SYNTHESIS OF THE SIX-MEMBERED TETRACARBONYL CARBENE-THIOETHER CHELATE [(CO)$_4$Cr{$\overline{C(OEt)C(OEt)=CHCHS(CH_2)_3S}$}] AND THE SEVEN-MEMBERED IMIDATE-THIOETHER CHELATES [(CO)$_4$Cr{$\overline{NR=C(OEt)C(OEt)=CHCHS(CH_2)_3S}$}] (R = H OR Me), BY CO OR NR INSERTION INTO METAL–CARBENE BONDS. CRYSTAL STRUCTURES OF [(CO)$_4$Cr{$\overline{S(CH_2)_3SC(OEt)C(OEt)=CHCH}$}] AND [(CO)$_4$Cr{$\overline{N(Me)=C(OEt)C(OEt)=CHCHS(CH_2)_3S}$}]

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Summary

The compounds [(CO)$_5$M{$\overline{C(OEt)CH_2CHS(CH_2)_3S}$}] (M = Cr (I) and M = W (II)) have been made by reaction of the carbene anions [(CO)$_5$M{C(OEt)CH$_2$}]$^-$ with Cl$\overline{CHS(CH_2)}$$_3$S. Deprotonation and subsequent alkylation of the chromium derivatives yield two diastereomers with the formula [(CO)$_4$$\overline{Cr{C(OEt)C(OEt)=CHCHS(CH_2)_3S}}$] (IIIa and IIIb). Upon deprotonation the tungsten precursor undergoes β-elimination and alkylation then gives the vinylcarbene complex [(CO)$_5$W{C(OEt)CH=CHS(CH$_2$)$_3$SEt}] (IV). Reaction of ClCH(SPh)Ph with the chromium carbene anion gives the vinylcarbene complex [(CO)$_5$Cr{C(OEt)CH=CHPh}] (VII). Reaction of the six-membered chelate [(CO)$_4$$\overline{Cr{C(OEt)C(OEt)=CHCHS(CH_2)_3S}}$] with MeNHNH$_2$ takes place with rearrangement to give the dithioether chelate [(CO)$_4$Cr{$\overline{S(CH_2)_3}$-$\overline{SC(OEt)C(OEt)=CHCH}$}] (VIII), with NMe insertion into the metal–carbene bond to give the imidate-sulphide complex [(CO)$_4$Cr{$\overline{N(Me)=C(OEt)C(OEt)=CHCHS(CH_2)_3S}$}] (IX), and by formal NH insertion to give the seven-membered chelate (CO)$_4$$\overline{Cr{NH=}}$ $\overline{C(OEt)C(OEt)=CHCHS(CH_2)_3S}$] (X). The structures of the complexes VIII and IX have been determined by X-ray diffraction.

Introduction

We previously described the preparation of five-membered chelate compounds of disubstituted chromium carbonyl containing bidentate carbene-thioether (for example A) and carbene-phosphine ligands (for example B) [2].

A   . B   C
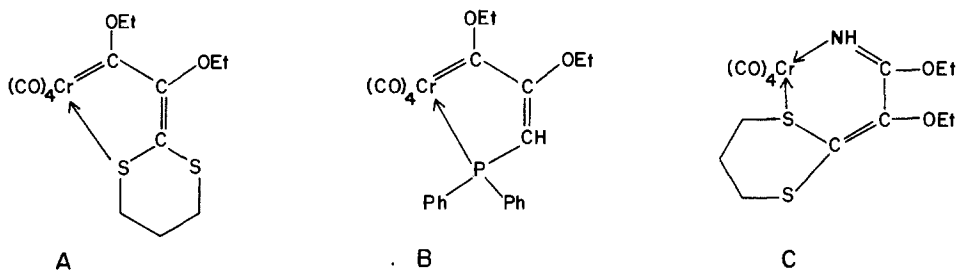
Both types of compound can be converted into coordinated imidate-containing compounds (for example **C**) by formal NH insertion into the metal–carbene bond upon treatment with $MeNHNH_2$.

During the formation of the compounds such as **A** (or the aminocarbene derivative thereof [3]) and **B**, a carbonyl (or isonitrile) group *cis* to a carbene carbon atom in the precursor complex (for example $[(CO)_5Cr\{C(OEt)CH_2PPh_2\}]$ (**D**)) is functionalised by deprotonation α to the carbene carbon atom (compare Casey's work on carbene anions [4]) and formally inserted into a metal–carbene bond while the sulphur or phosphorus atom β to the carbene carbon becomes coordinated at the vacated coordinated site. Alkylation gives the neutral products.

These results, as well as the fact that few CO insertions into metal–carbene bonds have been reported [5,6], prompted us to attempt the preparation of still unknown six-membered tetracarbonyl carbene-thioether chelates of chromium and tungsten from carbene complexes in which the sulphur atom is situated γ to the carbene carbon. We also describe here the preparation of seven-membered chelates (which are rare species [7]) by treatment of a six-membered chelate with methylhydrazine. This reaction also furnished an unexpected tetracarbonyl complex in low yield. Its complicated structure necessitated an X-ray crystallographic study, which revealed that a rather unusual $MeNHNH_2$-catalysed insertion of a carbene into a single C–S bond of the ligand had taken place.

Results and discussion

(a) Preparation of precursor complexes and their reaction with LiBu and $[Et_3O][BF_4]$

The complexes $[(CO)_5M\{C(OEt)CH_2\overline{CHS(CH_2)_3S}\}]$ (M = Cr (**I**) and W (**II**)) were prepared by addition of $ClCHS(CH_2)_3S$ to the carbene anions $[(CO)_5M\{C(OEt)CH_2\}]^-$ [2] followed by separation on a silica gel column and precipitation as oils from pentane at $-30°C$. No decomposition occurred under nitrogen during one month, but both compounds were less stable in solution. Mass spectrometry as well as IR (Table 1) and ^1H NMR (Table 2) spectroscopy and elemental analysis (see Experimental section) confirmed the structures shown in Scheme 1. The signals from the protons α to the carbene carbon atom lie upfield (δ 3.72 ppm in **I**) from that of the proton α to the two sulphur atoms (δ 4.43 ppm in **I**).

