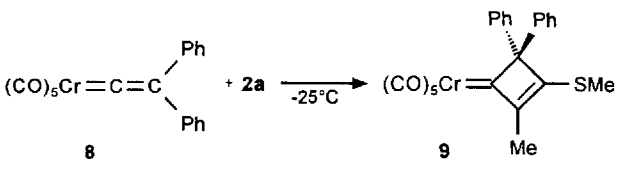
Analogous ylide formation and vinylidene substitution (Scheme 5) were observed in the reaction of **1** with tetrahydrothiophene (**6**). At −40 °C, the IR spectrum of the reaction mixture shows in addition to the CO absorption of the starting compound and the thioether complex **7**[34,35] bands of low intensity at 2058 cm^{-1} and 1910 cm^{-1} which we attribute to an S-ylide complex. This compound is very labile, decomposes at temperatures above −30 °C and, therefore, was not isolated.

Scheme 5



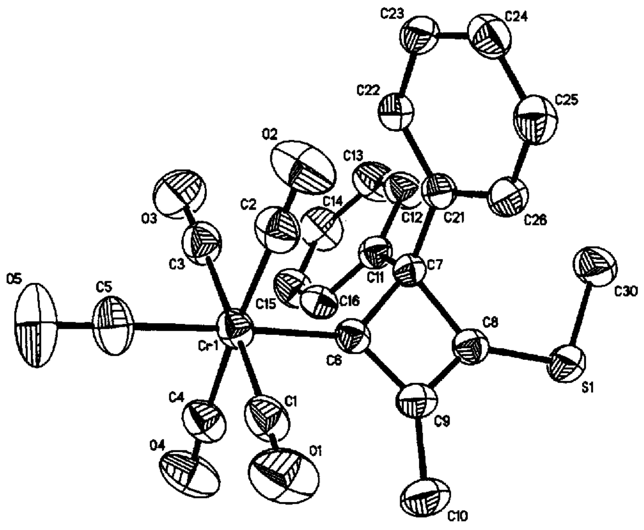
Although cyclobutenylidene complex **3** could not be isolated in pure form, the formation of **3** in the reaction of **1** with **2a** is plausible on the basis of the spectra and the isolation of the analogous cyclobutenylidene complex **9**. Ring expansion corresponding to **3** → **4a** is not possible in **9**. Complex **9** was obtained from **8** and **2a** and isolated in a pure form (Scheme 6).

Scheme 6



Complex **9** was characterized by spectroscopic means and additionally by an X-ray diffraction study (Figure 1). The cyclobutenylidene ring is only slightly puckered, the angle between the planes formed by the atoms C(6), C(7), C(9) and C(7), C(8), C(9) is 175.2°. The angle in the 3-amino-substituted cyclobutenylidene complex $[(CO)_5W{=}\overline{C{-}C(Me){=}C(NEt_2){-}C}(Me)tBu]$ is 165.3°[23]. The C(6)−C(9) bond in **9** [1.412(4) Å] is longer than the C(8)−C(9) bond [1.365(5) Å]. The reverse is true for the 3-amino-substituted cyclobutenylidene complex [1.371(8) Å versus 1.436(9) Å][23]. Torsion angles and corresponding C−C distances in **9** are, however, similar to those in the ethoxy-substituted cyclobutenylidene complex $[(CO)_5W{=}\overline{C{-}C(Me){=}C(OEt){-}C}Ph_2]$[23]. These structural features illustrate the smaller π-basicity of the methylthio substituent in **9** compared to the diethylamino group in $[(CO)_5W{=}\overline{C{-}C(Me){=}C(NEt_2){-}C}R_2]$ and the considerable sensitivity of the structure of the ring system to changes in the electronic properties of the substituents in position 3.

Figure 1. Structure of complex **9** in the crystal (hydrogen atoms omitted)[a]

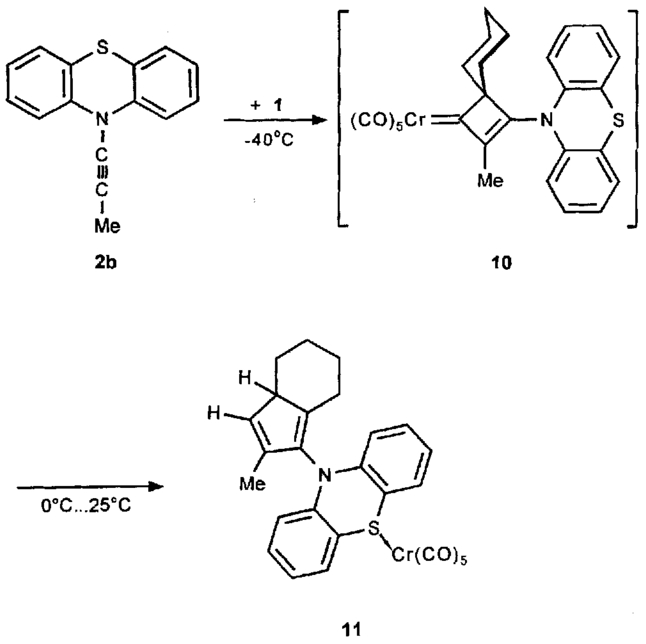


[a] Selected bond lengths [Å] and angles [°] (standard deviations in parentheses): Cr(1)−C(6) 1.999(3), C(6)−C(7) 1.608(4), C(7)−C(8) 1.538(4), C(8)−C(9) 1.365(5), C(6)−C(9) 1.412(4), C(9)−C(10) 1.508(5), C(8)−S(1) 1.702(3), S(1)−C(30) 1.794(4); Cr(1)−C(6)−C(7) 134.5(2), Cr(1)−C(6)−C(9) 136.0(2), C(6)−C(7)−C(8) 81.2(2), C(7)−C(8)−C(9) 94.2(2), C(6)−C(9)−C(8) 95.0(3).

