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Thiocarbene complexes of chromium: sulfur to carbon migration of an allyl group upon alkyne insertion

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Abstract

$(CO)_5Cr{=}C(CH_3)S(CH_2CH{=}CH_2)$ (7) reacts with diphenylacetylene by insertion of the alkyne and of CO to give the unsaturated thiolactones $H_2C{=}CHCH_3(CH_3)$-$\overline{CSC(=O)C(Ph)=CPh}$ and $CH_3(H)\overline{CSC(=O)C(Ph=CPh}$, the former arising from migration of the allyl group from sulfur to carbon and the latter by loss of the allyl group.

Introduction

In a series of papers [1–4] we have described the interesting reactions of disubstituted aminocarbene complexes of chromium towards alkynes. When they bear a coordinated double bond γ with respect to the carbene function, they undergo an alkyne-insertion double bond cyclopropanation reaction (Scheme 1). When the double bond is *trans* to the metal and cannot be coordinated to it, in addition to insertion of an alkyne and CO there is a nitrogen to carbon migration of the allyl group (Scheme 1). The latter reaction is reminiscent of a carbon–nitrogen centered ylid rearrangement of the Stevens type [5]. Since in organic chemistry, the same rearrangement has been observed in the case of sulfur centered ylids [6], we synthesized thiocarbene carbonylchromium complexes and examined their behaviour in the alkyne insertion reaction.

Results and discussion

The thiocarbene complexes **7** and **9** were prepared by a modification of the method used by Fischer [7]: rather than treating a large excess of thiol with the

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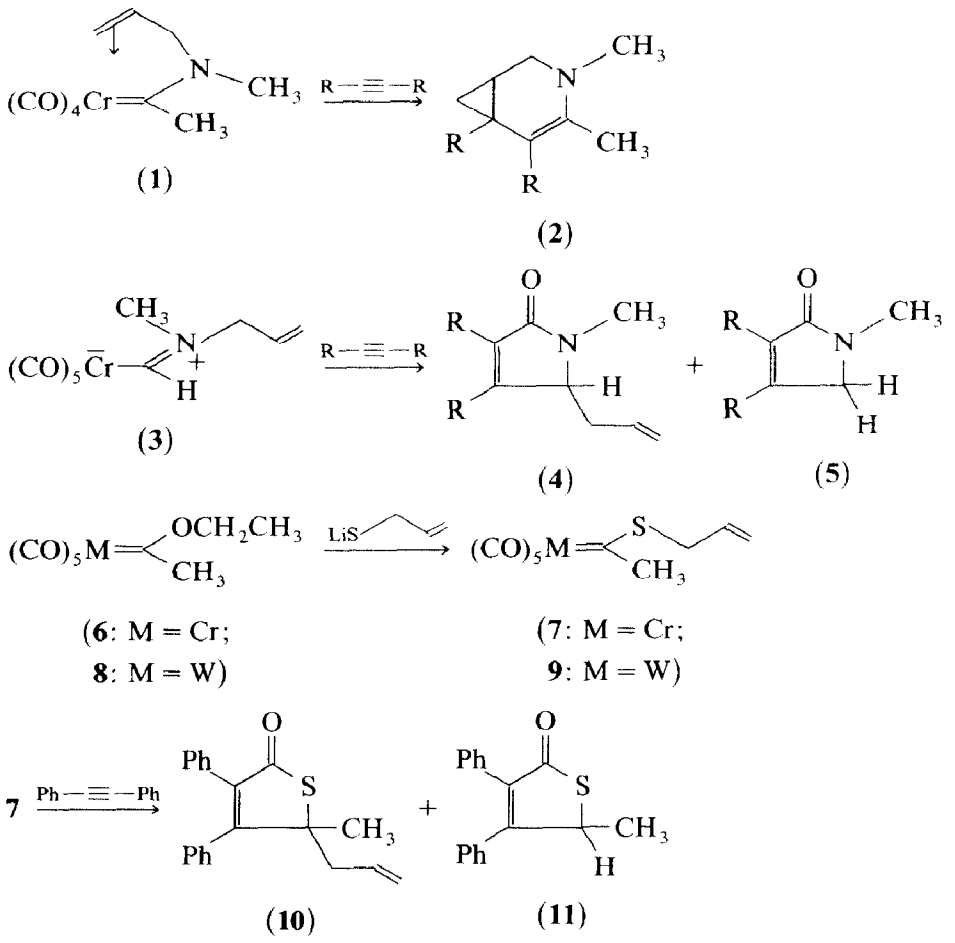


Scheme 1

methyl(ethoxy)carbene complexes **6** and **8**, we used instead a small excess of the magnesium or lithium allylthiolate. The allylthiolates were prepared either by treatment of allylthiol with BuLi, or that of allylmagnesium bromide with sulfur at $-40\,^{\circ}C$. Complexes **7** and **9** were thus obtained in 30 to 40% yield.