Deprotonation of **I** with LiBu in ether at $-60°C$ produced a bright yellow precipi-

tate which dissolved and turned red when the solution was allowed to warm up to room temperature. Alkylation with Meerwein's reagent, $[Et_3O][BF_4]$, and chromatography yielded two brown diastereomers (IIIa and IIIb, Scheme 1) each of which contained two chiral centres in its chelate ring, one at the coordinated sulphur atom and the other at the carbon in the position α to it. These compounds gave identical 70 eV mass spectra and very similar proton NMR resonances as well as IR absorption bands in the carbonyl region (Tables 1 and 2).

The tungsten analogue of III could not be prepared. Deprotonation of II followed by alkylation furnished the vinylcarbene, IV. Since both III and IV decomposed slowly and

I : M = Cr

orange, 60%

II : M = W

yellow-orange, 18%

III a,b

brown, 60%, 20%

IV

orange-red, 57%
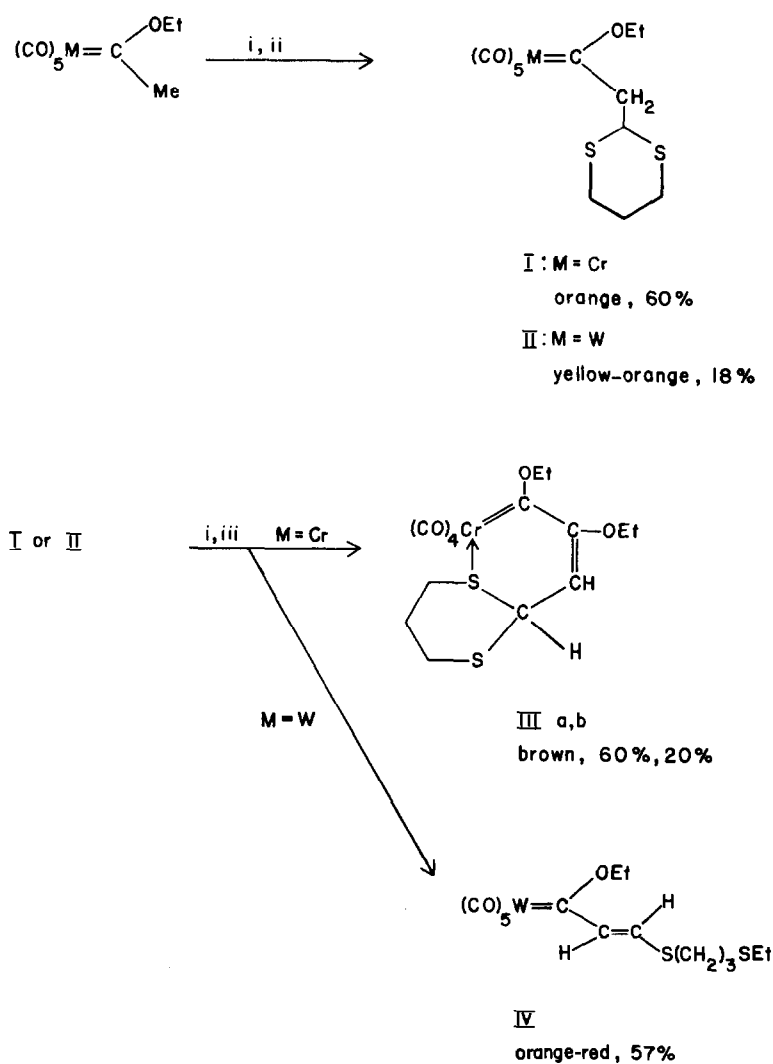
SCHEME 1. Reagents: (i) LiBu; (ii) ClCHS(CH$_2$)$_3$S; (iii) [Et$_3$O][BF$_4$].

TABLE 1

INFRARED DATA ^{a} (ν(CO), cm^{-1})

	Pentacarbonyl complexes			
	$A_1^{(1)}$	B_1	$A_1^{(2)}$	E
I	2060m	1978w	1950(sh)	1940s
II	2075m	1983w	1943(sh)	1940s
IV	2065m	1975w	1945(sh)	1938s
VI	2062m		1931(sh)	1929s
VII	2060m		1956s	1946s
	Tetracarbonyl complexes ^{b}			
	$A_1^{(1)}$	$A_1^{(2)}$	B_1	B_2
IIIa	2025m	1948ms	1916s	1896m
IIIb	2027ms	1950ms	1918s	1903ms
V	2015m	1942s	1918(sh)	1908m
VIII	2015m	1911m	1885s	1880(sh)
IX	2010m	1892s	1879s	1850m
X	2015m	1895s	1880s	1850m

^{a} I–VIII in hexane, IX and X measured in CS$_2$; m, medium; ms, medium-strong; s, strong; sh, shoulder.
^{b} Assignment based on pseudo-C_{2v}-symmetry.

yielded unsatisfactory elemental analyses, they were treated with ammonia in ether to afford the corresponding stable crystalline aminocarbene complexes V and VI in more than 80% yields (Tables 1 and 2).