To determine whether the direct connection of the sulfur atom to the C≡C bond is essential for ring expansion, the reaction of **1** with the ynamine *N*-(1-propynyl)phenothiazine (**2b**) was also investigated. In earlier studies, cyclobutenylidene complexes were obtained from **1** and ynamines such as 1-diethylamino-1-propyne and bis(diethylamino)ethyne, but ring expansion to 4,5,6,7-tetrahydroindenes was not observed[24].

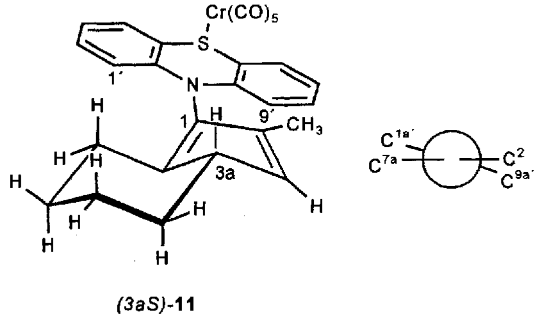
The vinylidene complex **1** reacts with **2b** even faster than with **2a**. After chromatography the *N*-(2-methyl-4,5,6,7-tetrahydroindenyl)phenothiazine complex **11** was obtained in moderate yield (Scheme 7). In contrast to the reaction of **1** with **2a**, neither substitution of the alkyne for the vinylidene ligand nor formation of an ylide complex at −40°C were observed. This is presumably due to steric hindrance of the sulfur atom by the phenothiazinyl *ortho* hydrogen atoms. A ν(CO) absorption at 2044 cm^{-1} indicates that the 3-(*N*-phenothiazinyl)cyclobutenylidene complex **10** was formed as an intermediate.

Scheme 7



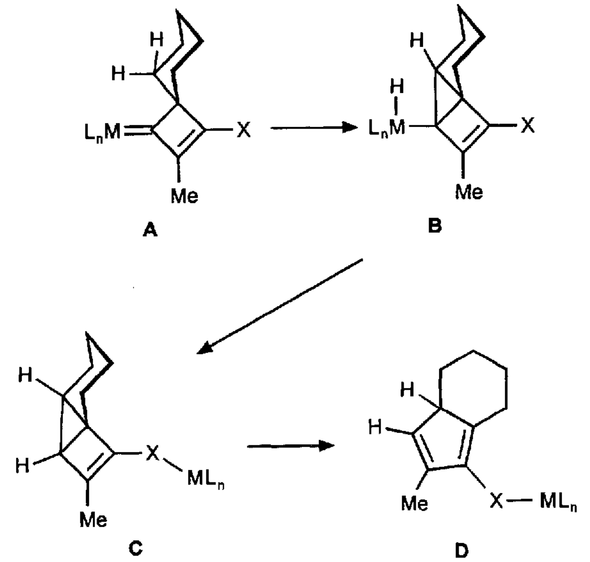
In contrast to **4**, tautomerization of **11** was not observed at room temperature. The structure of **11** shown in Scheme 7 corresponds to that of the tautomer **4a**. The detailed structure of **11** was established by ROESY. In solution only one conformer (with respect to the C1−N axis) could be detected (Scheme 8, only one enantiomer is shown). There are characteristic cross signals of the bridgehead proton (3a-H) with the axial 5- and 7-methylene protons as well as with the alkenyl proton (3-H). The positive sign of the intensity of the cross signals of the aromatic protons 1′-H and 9′-H with the axial 7-methylene proton and with the methyl group, respectively, indicates "genuine" ROE exchange signals. A negative sign for the cross signal would have been expected for a rapid interconversion of conformers.

Scheme 8



The formation of the analogous tautomer, both in the rearrangement of **3** and of **10**, suggests a common mechanism for the ring expansion. A direct connection of the sulfur atom to the C-3 atom of the cyclobutenylidene ring is not a precondition for the ring expansion to occur. Several rearrangement mechanisms are conceivable, e. g. the ring expansion could proceed by a stepwise mechanism via a strained tricyclo[4.3.0.$0^{1,7}$]nonane ring system (compare e. g. Gaoni and Tomazic[36]) or alternatively by a pericyclic ring opening preceded or followed by $Cr(CO)_5$ migration from carbon to sulfur. The ring expansion of spiro[4.4]nona-1,3-dienes to 4,5,6,7-tetrahydroindenes[20–22] was proposed to proceed by a pericyclic process. A possible reaction sequence which is consistent with all experimental results is shown in Scheme 9. 1,4-Migration of a hydrogen atom at C-2 of the cyclohexane ring to the metal to form complex **B** followed by reductive elimination affords the tricycle **C** and a solvens-stabilized ML_n fragment. Ring expansion and addition of the resulting (4,5,6,7-tetrahydroindenyl)thioether to ML_n or alternatively addition of **C** to ML_n and subsequent ring expansion give the tautomers **4a** and **11**.

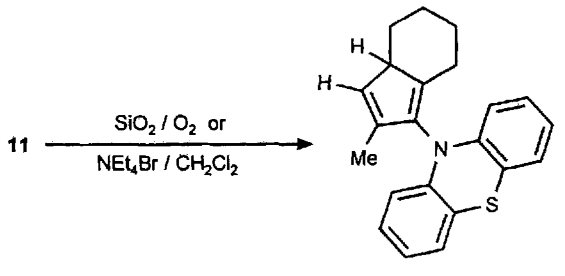
Scheme 9



In contrast to **3** and **10**, thermolysis of the 3-aminocyclobutenylidene complex $[(CO)_5Cr{=}\overline{C{-}C(Me){=}C(NEt_2)C}(CH_2)_5]$[24] did not afford a diethyl(4,5,6,7-tetrahydroindenyl)amine complex. After heating a solution of the complex in 1,1,2-trichloroethane at 60°C for four hours only small amounts of the complex had decomposed. After additional 16 hours at 115°C, the complex had completely decomposed. The formation of a 4,5,6,7-tetrahydroindene could not be detected. Ring expansion presumably requires a strongly electrophilic metal-bound ring-C atom. If this assumption was true we would expect the 3-alkoxycyclobutenylidene complex $[(CO)_5Cr{=}\overline{C{-}C(Me){=}C(OEt)C}(CH_2)_5]$[24] also to rearrange to 1-ethoxy-2-methyl-4,5,6,7-tetrahydroindene. The results of preliminary ^1H-NMR spectroscopic investigations of the thermolysis of $[(CO)_5Cr{=}\overline{C{-}C(Me){=}C(OEt)C}(CH_2)_5]$ support this conclusion.