The ^{1}H and ^{13}C NMR spectra indicate that complex **7** exists as a single isomer ***7E***, the carbene carbon giving a signal at 366.3 ppm. In the case of complex **9**, two isomers were detected in solution: both the protons of the double bond and of the $S-CH_2$ group appear at different field. The signals for the $S-CH_2$ protons at 2.76 and 2.57 ppm respectively indicate that 15% of the minor isomer ***8Z*** is present in solution along with ***8E***.

Attempts to coordinate the terminal double bonds of **7** and **9** to the metal by heating solutions in benzene failed. In the case of **7**, complete decomposition was observed, whereas **9** was recovered unchanged. Complex **9**, like its nitrogen analogue, was also stable in boiling benzene in the presence of diphenyl-acetylene, whereas under these conditions complex **7** underwent a fast reaction to give two organic compounds, which were separated by silica gel chromatography.

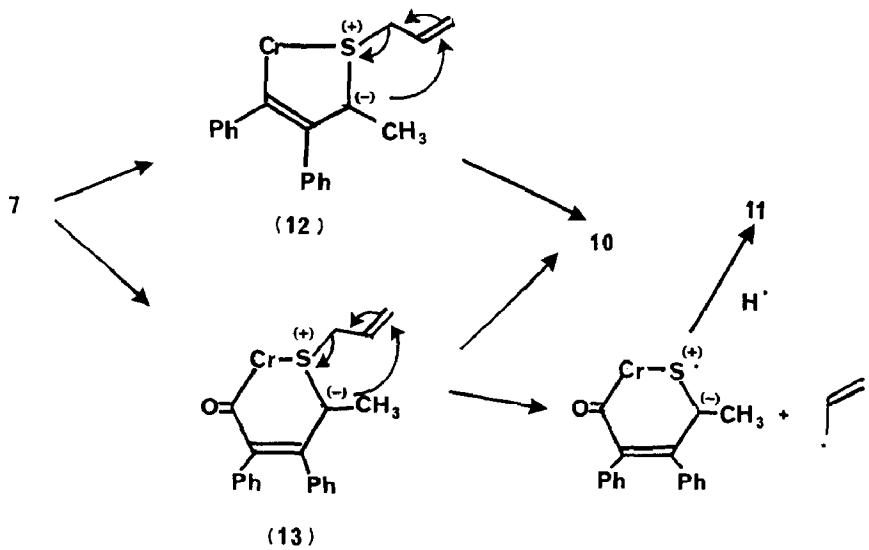
The first product (white crystals, m.p. 72° C, 40% yield), was assigned formula **10** on the following grounds. Both the elemental analysis and the mass spectrum ($m/z = 266$, M^+) are consistent with this formulation. The IR and ^{13}C NMR spectra confirm the presence of an α,β unsaturated lactone (ν(CO), 1670 cm^{-1}, δ(CO), 169.1 ppm). The ^1H NMR spectrum shows the presence of two phenyl groups (10H at 7.20 ppm), of an allyl group (1H at 5.87 ppm, 2H at 5.16 ppm and 2H at 2.62 ppm), and of a methyl group (singlet at 1.72 ppm), and is very similar to that of the nitrogen analogue **4** (R = Ph).

The second product (oil, 4% yield), was assigned structure **11**. The ^1H NMR spectrum, which is again similar to that of **5**, shows the presence of two phenyl groups (10H at 7.25 ppm), of an allyl group (1H at 5.85 ppm, 2H at 5.22 ppm, 2H at 2.65 ppm), of a hydrogen to a methyl group (1H at 4.83 ppm, as a quartet), and of a methyl group, as a doublet, at 1.44 ppm.

As far as the mechanism of this reaction is concerned, the formation of both compounds can be accounted for by analogy with the transformation **3** → **4** + **5**, in terms of the rearrangement of the ylids **12** or **13** obtained after the insertion of the alkyne, the rearrangement taking place before (via **12**) or after (via **13**) the CO insertion.

A parallel between the reaction described herein and the sulfonium ylid rearrangement would therefore provide a ready explanation of the formation of both **10** and **11**, **10** arising either from the 1,5- or 1,3-sigmatropic rearrangement.

It has been shown [8] that in the case of allylsulfonium ylids, a homolytic dissociation of the ylid can take place, and so in addition to afore-mentioned rearrangement, **11** could result from a homolytic rupture of the carbon sulfur bond of **12** or **13**, with loss of the allyl radical (Scheme 2). However, when the fact is borne in mind that a transition metal is involved in this reaction, a direct transfer of the allyl group from sulfur to chromium could also account for the formation of both **10** and **11**.