The mechanism of the formation of III via carbonyl insertion is depicted in Scheme 2. Contrary to the NMR results, the more acidic proton in I is assumed to be next to the carbene carbon atom, and not in the activated position α to the sulphur atoms. The same type of mechanism has been suggested previously to account for the formation of different five-membered chelates [2,3]. The formation of IV is in accord with the fact that the tungsten–carbene bond is stronger than the chromium–carbon bond and with the earlier observation that tungsten carbene complexes are less prone to react by formal CO insertion than their chromium counterparts [1].
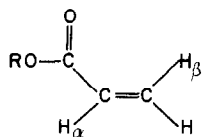
By introducing a better leaving group, we were able to synthesize a pentacarbonyl-vinylcarbene complex, [(CO)$_5$Cr{C(OEt)CH=CHPh}] (VII) in one step from the chromium carbene anion and ClCH(SPh)Ph. This reaction occurs with precipitation of LiCl and elimination of HSPh (Scheme 3). A similar complex, [(CO)$_5$Cr{C(OMe)CH=CHPh}], has been prepared previously by condensation of the carbene anion [(CO)$_5$Cr{C(OMe)CH$_2$}]$^-$ and benzaldehyde [8]. Spectroscopic data for complex VII are included in Tables 1 and 2.

In all the vinylcarbene complexes (IV, VI and VII) the two vinyl protons are situated *trans* to each other (J(CHCH) $\geq$ 15 Hz). The assignments of these protons are based on the work of Wilson and Fischer [9]. We note in passing that the analogy between carbene complexes and esters [10] breaks down when the chemical shifts of vinylcarbene complexes and vinyl esters are compared [11]:
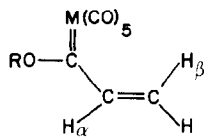
TABLE 2. ^{1}H NMR CHEMICAL SHIFTS ^{a} (CDCl$_3$; δ rel. to int. SiMe$_4$)

[(CO)$_5$Cr{C(OEt)CH$_2$$\overline{\text{CHS(CH}_2)_3\text{S}}$}] (I)	1.66 (t, 3H, OCH$_2$CH$_3$), 2.0 (m, 2H, CH$_2$CH$_2$CH$_2$), 2.8 (m, 4H, CH$_2$CH$_2$CH$_2$), 3.72 (d, 2H, C$_{carb}$ CH$_2$), 4.43 (t, 1H, CH$_2$CH), 5.17 (q, 2H, OCH$_2$)
[(CO)$_5$W{C(OEt)CH$_2$$\overline{\text{CHS(CH}_2)_3\text{S}}$}] (II)	1.65 (t, 3H, OCH$_2$CH$_3$), 2.0 (m, 2H, CH$_2$CH$_2$CH$_2$), 2.8 (m, 4H, CH$_2$CH$_2$CH$_2$), 3.53 (d, 2H, C$_{carb}$ CH$_2$), 4.43 (t, 1H, CHS), 4.93 (q, 2H, OCH$_2$)
[(CO)$_4$$\overline{\text{Cr{C(OEt)C(OEt)CHCHS(CH}_2)_3\text{S}}}$}] (IIIa)	1.33 (t, 3H, OCH$_2$CH$_3$), 1.62 (t, 3H, C$_{carb}$ OCH$_2$CH$_3$), 2.1 (m, 2H, CH$_2$CH$_2$CH$_2$), 2.8 (m, 4H, CH$_2$CH$_2$CH$_2$), 3.78 (q, 2H, OCH$_2$CH$_3$), 4.15 (d, 1H, CHS), 4.70 (d, 1H, C=CH), 5.12 (q, 1H, C$_{carb}$ OCH$_2$CH$_3$)
(IIIb)	1.33 (t, 3H, OCH$_2$CH$_3$), 1.63 (t, 3H, C$_{carb}$ OCH$_2$CH$_3$), 2.1 (m, 2H, CH$_2$CH$_2$CH$_2$), 2.8 (m, 4H, CH$_2$CH$_2$CH$_2$), 3.80 (q, 2H, OCH$_2$CH$_3$), 4.15 (d, 1H, CHS), 4.72 (d, 1H, C=CH), 5.15 (q, 2H, C$_{carb}$ OCH$_2$CH$_3$)
[(CO)$_5$W{C(OEt)CHCHS(CH$_2$)$_3$SEt}] ^{b} (IV)	1.25 (t, 3H, SCH$_2$CH$_3$), 1.55 (t, 3H, OCH$_2$CH$_3$), 2.0 (m, 2H, CH$_2$CH$_2$CH$_2$), 2.5 (m, 4H, CH$_2$CH$_2$CH$_2$), 2.92 (q, 2H, SCH$_2$CH$_3$), 4.75 (q, 2H, OCH$_2$CH$_3$), 7.15 (d, 1H, CHS), 7.52 (d, 1H, C$_{carb}$ CH)
[(CO)$_4$$\overline{\text{Cr{C(NH}_2)\text{C(OEt)CHCHS(CH}_2)_3\text{S}}}$}] (V)	1.37 (t, 3H, OCH$_2$CH$_3$), 2.1 (m, 2H, CH$_2$CH$_2$CH$_2$), 2.9 (m, 4H, CH$_2$CH$_2$CH$_2$), 3.75 (q, 2H, OCH$_2$CH$_3$), 4.65 (d, 1H, CHS), 5.10 (d, 1H, C=CH), 8.8 (br, 2H, NH$_2$)
[(CO)$_5$W{C(NH$_2$)CHCHS(CH$_2$)$_3$SEt}] ^{c} (VI)	1.23 (t, 3H, SCH$_2$CH$_3$), 1.9 (m, 2H, CH$_2$CH$_2$CH$_2$), 2.5 (m, 4H, CH$_2$CH$_2$CH$_2$), 2.90 (q, 2H, SCH$_2$CH$_3$), 6.35 (d, 1H, CHS), 7.82 (d, 1H, C$_{carb}$ CH), 8.0 (br, 2H, NH$_2$)
[(CO)$_5$Cr{C(OEt)CHCHPh}] ^{b} (VII)	1.67 (t, 3H, OCH$_2$CH$_3$), 5.03 (q, 2H, OCH$_2$CH$_3$), 6.80 (d, 1H, CHPh), 7.3 (m, 5H, Ph), 7.80 (d, 1H, C$_{carb}$ CH)
[(CO)$_4$$\overline{\text{Cr{S(CH}_2)_3\text{SC(OEt)C(OEt)CHCH}}}$}] (VIII)	1.27 (t, 3H, SCOCH$_2$CH$_3$), 1.37 (t, 3H, OCH$_2$CH$_3$), 2.3 (m, 2H, CH$_2$CH$_2$CH$_2$), 3.0 (m, 4H, CH$_2$CH$_2$CH$_2$), 3.90 (s, 1H, CHS), 3.92 (q, 2H, SCOCH$_2$), 4.00 (q, 2H, OCH$_2$), 4.65 (s, 1H, C=CH)
[(CO)$_4$$\overline{\text{Cr{N(Me)C(OEt)C(OEt)CHCHS(CH}_2)_3\text{S}}}$}] (IX)	1.35 (t, 6H, 2 × OCH$_2$CH$_3$), 2.1 (m, 2H, CH$_2$CH$_2$CH$_2$), 2.9 (m, 4H, CH$_2$CH$_2$CH$_2$), 3.8 (m, 5H, 2×OCH$_2$CH$_3$ and CHS), 4.72 (d, 1H, C=CH), 7.4 (br, 1H, NH)
[(CO)$_4$$\overline{\text{Cr{NHC(OEt)C(OEt)CHCHS(CH}_2)_3\text{S}}}$}] (X)	1.35 (t, 6H, 2×OCH$_2$CH$_3$), 2.1 (m, 2H, CH$_2$CH$_2$CH$_2$), 2.9 (m, 4H, CH$_2$CH$_2$CH$_2$), 3.8 (m, 5H, 2×OCH$_2$CH$_3$ and CHS), 4.72 (d, 1H, C=CH), 7.4 (br, 1H, NH)