The decoordination of the thioether was investigated with the example of **11**. Exposure of **11** adsorbed on silica gel to air for two days and chromatography afforded the 4,5,6,7-tetrahydroindene derivative **12** in 35% yield (Scheme 10). Reaction of **11** with tetraethylammonium bromide in dichloromethane for half an hour and subsequent chromatographic work-up gave **12** in 67% yield.

Scheme 10



12

The ^{1}H- and ^{13}C-NMR spectra confirmed that the decomplexation proceeded without structural changes of the (4,5,6,7-tetrahydroindenyl)phenothiazine ligand.

These results show that thio- and amino-substituted 4,5,6,7-tetrahydroindenes are readily accessible from pentamethylenevinylidene complexes and alkylthio alkynes respectively ynamines containing a thioether moiety.

Support of this work by *Volkswagen-Stiftung* and the *Fonds der Chemischen Industrie* is gratefully acknowledged. We thank Dr. *A. Geyer* and Ms. *M. Cavegen* for performing the 2D-NMR measurements.

Experimental

All operations were performed under inert gas (N_2 or Ar) by using standard Schlenk techniques. Solvents were dried by refluxing over sodium/benzophenone ketyl or CaH_2 and were freshly distilled prior to use. The silica gel used for chromatography (J. T. Baker, silica gel for flash chromatography) was argon-saturated. Flash chromatography was performed at an argon pressure of 1.3 bar (column length: 60 cm, column diameter: 2.5 cm). Preparative thin-layer chromatography (TLC, 2 mm) was carried out with a Harrison Research chromatotrone under a nitrogen atmosphere. The yields refer to analytically pure compounds and were not optimized. C_8K[26] and the alkynes **2a**[37] and **2b**[38,39] were prepared according to literature procedures, tetrahydrothiophene (THT, **6**) was purchased from Fluka. – IR: FT-IR spectrophotometer FTS 70, Fa. Bio-Rad. – ^{1}H and ^{13}C NMR: Bruker WM 250, AC 250, DRX 600, Jeol JNX 400. ^{1}H- and ^{13}C-NMR chemical shifts are reported relative to the residual solvent peaks of [D$_2$]dichloromethane or [D$_1$]chloroform. *J*-modulated spin-echo experiments were performed with JMODXH (program released by Bruker) and are "+"-calibrated relative to [D$_2$]dichloromethane. ^{1}H-NMR signal assignment was performed by DQF-COSY, selective TOCSY, and TOCSY. NOE experiments were carried out with the ROESY technique and heteronuclear correlation was assigned by HMQC and J-modulated spin-echo experiments[29]. – UV/Vis: Hewlett-Packard diode array spectrophotometer 8452A. – MS: Finnigan MAT 312, modified for EI (70 eV).

Pentacarbonyl[pentamethylenevinylidene]chromium (**1**), *and Pentacarbonyl[diphenylvinylidene]chromium* (**8**): 1.54 g (7.0 mmol) of $Cr(CO)_6$ was added at −78 °C to a suspension of 2.09 g (15.4 mmol) of C_8K in 50 ml of THF. After 15 min the suspension was warmed to 0 °C. Within 10 min the color of the slurry changed from dark-brown to silver-green. After 1 1/2 h formation of $K_2[Cr(CO)_5]$ was complete as indicated by IR spectroscopy. The suspension was cooled to −78 °C and 0.95 ml (7.0 mmol) of cyclohexylcarbonyl chloride [synthesis of **8**: 1.61 g (7.0 mmol) of diphenylacetyl chloride dissolved in 3 ml of THF] was added. The mixture immediately turned olive-green. The solution was warmed to 0 °C and kept for 0.5 h at that temp. [IR (THF): ν(CO) = 2031 cm^{-1} s, 1895 vs (**1**); 2027 cm^{-1} s, 1894 vs (**8**)]. – The solvent was removed in vacuo at room temp. and the black residue was dissolved in 50 ml of dichloromethane. 0.98 ml (7.0 mmol) of trifluoroacetic anhydride was added at −78 °C. The solution was stirred for 5 min. Then 1.09 ml (7.0 mmol) of DBU and 50 ml of *n*-pentane precooled to −40 °C were added. The solution was filtered over a short column of a 2-cm layer of kieselgur and a 2 cm layer of neutral Al_2O_3. Rapid elution with additional 50 ml of *n*-pentane/dichloromethane (2:1) at −40 °C gave a dark-green solution of **1** and **8**, respectively. The volume of the combined eluates was reduced in vacuo at −45 °C to approximately 40%. Since the vinylidene complexes are labile these solutions were immediately used for the subsequent reactions. The yield (indirectly determined by quenching with ynamines[24]) ranged from 60 to 65%. – **1**: IR (CH_2Cl_2): ν(CO) = 2082 cm^{-1} s, 2011 sh, 1994 vs, 1973 vs. – ^{1}H NMR (CD_2Cl_2, 193 K): δ = 1.54 (m, 6H), 2.14 (m, 4H). – ^{13}C NMR (CD_2Cl_2, 193 K): δ = 21.7, 25.1, 25.7 (CH_2), 121.3 (C_β), 213.1 (*cis*-CO), 225.9, (*trans*-CO), 399.3 (C_α). – **8**: IR (CH_2Cl_2): ν(CO) = 2088 cm^{-1} s, 2027 sh, 2002 vs, 1977 vs. – ^{1}H NMR (CD_2Cl_2, 228 K): δ = 7.51–7.45 (m, Ph). – ^{13}C NMR ($CDCl_3$, 223 K): δ = 127.1, 128.1, 129.0, 130.6 (Ph), 133.7 (C_β), 211.9 (*cis*-CO), 222.8 (*trans*-CO), 405.9 (C_α).