Scheme 2

Experimental

All reactions were carried out in oven-dried glassware under nitrogen. Benzene, diethyl ether (Et_2O), and tetrahydrofuran (THF) were distilled from $LiAlH_4$. Preparative column chromatography was performed with 70–230 mesh Merck silica gel, and preparative (PLC) and thin layer chromatography (TLC) with Merck G60 silica gel. Light petroleum ether (PE) was used as eluent.

NMR spectra were recorded on a JEOL FX-90 spectrometer or on a Bruker WM 200 spectrometer. IR spectra were recorded with a Beckman 4240 spectrophotometer, and mass spectra with a Kratos MS 3P. Melting points were determined on a Reichert Köfler block and are uncorrected.

Pentacarbonyl((thioallyl)(methyl)carbene)chromium(0) (7)

a) Sulfur (0.32 g, 10 mmol) was added to a solution of allylmagnesium bromide (10 mmol) in THF (50 ml), at −40 °C and the solution was then warmed to room temperature. The homogeneous solution was then added through a cannula to a solution of complex **6** (2.64 g, 10 mmol) in THF (50 ml) at −40 °C. The mixture was allowed to warm to room temperature and water was added. After extraction with petroleum ether the extract was evaporated under vacuum to give a dark red oil, which was purified by silica gel chromatography. Elution with petroleum ether gave complex **7** (0.88 g, 30%) as a red oil. ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.80 (1H, m, C*H*=CH_2), 5.34 (2H, m, CH_2=CH), 3.83 (2H, d, S–CH_2), 3.57 (3H, s, CH_3). ^{13}C NMR (50.1 MHz, C_6D_6) δ 366.6 (Cr=*C*), 227.3, 216.5 (CO), 129.4, 120.3 (*C*H=*C*H_2), 45.8 (S–*C*H_2, *C*H_3). Anal. Found: C, 41.67; H, 3.28. $C_{10}H_8O_5S$ calcd.: C, 41.08; H, 2.74%. *m/z*: 292 (M^+).

(b) BuLi (12.5 mmol) in hexane (7.8 ml) was added to a solution of allylthiol (0.93 g, 12.5 mmol) in THF (50 ml) at −40 °C. The solution was added to a solution of complex **6** (3.1 g, 11.7 mmol) in THF (150 ml) at −40 °C. Work-up and purification as above gave complex **7** (1.02 g, 30%) as an oil.

Pentacarbonyl((thioallyl)(methyl)carbene)tungsten(0) (9)

Complex **9** was prepared according by the same procedure. **9***E*: ^{1}H NMR (200 MHz, C_6D_6) δ 5.09 (1H, m, C*H*=CH_2), 4.78 (2H, m, CH_2=CH), 2.61 (3H, s, CH_3), 2.57 (2H, d, S–CH_2). ^{13}C NMR (50.1 MHz, C_6D_6) δ 332.1 (W=*C*), 207.2, 197.9 (CO), 128.4, 120.4 (*C*H=*C*H_2), 47.6 (S–*C*H_2), 46.3 (*C*H_3). *m/z*: 424 (M^+)

Insertion of diphenylacetylene

A solution of complex **7** (0.75 g, 2.5 mmol) in benzene (50 ml) containing diphenylacetylene (0.6 g, 3 mmol) was boiled for 12 h. Most of the solvent was then evaporated under vacuum and the residue chromatographed on silica gel. Elution with petroleum ether/methylene chloride (70/30) first gave **10** (0.3 g, 40%) as a white solid m.p. 72 °C. ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.27–7.05 (10H, m, Ph), 5.87 (1H, m, C*H*=CH_2), 5.20 (2H, m, CH_2=CH), 2.64 (2H, d, CH_2), 1.71 (3H, s, CH_3). ^{13}C NMR (50.1 MHz, $CDCl_3$) δ 169.1 (CO), 140.6, 134.4, 133.2, 131.4, 130.0, 128.8, 128.4, 127.9, 127.8, 119.9 (*C*=*C*, Ph), 60.8 (S–*C*), 43.9 (*C*H_2), 26.3 (*C*H_3). Anal. Found: C, 78.15; H, 5.89. $C_{20}H_{18}OS$ calcd.: C, 78.43; H, 5.88%. *m/z*: 306 (M^+). Subsequently compound **11** (0.03 g) was eluted as an oil. ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.29–7.13 (10H, m, Ph), 5.9 (1H, m, C*H*=CH_2), 5.22 (2H, m, CH_2=CH),

4.63 (1H, q, J 7.2 Hz, CH–CH_3), 2.63 (2H, d, CH_2), 1.43 (3H, d, J 7.2 Hz, CH–CH_3). m/z: 266 (M^+).

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