^{a} Abbreviations: br, broad; d, doublet; m, multiplet; s, singlet; t, triplet; q, quartet. ^{b} Coupling constant, J(CHCH) 15 Hz. ^{c} Coupling constant, J(CHCH) 15.1 Hz.
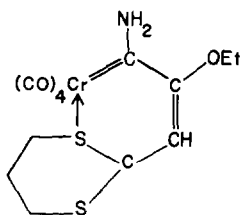
E

F

The deshielding effect of the O=C–OR moiety on H_β in **E** is larger than on H_α whereas the α-effect of the $(CO)_5M=C–OR$ unit in **F** is larger than any effect of the carbonyl carbon and also much larger than the β-effect which it exerts on H_β.

(b) Preparation of seven-membered chelates

Compound IIIa reacted at $-60\,^\circ\mathrm{C}$ with an equimolar amount of $MeNHNH_2$ to give

$\underline{V}$

red-brown, 68%

$\underline{VI}$

yellow, 84%

$\underline{III}$

SCHEME 2. Reagents: (i) LiBu; (ii) $[Et_3O][BF_4]$.

SCHEME 3. Reagents: (i) LiBu; (ii) ClCH(Ph)SPh.

SCHEME 4. Reagent: (i) MeNHNH$_2$.

$$M=C \begin{smallmatrix} NHNHPh \\ \\ R^2 \end{smallmatrix}$$

$M\leftarrow N\equiv CR^2$

57–86 %

$$M\leftarrow S\begin{smallmatrix} \\ C \\ R^1O \quad R^2 \end{smallmatrix}$$

5 %

$$M=C \begin{smallmatrix} OR^1 \\ \\ R^2 \end{smallmatrix}$$

v   vi   i   ii   iii   iv

$$M\leftarrow NH=C \begin{smallmatrix} NHMe \\ \\ R^2 \end{smallmatrix}$$

20 %

$$M\leftarrow NH=C \begin{smallmatrix} OR^1 \\ \\ R^2 \end{smallmatrix}$$

26–90 %

$$M\leftarrow N=C \begin{smallmatrix} Me \quad OR^1 \\ \\ R^2 \end{smallmatrix}$$

35–50 %

SCHEME 5. Hydrazines and carbenes: (i) MeNHNH$_2$, R^1 = Et, R^2 = part of chelate ring; (ii) MeNHNH$_2$, R^1 = Et, R^2 = part of chelate ring; (iii) MeNHNH$_2$ or Me$_2$NNH$_2$, R^1 = Et, R^2 = part of chelate ring; (iv) MeNHNH$_2$, R^1 = Et R^2 = part of chelate ring; (v) Me$_2$NNH$_2$, R^1 = Me, R^2 = Me; (vi) PhNHNH$_2$, R^1 = Et, R^2 = NHBu^t.

three yellow, crystalline products [(CO)$_4$Cr{S(CH$_2$)$_3$SC(OEt)C(OEt)=CHCH}] (VIII), [(CO)$_4$Cr{N(Me)=C(OEt)C(OEt)=CHCHS(CH$_2$)$_3$S}] (IX) and [(CO)$_4$Cr{NH=C(OEt)-C(OEt)=CHCHS(CH$_2$)$_3$S}] (X) (Scheme 4) in 5 to 35% yields. The hydrazine-catalysed formation of VIII involves an unusual carbene insertion into a single C–S bond and the coordination of this sulphur atom at the vacant site. Although spectral data (the molecular ion and loss of four CO groups were observed in the mass spectrometer; infrared and nuclear magnetic data are shown in Tables 1 and 2) and elemental analysis indicated that VIII was a rearrangement product of III, an X-ray crystallographic study was necessary to establish the detailed structure. The seven-membered chelates IX and X are respectively formed by formal NMe or NH insertion into the carbene bond. To obtain more structural information about such rare species, we also determined the crystal structure of IX.