Pentacarbonyl[2-methyl-1-methylthio-4,5,6,7-tetrahydroindene-S]-chromium (**4**): 1.14 ml (13.2 mmol) of **2a** was added dropwise at 0 °C to a freshly solution of **1** (see above). The color changed immediately from dark-green to dark-red. After 1 h the conversion of **1** was complete as evidenced by the ν(CO) spectrum. Within another hour at room temp. the color changed from dark-red to dark-yellow. The solvent was removed in vacuo, the residue dissolved in 40 ml of *n*-pentane and the solution chromatographed at −20 °C with *n*-pentane/dichloromethane (ratio decreasing from 9:1 to 2:1). A yellow band was eluted and the solvent removed in vacuo at room temp. The residue was chromatographed once more under the same conditions giving a yellow oil containing a tautomeric mixture of **4a**–**e**. At −30 °C the oil partially crystallized in yellow rhombi. Yield: 0.35 g (13% based on $Cr(CO)_6$), m.p.: 34 °C. – IR (*n*-pentane): ν(CO) = 2068 cm^{-1} w, 1987 w, 1945 vs, 1932 s. – UV/Vis: λ_{max} (lg ε) = (CH_2Cl_2) 402 nm (3.326), (n-pentane) 406 nm (3.294), (DMF) 430 nm (3.354). – ^{1}H NMR (CD_2Cl_2, 228 K): δ = 0.65–1.88 (m, 20H, **4a**–**e**, 4,5,6,7-H), 1.94 (s, 3H, **4c**, 2-CH_3), 2.00 (d, *J* = 3.0 Hz, 3H, **4d**, CHC*H*$_3$), 2.08 (s, 3H, **4e**, 2-CH_3), 2.14 (s, 3H, **4a**, 2-CH_3), 2.15 (s, 3H, **4b**, 2-CH_3), 2.16 (m$_c$, 1H, **4d**, C*H*CH$_3$), 2.21–2.63 (m, 18H, **4a**–**e**, 5,6,7-H, **4b,c,e**, 4-H), 2.27 (m$_c$, 2H, **4a**, **d**, 4-H), 2.36, 2.40, 2.46, 2.49, 2.52 (s, each 3H, **4a**–**e**, S-CH_3), 2.58 (s, 1H, **4c**, C*H*SCH$_3$), 2.67 (m$_c$, 1H, **4a**, 3a-H), 2.86 (m$_c$, 1H, **4e**, 3-CH_2), 2.97 (m$_c$, 1H, **4b**, 7a-H), 5.57 (d, *J* = 5.6 Hz, 1H, **4b**, 3-H), 5.64 (m$_c$, 1H, **4d**, 3-H), 5.88 (s, br., 1H, **4c**, 3-H), 6.03 (s, br., 1H, **4a**, 3-H). (For **4a/4b/4c/4d/4e** ≈ 2.5/1.0/1.5/2.0/5.9). – ^{13}C NMR (CD_2Cl_2, 228 K, JMODXH): δ = 14.2, 15.3, 16.1 (−, **4a**–**d**, 2-CH_3), 14.8 (−, **4e**, 2-CH_3), 21.0, 22.1, 25.5 (−, **4a**–**d**, SCH_3), 24.3 (−, **4e**, SCH_3), 22.6, 22.8, 24.7, 25.3 (+, **4e**, C-4–C-7), 22.4, 24.9, 27.4, 27.8, 28.2, 28.4, 29.0, 31.8, 32.7, 39.4, 42.4 (+, **4a**–**d**, C-4–C-7), 39.4 (−, **4d**, C-2), 40.0 (−, **4c**, C-1), 46.8 (+,

4e, C-3), 51.8 (−, **4a**, C-3a), 55.0 (−, **4b**, C-7a), 116.4, 119.8, 125.0, 132.4 (−, **4a−d**, C-3), 131.0, 137.0, 138.7, 143.8 (+, **4e**, C-2, C-3, C-3a, C-7a), 127.0, 128.9, 130.7, 140.6, 141.6, 142.6, 142.8, 145.5, 150.3, 151.6, 155.4, 155.6 (+, **4a−d**, sp^2-C), 214.6, 214.7, 214.8, 214.9 (+, **4a−e**, *cis*-CO), 221.8 (+, **4a−e**, *trans*-CO). − MS (EI, 70 eV), *m/z* (%): 372 (7) [M$^+$], 316 (8) [M$^+$ − 2 CO], 288 (1) [M$^+$ − 3 CO], 260 (18) [M$^+$ − 4 CO], 232 (63) [M$^+$ − 5 CO], 180 (98) [M$^+$ − 5 CO − Cr], 165 (27) [M$^+$ − 5 CO − Cr − CH_3], 132 (58) [M$^+$ − 5 CO − Cr − CH_3SH]. − $C_{16}H_{16}CrO_5S$ (372.36): calcd. C 51.61, H 4.33; found C 51.38, H 4.56.