Various routes by which coordinated carbenes may interact with hydrazines are shown in Scheme 5. Reactions (i) and (ii) were found exclusively with the six-membered carbene-thioether chelate described in this paper. Reaction (iii) was found with five-membered carbene-thioether chelates (A) and carbene-phosphines chelates (B) (vide supra), whereas the former species also afforded an amidine-thioether complex (see (iv)) when treated with McNHNH$_2$. Fischer and Aumann [12] reported the formation of a

nitrile compound (see (v)) via addition of the hydrazine, loss of HOR^1, and subsequent N–N bond cleavage. With the carbene complex [Cl$_2$(Bu^{t}NC)Pt{C(NHBu^t)OEt}], N–N bond breaking does not occur (see (vi)) [13]. Because loss of HOR^1 does not precede N–N bond cleavage, in most chelates the undesired rehybridization of the carbene carbon from sp^2 to sp, which then excludes N coordination, occurs only in the formation of minor by-products [3]. Hydrazines are protonated or alkylated by epoxides at the highest substituted nitrogen atom [14]. If the alkylating agent is bulky, the other nitrogen atom may be attacked. With six-membered chelates and MeNHNH$_2$, NH and NMe insertion occurred in equal proportions at $-60°$C. At $-80°$C only the NMe insertion product was formed, in 50% yield. From these results we conclude that steric factors only become unimportant enough to allow the substituted nitrogen of the hydrazine to attack the carbene carbon, in the case of six-membered chelates.

(c) The molecular structures of [(CO)$_4$Cr{$\overline{S(CH_2)_3}$$\overline{SC(OEt)C(OEt)=CHCH}$}] (VIII) and [(CO)$_4$Cr{$\overline{N(Me)=C(OEt)C(OEt)=CHCHS(CH_2)_3S}$}] (IX)

The structure of VIII contains monomeric units of the complex separated by Van der Waals distances. The chromium atom in the complex is approximately octahedrally coordinated by four carbonyl groups and a bidentate dithioether ligand (Fig. 1). The deviation from the idealised 90° angles about Cr ranges from 83.7(3)° for C(1)–Cr–C(3) (Table 3) to 97.1(2)° for S(2)–Cr–C(3). The average Cr–S separation (Table 3) of 2.424(2) Å agrees well with the average value of 2.419(3) Å in the complex [(CO)$_4$Cr{$\overline{S(Et)(CH_2)_2SEt}$}] [15] and with those for Cr–S bonds in other tetracarbonyl thioether complexes [16]. Each sulphur donor atom forms part of a five- and a
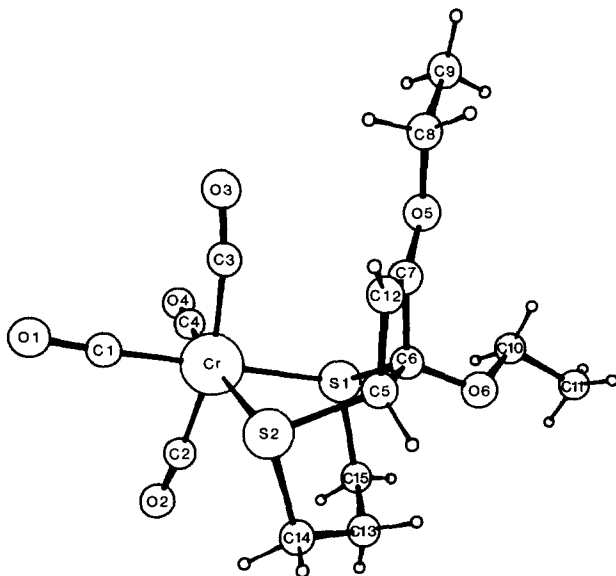

Fig. 1. A perspective view of a molecule of [(CO)$_4$Cr{$\overline{S(CH_2)_3}$$\overline{SC(OEt)C(OEt)=CHCH}$}] (VIII).

TABLE 3

BOND LENGTHS (Å) AND ANGLES (°) FOR COMPOUND VIII

Cr–S(1)	2.408(2)	S(2)–C(14)	1.849(9)
Cr–S(2)	2.441(2)	C(5)–C(6)	1.545(8)
Cr–C(1)	1.841(8)	C(5)–C(12)	1.503(10)
Cr–C(2)	1.876(8)	C(6)–C(7)	1.507(9)
Cr–C(3)	1.864(7)	C(6)–O(6)	1.387(7)
Cr–C(4)	1.840(8)	C(7)–C(12)	1.314(9)
C(1)–O(1)	1.150(9)	C(7)–O(5)	1.354(8)
C(2)–O(2)	1.143(9)	C(8)–C(9)	1.509(13)
C(3)–O(3)	1.161(9)	C(8)–O(5)	1.443(8)
C(4)–O(4)	1.155(10)	C(10)–C(11)	1.480(12)
S(1)–C(6)	1.841(6)	C(10)–O(6)	1.448(9)
S(1)–C(15)	1.842(8)	C(13)–C(14)	1.485(11)
S(2)–C(5)	1.831(7)	C(13)–C(15)	1.540(12)
S(1)–Cr–S(2)	79.1(1)	Cr–S–C(14)	105.7(3)
S(1)–Cr–C(2)	175.2(2)	C(6)–S(1)–C(15)	97.7(3)
S(1)–Cr–C(2)	95.1(2)	C(5)–C(2)–C(14)	98.0(3)
S(1)–Cr–C(3)	95.0(2)	S(1)–C(6)–C(5)	114.2(4)
S(1)–Cr–C(4)	93.4(2)	S(1)–C(15)–C(13)	115.7(5)
S(2)–Cr–C(1)	96.4(2)	S(2)–C(5)–C(6)	115.5(4)
S(2)–Cr–C(2)	92.6(3)	C(6)–C(5)–C(12)	87.0(5)
S(2)–Cr–C(3)	97.1(2)	S(2)–C(5)–C(12)	113.7(5)
S(2)–Cr–C(4)	172.5(2)	S(2)–C(14)–C(13)	114.9(7)
C(1)–Cr–C(2)	86.7(3)	C(7)–O(5)–C(8)	133.2(5)
C(1)–Cr–C(3)	83.7(3)	C(6)–O(6)–C(10)	115.0(5)
C(1)–Cr–C(4)	91.0(3)	C(7)–C(6)–O(6)	116.3(5)
C(2)–Cr–C(3)	167.1(3)	C(5)–C(6)–O(6)	113.1(5)
C(2)–Cr–C(4)	87.3(3)	C(5)–C(6)–C(7)	84.1(4)
C(3)–Cr–C(4)	84.2(3)	C(6)–C(7)–C(12)	95.9(6)
Cr–C(1)–O(1)	177.5(8)	C(6)–C(7)–O(5)	127.1(5)
Cr–C(2)–O(2)	174.1(8)	C(12)–C(7)–O(5)	136.9(6)
Cr–C(3)–O(3)	171.0(6)	C(9)–C(8)–O(5)	108.3(6)
Cr–C(4)–O(4)	177.9(6)	C(11)–C(10)–O(6)	109.9(7)
Cr–S(1)–C(6)	105.2(2)	C(5)–C(12)–C(7)	92.8(5)
Cr–S(1)–C(15)	107.7(3)	C(14)–C(13)–C(15)	120.6(8)
Cr–S(2)–C(5)	105.1(2)		

six-membered ring; the latter ring having a chair conformation. The two carbon atoms of the former ring also form part of a substituted cyclobutene ring. As expected [15], the metal–carbonyl distances are shorter for the *trans* CO (av. 1.841(8) Å) than for the *cis* CO ligands, (av. 1.870(8) Å).

The two *cis* CO ligands are significantly bent away from the chelate ring and the C(2)–Cr–C(3) angle is 167.1(3)°. The dimensions of the butene ring are very similar to those reported for cyclobutene [17]. The length of the C(7)–C(12) double bond is 1.314(9) Å, compared to 1.325(46) Å in the parent ring system, and the average single bond is 1.505(10) Å, compared with 1.537(10) Å. The angles about the carbon atoms

with the highest p-character vary between 84.1(4) and 87.3(3)°, and the C=C–C angles between 92.8(5) and 95.9(6)° (angle in cyclobutene 94.0(8)°).

Relatively high R-factors (R 9.4, R_w 6.1%) for IX preclude detailed comparison of structural parameters with similar structures. Only the most important features of structure IX (Fig. 2) are compared with those for the six-membered chelate [(CO)$_4$-Cr{NH=C(OEt)C(OEt)=CS(CH$_2$)$_3$S}] (G) which have previously been discussed in detail [18], in order to establish structural trends which are as follows: (i) The N–Cr–S angle in the seven-membered chelate (91.7(4)°, Table 4) is larger than in the six-mem-