Pentacarbonyl[2-methyl-3-methylthio-spiro[3.5]non-2-ene-1-ylidene]chromium (**3**), *Pentacarbonyl[2-methyl-1-methylthio-4,5,6,7-tetrahydro-3aH-indene-S]chromium* (**4a**), and *Pentacarbonyl-[methyl(1-propynyl)thioether-S]chromium* (**5**): 0.88 ml (10.2 mmol) of **2a** was added dropwise at −30 °C to a freshly prepared solution of **1** (see above). Within 10 min the color changed from dark-green to red-brown. After 1 h the solvent was removed in vacuo at −30 °C. The brown residue was chromatographed at −35 °C with *n*-pentane/dichloromethane (ratio decreasing from 1:0 to 9:1). First a brown-yellow band [$Cr(CO)_6$], then a red band (containing **3**, **4a**, and **5**), and finally a yellow band which contained pure **4a** were eluted. The solvents of each fraction were removed in vacuo at −30 °C. **4a** was isolated from the third fraction as a yellow oil. The red, oily residue from the second fraction was redissolved in 8 ml of *n*-pentane/dichloromethane (5:3) and again chromatographed under identical conditions. The red zone which was directly followed by a yellow one was collected. Removal of the solvent in vacuo afforded **3** as a red powder which, however, was still contaminated by **4a** and **5** as indicated by its IR spectrum. − MS (EI, 70 eV), *m/z* (%): 372 (5) [M$^+$], 316 (7) [M$^+$ − 2 CO], 260 (14) [M$^+$ − 4 CO], 232 (56) [M$^+$ − 5 CO], 180 (58) [M$^+$ − 5 CO − Cr], 165 (17) [M$^+$ − 5 CO − Cr − CH_3], 132 (38) [M$^+$ − 5 CO − Cr − CH_3SH]. − **3**: IR (CH_2Cl_2): ν(CO) = 2051 cm^{-1} m, 1978 w, 1950 vs, 1938 sh. − ^{1}H NMR (CD_2Cl_2, 228 K): δ = 1.24−1.87 (m, 10H, CH_2), 2.29 (s, 3H, 2-CH_3), 2.61 (s, 3H, SCH_3). − ^{13}C NMR (CD_2Cl_2, 228 K, JMODXH): δ = 14.5 (−, SCH_3), 15.2 (−, CH_3), 25.0 (+, C-7), 25.2 (+, C-6, C-8), 35.3 (+, C-5, C-9), 69.6 (+, C-4), 169.5 (+, C-2), 178.1 (+, C-3), 217.6 (+, *cis*-CO), 228.1 (+, *trans*-CO), 323.5 (+, C-1). − **4a**: IR (CH_2Cl_2): ν(CO) = 2068 cm^{-1} m, 1987 w, 1945 vs, 1932 s. − ^{1}H NMR (CD_2Cl_2, 298 K): δ = 0.82 (m$_c$, 2H, 4,7-H), 1.21 (m$_c$, 2H, 5-CH_2), 1.45 (m$_c$, 2H, 6,7-H), 2.15 (s, 3H, 2-CH_3), 2.54 (s, 3H, SCH_3), 2.21−2.33 (m, 2H, 4,6-H), 2.93−3.03 (m, 1H, 3a-H), 6.03 (s, br., 1H, 3-H); (CD_2Cl_2, 228 K): δ = 0.78 (m$_c$, 2H, 4,7-H), 1.08−1.63 (m, 4H, 5-CH_2, 6,7-H), 2.12 (s, 3H, 2-CH_3), 2.51 (s, 3H, SCH_3), 2.16−2.28 (m, 2H, 4,6-H), 2.85−2.97 (m, 1H, 3a-H), 6.00 (s, br., 1H, 3-H). − ^{13}C NMR (CD_2Cl_2, 228 K, JMODXH): δ = 14.5 (−, 2-CH_3), 24.1 (−, SCH_3), 24.8, 27.2, 27.6, 31.7 (+, C-4−C-7), 51.7 (−, C-3a), 132.2 (−, C-3), 140.5, 148.0, 156.2 (+, sp^2-C), 214.5 (+, *cis*-CO), 221.7 (+, *trans*-CO); (CD_2Cl_2, 298 K, JMODXH): δ = 15.3 (−, 2-CH_3), 25.3 (−, SCH_3), 32.3, 28.2, 28.0, 25.5 (+, C-4−C-7), 52.7 (−, C-3a), 132.8 (−, C-3), 140.9, 156.7 (+, sp^2-C), 215.2 (+, *cis*-CO), 222.1 (+, *trans*-CO). − Other spectroscopical and analytical data were identical with those of **4**. − **5**: IR (*n*-pentane): ν(CO) = 2073 cm^{-1} m, 1987 w, 1950 vs, 1938 s. − ^{1}H NMR (CD_2Cl_2, 228 K): δ = 1.98 (s, 3H, $\equiv CCH_3$), 2.56 (s, 3H, SCH_3); (CD_2Cl_2, 298 K): δ = 2.01 (s, 3H, $\equiv CCH_3$), 2.59 (s, 3H, SCH_3). − ^{13}C NMR (CD_2Cl_2, 228 K, JMODXH): δ = 14.1 (−, SCH_3), 29.4 (−, $\equiv CCH_3$), 66.2 (+, $S\mathit{C}\equiv C$), 92.7 (+, $SC\equiv \mathit{C}$), 214.1 (+, *cis*-CO), 221.6 (+, *trans*-CO); (CD_2Cl_2, 298 K, JMODXH): δ = 14.5 (−, SCH_3), 29.9 (−, $\equiv CCH_3$), 214.7 (+, *cis*-CO).

Pentacarbonyl[tetrahydrothiophene]chromium (**7**): 1.33 ml (15.1 mmol) of **6** was added slowly at −40 °C to a freshly prepared solution of **1** (see above). Although there was no noticeable change in the color of the solution the IR spectrum showed two new ν(CO) absorptions at 2068 cm^{-1} and 2058 cm^{-1}. Within 1 h the solution was warmed to −20 °C. The IR absorption at 2058 cm^{-1} disappeared. Additonal 5.33 ml (60.3 mmol) of **6** was added. The solution was kept for 1.5 h at −10 °C. Then the solvent was removed in vacuo. The yellow-green oily residue was dissolved in 5 ml of *n*-pentane/dichloromethane (1:1) and the solution chromatographed twice with *n*-pentane/dichloromethane (ratio decreasing from 1:0 to 4:1). A yellow band was eluted and the solvent was removed in vacuo at −40 °C yielding a yellow powder. Recrystallization from *n*-pentane/dichloromethane (20:1) at −30 °C afforded **7** as yellow deliquescent cubes[31,32]. Yield 0.33 g (17% based on $Cr(CO)_6$), m.p. 27−28 °C. − IR (*n*-pentane): ν(CO) = 2069 cm^{-1} w, 1984 w, 1945 vs, 1934 m. − ^{1}H NMR ($CDCl_3$, 228 K): δ = 2.09 (s, br., 4H, CH_2), 2.99 (s, br., 4H, SCH_2); ($CDCl_3$, 298 K): δ = 2.07 (m$_c$, 4H, CH_2), 2.96 (m$_c$, 4H, SCH_2). − ^{13}C NMR ($CDCl_3$, 228 K): δ = 30.4 (CH_2), 42.1 (S-CH_2), 214.7 (*cis*-CO), 221.4 (*trans*-CO). − MS (EI, 70 eV), *m/z* (%): 280 (28) [M$^+$], 252 (5) [M$^+$ − CO], 224 (5) [M$^+$ − 2 CO], 196 (14) [M$^+$ − 3 CO], 168 (46) [M$^+$ − 4 CO], 140 (26) [M$^+$ − 5 CO], 88 (48) [M$^+$ − 5 CO − Cr]. − $C_9H_8CrO_5S$ (279.95): calcd. C 38.58, H 2.88; found C 38.49, H 2.89.

Pentacarbonyl[2-methyl-3-methylthio-4,4-diphenylcyclobut-2-enylidene]chromium (**9**): At −30 °C 1.91 ml (22.3 mmol) of **2a** was slowly added to a freshly prepared solution of **8** (see above). The solution was warmed to room temp. and stirred for 1 h. The solution was subsequently concentrated in vacuo to 5 ml and kept for another hour. The color changed from green to dark red. The solvent was completely removed in vacuo. The red residue was dissolved in 40 ml of *n*-pentane and the solution chromatographed at −35 °C with *n*-pentane/dichloromethane (ratio decreasing from 1:0 to 9:2). First a yellow band [$Cr(CO)_6$], then a red band containing **9** were eluted. The solvent of the second fraction was removed in vacuo. Crystallization of the residue at −30 °C from 15 ml of *n*-pentane yielded 290 mg of **9** (0.44 mmol; 10% based on $Cr(CO)_6$) as black rhombi, m.p.: 72−75 °C (dec.). − IR (*n*-pentane): ν(CO) = 2053 cm^{-1} m, 1979 w, 1959 vs, 1944 s. − UV/Vis (solvent): λ_{max} (lg ε) = (*n*-pentane) 512 nm (4.302), (EtOH) 508 nm (4.279), (DMF) 502 nm (4.267). − ^{1}H NMR (CD_2Cl_2, 228 K): δ = 2.14, 2.31 (s, 2 × 3H, 2-CH_3, SCH_3), 7.33−7.47 (m, 10H, Ph). − ^{13}C NMR (CD_2Cl_2, 228 K, JMODXH): δ = 13.6 (−, 2-CH_3), 14.3 (−, SCH_3), 76.0 (+, C-4), 127.6, 128.4, 129.3 (−, =CH, Ph), 140.3 (+, =CHPh), 170.6 (+, C-2), 177.5 (+, C-3), 216.6 (+, *cis*-CO), 228.4 (+, *trans*-CO), 331.7 (+, C-1). − MS (EI, 70 eV): *m/z* (%): 456 (2) [M$^+$], 428 (1) [M$^+$ − CO], 372 (8) [M$^+$ − 3 CO], 344 (6) [M$^+$ − 4 CO], 316 (28) [M$^+$ − 5 CO], 301 (20) [M$^+$ − 5 CO − CH_3], 264 (19) [M$^+$ − 5 CO − Cr]. − $C_{23}H_{16}CrO_5S$ (456.19): calcd. C 60.52, H 3.54; found C 60.53, H 3.59.

Pentacarbonyl[2-methyl-1-(N-phenothiazinyl)-4,5,6,7-tetrahydro-3aH-indene-S]chromium (**11**): A solution of 1.11 g (4.6 mmol) of **2b** in 3 ml of dichloromethane was added at −40 °C to a freshly prepared solution of **1** that was concentrated to a volume of 10 ml. The solution was kept for 10 min at −40 °C, then for 1 h at 0 °C and finally for another 1/2 h at room temp. 5 g of silica gel was added and the solvent was removed in vacuo. The residue was chromatographed at −20 °C. With *n*-pentane/dichloromethane (ratio decreasing from 1:0 to 7:3) a yellow band was eluted. The solvent was removed in vacuo and the residue chromatographed once more under identical conditions. Crystallization from *n*-pentane gave a yellow powder. Yield 1.17 g (48% based on **2b**), m.p. 37−39 °C. − IR (*n*-pentane): ν(CO) = 2068 cm^{-1} m, 1986 w, 1947 vs, 1932 s. − UV/Vis (solvent): λ_{max} (lg ε) = (CH_2Cl_2) = 404 nm (3.259), (*n*-pentane) 412 nm (3.227), (DMF) 436 nm (3.512). − ^{1}H NMR