TABLE 4

BOND LENGTHS (Å) AND ANGLES (°) FOR COMPOUND IX

Cr–C(1)	1.887(21)	S(1)–C(13)	1.843(18)
Cr–C(2)	1.729(21)	S(1)–C(16)	1.800(17)
Cr–C(3)	1.903(23)	S(2)–C(13)	1.787(16)
Cr–C(4)	1.821(21)	S(2)–C(14)	1.783(20)
Cr–S(1)	2.433(5)	N–C(5)	1.471(18)
Cr–N	2.133(15)	N–C(6)	1.331(21)
C(1)–O(1)	1.156(19)	C(6)–C(9)	1.451(22)
C(2)–O(2)	1.170(19)	C(7)–C(8)	1.479(22)
C(3)–O(3)	1.137(21)	C(10)–C(11)	1.479(22)
C(4)–O(4)	1.146(20)	C(9)–C(12)	1.351(24)
O(5)–C(6)	1.329(19)	C(12)–C(13)	1.458(24)
O(5)–C(7)	1.423(18)	C(14)–C(15)	1.493(24)
O(6)–C(9)	1.372(19)	C(15)–C(16)	1.523(22)
O(6)–C(10)	1.400(18)		
C(1)–Cr–C(2)	88.3(8)	Cr–N–C(6)	128.4(14)
C(1)–Cr–C(3)	169.2(10)	O(5)–C(7)–C(8)	106.9(15)
C(1)–Cr–C(4)	82.2(9)	O(5)–C(6)–C(9)	117.0(19)
C(1)–Cr–S(1)	93.9(6)	O(5)–C(6)–N	120.7(18)
C(1)–Cr–N	96.2(8)	O(6)–C(10)–C(11)	110.1(17)
C(2)–Cr–C(3)	87.0(9)	O(6)–C(9)–C(6)	112.0(16)
C(2)–Cr–C(4)	88.3(8)	O(6)–C(9)–C(12)	127.1(17)
C(2)–Cr–S(1)	176.4(6)	S(1)–C(16)–C(15)	112.2(13)
C(2)–Cr–N	90.9(7)	S(1)–C(13)–S(2)	111.3(10)
C(3)–Cr–C(4)	87.9(10)	S(1)–C(13)–C(12)	108.2(13)
C(3)–Cr–S(1)	90.4(7)	S(2)–C(14)–C(15)	114.7(15)
C(3)–Cr–N	93.6(9)	S(2)–C(13)–C(12)	110.5(13)
C(4)–Cr–S(1)	89.2(6)	N–C(6)–C(9)	122.1(18)
C(4)–Cr–N	178.2(8)	C(6)–C(9)–C(12)	120.8(18)
S(1)–Cr–N	91.7(4)	C(9)–C(12)–C(13)	124.2(17)
O(4)–C(4)–Cr	175.6(20)	C(13)–S(2)–C(14)	98.9(9)
O(2)–C(2)–Cr	177.1(18)	C(13)–S(1)–C(6)	97.5(9)
O(1)–C(1)–Cr	173.5(19)	C(16)–C(15)–C(14)	114.4(17)
O(3)–C(3)–Cr	164.0(24)	C(5)–N–C(6)	113.5(15)
Cr–S(1)–C(16)	112.1(7)	C(6)–O(5)–C(7)	120.9(15)
Cr–S(1)–C(13)	107.7(6)	C(9)–O(6)–C(10)	117.8(14)
Cr–N–C(5)	117.8(12)		
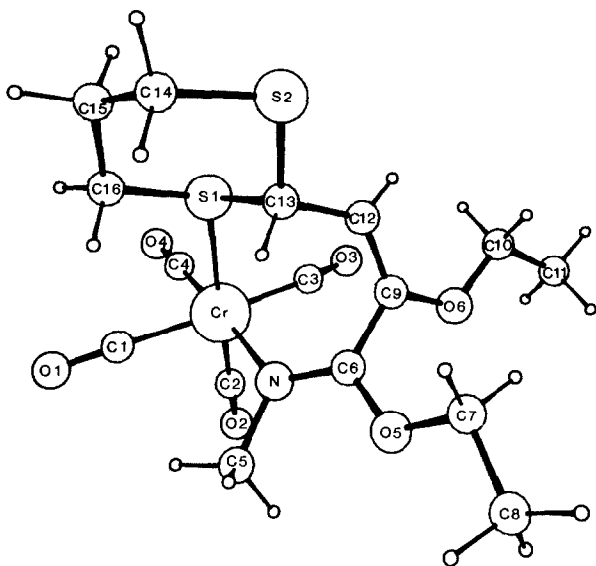
Fig. 2. A perspective view of a molecule of [(CO)₄Cr{N(Me)=C(OEt)C(OEt)=CHCHS(CH₂)₃S}] (IX).

bered chelate (84.9(1)°) although the C–N–Cr and C(ring)–S–Cr angles (117.8(12) and 107.7(6)°) are smaller than in **G** (134.4(4) and 110.6(2)°, respectively); (ii) The methyl group attached to the nitrogen atom in the new compound may be responsible for the larger deviations from linearity of the two *cis* carbonyls (169.2(10) vs. 176.9(3)°); (iii) The *cis* carbonyl ligands are further from the metal (av. 1.895(22) Å, Table 4) than the carbonyl *trans* to the heteroatoms (av. 1.775(31) Å; in **G**: *cis*, 1.889(2) Å; *trans*, 1.828(3) Å); (iv) Cr–S and Cr–N separations of 2.433(5) and 2.133(15) Å in IX compare with 2.392(2) and 2.095(5) Å, respectively in **G**; (v) The new chelate rings contain one sp^3 carbon atom (angle S(1)–C(13)–C(12) 108(1)°) and three sp^2 carbons (124(1), 120(1), 126(1)°), whereas all three carbons in **G** are sp^2 hybridized, with angles between 122(1) and 127(1)°.

Experimental

All manipulations were carried out under purified nitrogen using Schlenk-techniques [19]. Solvents were dried and distilled under nitrogen before use. [(CO)₅M{C(OEt)Me}] (M = Cr or W) [20], [Et₃O][BF₄] [21], ClCHS(CH₂)₃S [22] and ClCH(SPh)Ph [23] were prepared by published methods and stored under nitrogen. Commercial starting materials were not purified before use. Column chromatography was carried out with silica gel (60 mesh, particle size 0.063–0.200 mm, Merck) as stationary phase at −10°C. IR spectra were measured on a Perkin–Elmer 297 spectrometer, ¹H and NMR spectra on a Varian T60 instrument with SiMe₄ as internal standard and CDCl₃ as solvent. Mass spectra, which showed the molecular ions as well indicated the number of coordinated carbonyl groups, were determined on a Hitachi–Perkin–Elmer RMU-6H mass spec-

trometer (at 70 eV). Elemental analyses were carried out by Mikroanalytische Laboratory, Bonn. Melting points (Kofler hot-stage) are uncorrected.

(a) Preparation of precursor complexes and their reaction with LiBu and [Et₃O][BF₄]

LiBu (10.9 mmol) in hexane was added dropwise to a cooled ($-60°$C) solution (10 ml) of [(CO)₅Cr{C(OEt)Me}] (2.90 g, 10.9 mmol in THF), and the mixture was stirred for 5 min then ClCHS(CH₂)₃S (1.69 g, 11 mol) in 15 ml THF was added slowly. The solvent was removed under reduced pressure at 0°C and the residue dissolved in 50 ml CH₂Cl₂. The solution was filtered through SiO₂ (0°C) then evaporated, and the residue was chromatographed with hexane/CH₂Cl₂ (2/1) as eluant. The first yellow fraction contained some starting material and was discarded. The second orange fraction was concentrated and recrystallized from ether/hexane (1/2) at $-30°$C. Yellow needle-like air stable crystals (2.50 g, 60%) of I were filtered off and dried in vacuo. M.p. 75–77°C. Anal. Found: C, 40.70; H, 3.75; S, 16.98. CrC₁₃H₁₄O₆S₂ calcd.: C, 40.84; H, 3.69; S, 16.77%.