(CD_2Cl_2, 223 K): δ = 0.96 (m_c, 2H, 4-H_{ax}, 7-H_{ax}), 1.43 (m_c, 1H, 5-H_{eq}), 1.52 (s, br., 3H, CH_3), 1.73 (m_c, 1H, 5-H_{ax}), 1.87 (m_c, 1H, 7-H_{cq}), 2.05 (m_c, 1H, 6-H_{eq}), 2.40 (m_c, 1H, 4-H_{eq}), 2.87 (m_c, 1H, 3a-H_{ax}), 2.94 (m_c, 1H, 6-H_{ax}), 6.25 (s, br., 3-H), 6.59 (m_c, 2H, 1'-H, 9'-H), 6.70−7.28 (m, 6H, phenothiazinyl H). − ^{13}C NMR (CD_2Cl_2, 228 K, JMODXH): δ = 13.3 (−,CH_3), 25.0 (+, C-5), 25.5 (+, C-6), 27.0 (+, C-7), 31.7 (+, C-4), 49.8 (−, C-3a), 115.0, 115.4 (+, C-4a', C-5a'), 115.2, 115.6, 122.9, 123.0, 126.6, 129.4, 129.6 (−, phenothiazinyl CH), 132.2 (+, C-Cp), 132.7 (−, C-3), 140.4 (+, *C*CH_3), 143.0, 143.1 (+, C-9a', C-10a'), 149.2 (+, N*C*CCH_3), 214.0 (+, *cis*-CO), 222.4 (+, *trans*-CO). − MS (EI, 70 eV): *m/z* (%): 523 (1) [M^+], 467 (1) [M^+ − 2 CO], 383 (6) [M^+ − 5 CO], 331 (76) [M^+ − 5 CO − Cr], 198 (100) [phenothiazine$^+$]. − $C_{27}H_{21}CrNO_5S$ (523.5): calcd. C 61.95, H 4.04, N 2.68; found C 62.01, H 4.16, N 2.96.

2-Methyl-1-(N-phenothiazinyl)-4,5,6,7-tetrahydro-3aH-indene (**12**): a) 0.39 g (0.7 mmol) of **11** was dissolved in 80 ml of acetone. 100 ml of silica gel was added to the obtained solution. Acetone was evaporated and the complex, adsorbed on silica gel, was exposed to air at room temp. for 2 d. The intensive yellow color of the silica gel vanished. Silica gel was extracted with 400 ml of acetone and the extract filtered. Removal of the solvent in vacuo yielded a yellow-brown oil which was dissolved in dichloromethane. The solution was filtered over silica gel with *n*-pentane/dichloromethane (2:1). The solvent was removed in vacuo and the yellow oily residue was purified by TLC with *n*-pentane/dichloromethane (2:1) to give **12** as a white powder. Yield 0.08 g (35% based on **11**), m.p. 93−95°C. − b) 0.14 g (0.27 mmol) of **11** was dissolved in 5 ml of dichloromethane. Then 2.84 g (13.5 mmol) of tetraethylammonium bromide was added to the resulting solution at room temp. After 0.5 h the ν(CO) spectrum indicated that the starting complex had completely been consumed. The solvent was removed in vacuo and the residue was extracted three times with 30-ml portions of *n*-pentane. The combined extracts were filtered, and the solvent was removed in vacuo. The residue was dissolved in 3 ml of *n*-pentane/dichloromethane (3:1) and purified by TLC using the same solvent mixture. The first light yellow band was collected. Removal of the solvent in vacuo yielded **12** hemihydrate as a white powder. Yield 0.06 g (67% based on **11**), m.p. 93−95°C. − IR (CH_2Cl_2): ν(C=C) = 1593 cm^{-1} m, 1571 m. − ^1H NMR (CD_2Cl_2, 228 K): δ = 0.83−1.60 (m, 4H, 4,5,6,7-H), 1.70 (s, 3H, CH_3), 1.75−2.67 (m, 4H, 4,5,6,7-H), 2.83 (m_c, 1H, 3a-H), 6.20 (s, 1H, 3-H), 6.35−6.96 (m, 8H, phenothiazinyl H). − ^{13}C NMR (CD_2Cl_2, 228 K, JMODXH): δ = 13.3 (−, CH_3), 25.1, 25.4, 27.3, 31.6 (+, C-4−C-7), 49.5 (−, C-3a), 118.4 (+, phenothiazinyl C), 114.4, 114.7, 122.0, 126.3, 127.1, 127.3 (−, phenothiazinyl CH), 132.0 (−, C-3), 133.3, 140.8 (+, *C*CH_3), 142.8, 143.0, (+, C-9a', C-10a'), 148.5 (+, N*C*CCH_3). − MS (EI, 70 eV): *m/z* (%): 331 (28) [M^+], 198 (100) [M^+ − indenyl]. − $C_{22}H_{21}NS \cdot 1/2\ H_2O$ (331.24 + 9.01): calcd. C 77.59, H 6.52, N 4.12; found C 77.54, H 6.46, N 4.35.

X-ray Structural Analysis of **9**: $C_{23}H_{16}CrO_5S$, molecular mass 456.4, crystal size 0.3 × 0.3 × 0.3 mm (obtained from *n*-pentane at −30°C), monoclinic, *C2/c*, a = 15.500(6), b = 12.188(4), c = 23.261(9) Å, β = 99.81(3)°, V = 4330(3) $Å^3$, Z = 8, d_{calcd} = 1.400 g cm^{-1}; μ(Mo-K_α) = 0.637 mm^{-1}, $F(000)$ = 1872; Wyckoff scan, 2Θ range 4.0−54.0°, scan rate variable 2.0−29.3° min^{-1} in ω; Δω = 0.75°, temp. 245 K, 10275 reflections collected, 4735 independent reflections, 3103 reflections with $F > 4.0\sigma(F)$; 271 refined parameters; R = 0.045, R_w = 0.047. Largest difference peak (hole): +0.33 e $Å^{-3}$ (−0.34 e $Å^{-3}$). − The measurements were made with a crystal mounted in a glass capillary on a Siemens R3m/V diffractometer (graphite monochromator, Mo-K_α radiation, λ = 0.71073 Å). The structure was solved by direct methods using the SHELXTL PLUS (VMS) program package. 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 full-matrix least-squares techniques. Complete lists of atomic coordinates and thermal parameters were deposited[40].

---

[1] W. Kaminsky, K. Külper, H. H. Brintzinger, F. R. W. P. Wild, *Angew. Chem.* **1985**, *97*, 507; *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 507.

[2] S. Collins, B. A. Kuntz, N. J. Taylor, D. G. Ward, *J. Organomet. Chem.* **1988**, *342*, 21.

[3] W. Mengele, J. Diebold, C. Troll, W. Röll, H.-H. Brintzinger, *Organometallics* **1993**, *12*, 1931.

[4] K. Tsukida, M. Ito, F. Tomeoka, A. Kodama, *J. Chem. Soc., Perkin Trans. 1*, **1981**, 2472.

[5] M. Ito, T. Hiroshima, K. Tsukida, Y. Shichida, T. Yoshizawa, *J. Chem. Soc., Chem. Commun.* **1985**, 1443.

[6] T. Iwasa, M. Ito, F. Tokunaga, *Photochem. Photobiol.* **1992**, *56*, 921.

[7] K. Matcheva, M. Beckmann, D. Schomburg, E. Winterfeldt, *Synthesis* **1989**, 814.

[8] S. P. Green, D. A. Whiting, *J. Chem. Soc., Chem. Commun.* **1992**, 1753.

[9] M. Beckmann, T. Meyer, F. Schulz, E. Winterfeldt, *Chem. Ber.* **1994**, *127*, 2505.

[10] F. R. W. P. Wild, L. Zsolnai, G. Huttner, H. H. Brintzinger, *J. Organomet. Chem.* **1982**, *232*, 233.

[11] Y. Masuyama, K. Yamada, H. Tanaka, Y. Kurusu, *Synth. Commun.* **1987**, *17*, 1525.

[12] M. Hatanaka, Y. Himeda, R. Imashiro, Y. Tanaka, I. Ueda, *J. Org. Chem.* **1994**, *59*, 111.

[13] R. T. Halterman, T. M. Ramsey, *J. Organomet. Chem.* **1994**, *465*, 175.

[14] J. P. Marino, R. J. Lindermann, *J. Org. Chem.* **1981**, *46*, 3696.

[15] A. Abouabdellah, J.-P. Bégué, D. Bonnet-Delpon, T. Lequeux, *J. Org. Chem.* **1991**, *56*, 5800.

[16] R. N. Austin, T. J. Clark, T. E. Dickson, C. M. Killian, T. A. Nile, D. J. Schabacker, A. T. McPhail, *J. Organomet. Chem.* **1995**, *491*, 11.

[17] R. B. Reinarz, G. J. Fonken, *Tetrahedron Lett.* **1973**, 4591.

[18] K. H. Holm, L. Skattebøl, *Acta Chem. Scand. B* **1984**, *38*, 783.

[19] V. A. Mironov, A. P. Ivanov, Ya. M. Kimelfeld, L. I. Petrovskaya, A. A. Akhrem, *Tetrahedron Lett.* **1969**, 3347.

[20] L. M. Dané, J. W. de Haan, H. Kloosterziel, *Tetrahedron Lett.* **1970**, 2755.

[21] M. F. Semmelhack, H. N. Weller, J. S. Foos, *J. Am. Chem. Soc.* **1977**, *99*, 292.

[22] K. S. Replogle, B. K. Carpenter, *J. Am. Chem. Soc.* **1984**, *106*, 5751.

[23] H. Fischer, O. Podschadly, A. Früh, C. Troll, R. Stumpf, A. Schlageter, *Chem. Ber.* **1992**, *125*, 2667.

[24] H. Fischer, O. Podschadly, unpublished results.

[25] M. A. Schwindt, T. Lejon, L. S. Hegedus, *Organometallics* **1990**, *9*, 2814.

[26] M. F. Semmelhack, G. R. Lee, *Organometallics* **1987**, *6*, 1839.

[27] B. E. Boland, S. A. Fam, R. P. Hughes, *J. Organomet. Chem.* **1979**, *172*, C29.

[28] H. Fischer, A. Schlageter, W. Bidell, A. Früh, *Organometallics* **1991**, *10*, 389.

[29] E. W. Abel, S. K. Bhargava, K. G. Orrell, *Progr. Inorg. Chem.* **1984**, *32*, 1.

[30] J. H. Eekhof, H. Hogeveen, R. M. Kellogg, E. Klei, *J. Organomet. Chem.* **1978**, *161*, 183.

[31] H. Kessler, M. Gehrke, C. Griesinger, *Angew. Chem.* **1988**, *100*, 507; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 490.

[32] See e.g.[32a] *Transition Metal Carbene Complexes* (Eds. K. H. Dötz, H. Fischer, P. Hofmann, F. R. Kreissl, U. Schubert, K. Weiss), Verlag Chemie, Weinheim, **1983**. − [32b] M. I. Bruce, A. G. Swincer, *Adv. Organomet. Chem.* **1983**, *22*, 59. − [32c] M. I. Bruce, *Chem. Rev.* **1991**, *91*, 197.

[33] H. Fischer, J. Schmid, S. Zeuner, *Chem. Ber.* **1987**, *120*, 583.

[34] W. Strohmeier, J. F. Guttenberger, G. Popp, *Chem. Ber.* **1965**, *98*, 2248.

[35] J. H. Eekhof, H. Hogeveen, R. M. Kellogg, *J. Organomet. Chem.* **1978**, *161*, 361.

[36] Y. Gaoni, A. Tomazic, *J. Org. Chem.* **1985**, *50*, 2948.
[37] L. Brandsma, *Preparative Acetylenic Chemistry*, Elsevier, Amsterdam, **1988**.
[38] J. L. Dumont, M. G. Champetier, *C. R. Acad. Sci.* **1965**, *261*, 1710.
[39] J. L. Dumont, W. Chodkiewicz, P. Cadiot, *Bull. Soc. Chim. Fr.* **1967**, 1197.
[40] Further details of the crystal structure investigations are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Informationen mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-404648, the authors and the journal citation.

[96010]