Compound II was prepared similarly from 4.22 g (12 mmol) [(CO)₅W{C(OEt)Me}]; 1.10 g (18%) of yellow-orange crystals were obtained. M.p. 79–81°C. Anal. Found: C, 30.12; H, 3.08; S, 12.35. WC₁₃H₁₄O₆S₂ calcd.: C, 30.37; H, 2.74; S, 12.47%.

Reaction of LiBu (6.3 mmol) with 2.40 g (6.30 mmol) I in 100 ml ether at $-60°$C produced a yellow precipitate, which dissolved, to give a red solution when the mixture was allowed to warm slowly to room temperature (22°C). After removal of the solvent under vacuum, the residue was dissolved in CH₂Cl₂ (20 ml) and alkylated with [Et₃O][BF₄], with monitoring by TLC, which indicated the formation of one brown product. Column chromatography (hexane/CH₂Cl₂; 4/1) yielded two brown oils. The less polar compound IIIa (1.55 g, ca. 60%) was more stable than the second product IIIb (0.52 g, ca. 20%), and was used as isolated in further reactions. The oils were characterized spectroscopically (Table 1 and 2). When ammonia was bubbled for 5 min through an ether solution of IIIa (0.50 g, 1.2 mmol), removal of the solvent and recrystallization of the residue from ether/hexane (1/5) yielded red-brown crystals of V (10.4 g, ca. 88%). M.p. 110°C (with decomp.) Anal. Found: C, 40.77; H, 4.06; N, 3.74. CrC₁₃H₁₅NO₅S₂ calcd.: C, 40.94; H, 3.96; N, 3.67%.

When [(CO)₅W{C(OEt)CH₂CHS(CH₂)₃S}] (II) (1.00 g, 1.9 mmol) was treated in the way described for I above only 0.60 g (ca. 57%) of IV was obtained as an orange-red oil. Treatment with NH₃, similar to that of IIIa, afforded yellow crystals of VI (0.32 g, ca. 84%). M.p. 64–65°C. Anal. Found: C, 30.05; H, 3.11; N, 3.01. WC₁₃H₁₅NO₅S₂ calcd.: C, 30.42; H, 2.95; N, 2.73%.

(b) Preparation of the vinylcarbene complex VII

[(CO)₅Cr{C(OEt)Me}] (3.73 g, 14.0 mmol) was deprotonated with an equimolar amount of LiBu ($-78°$C) in THF and the mixture treated with a suspension of 14 mmol ClCH(SPh)Ph and 14 mmol LiI in 10 ml THF (0°C). After 10 min stirring at 0°C, filtration through SiO₂ and washing with THF the dark red mixture was transferred to a SiO₂ column, and elution with hexane gave a clear red fraction. Concentration in vacuo, followed by recrystallization from ether/hexane ($-30°$C), yielded 1.55 g (31%) of (VII)

as red crystals. M.p. 92–93° C. Anal. Found: C, 54.51; H, 3.50. $CrC_{16}H_{12}O_6$ calcd.: C, 54.56; H, 3.43%.

(c) Preparation of compound VIII and the seven-membered chelates IX and X

Methylhydrazine (0.13 ml, 2.4 mmol) was added to a cooled ($-60°$ C) ether solution of III (1.0 g, 2.4 mmol). As the temperature rose to room temperature the mixture darkened. A column chromatographic separation (hexane/ether; 5/3) yielded three yellow products, which were recrystallized from ether/hexane ($-30°$ C).

TABLE 5

CRYSTALLOGRAPHIC DATA FOR THE COMPOUNDS [(CO)$_4$Cr{S̄(CH$_2$)$_3$S̄C(OEt)C(OEt)=CHCH}] (VIII) AND [(CO)$_4$Cr{N̄(Me)=C(OEt)C(OEt)=CHCHS̄(CH$_2$)$_3$S}] (IX)

	VIII	IX
Unit cell parameters		
Crystal system	triclinic	monoclinic
Space group	$P1$	$P2_1/c$
a (Å)	10.10(1)	9.23(1)
b (Å)	10.20(1)	10.60(1)
c (Å)	9.28(1)	21.57(2)
α (°)	105.8(1)	
β (°)	92.9(1)	101.2(3)
γ (°)	95.3(1)	
V (Å^3)	913.4	2058.5
Formula	$C_{15}H_{18}O_6S_2Cr$	$C_{16}H_{21}NO_6S_2Cr$
Molecular wt	410.42	439.46
Z	2	4
D(calc) (g cm^{-3})	1.59	1.41
μ(Mo-K_α)	8.21	7.23
Data collection		
Diffractometer	Philips PW 1100	
Radiation	Mo-K_α (λ 0.7107 Å)	
Crystal size (mm^3)	0.1 × 0.05 × 0.05	0.08 × 0.05 × 0.05
Reflections measured ($\theta \leq 23°$)	2566	3090
"Unobserved" reflections, $I < 2\sigma$	538	1566
Scan type	$\omega - 2\theta$	$\omega - 2\theta$
Scan width (°θ)	1.8	1.0
Scan speed (°θ s^{-1})	0.072	0.038
Standards 3 measured every 60 min, no significant drift observed		
Refinement		
Least-squares matrix	blocked	full
Weights	$(\sigma(F))^{-2}$	$(\sigma(F))^{-2}$
Reflections used	2474	1513
Weighted $R(R_w)$	0.067	0.061
R	0.083	0.094

VIII. Yield: 0.05 g (5%). M.p. 105°C (dec.). Anal. Found: C, 53.73; H, 4.51. $CrC_{15}H_{18}O_6S_2$ calcd.: C, 43.90; H, 4.42%.

IX. Yield: 0.37 g (35%). M.p. 120°C (dec.). Anal. Found: C, 43.76; H, 4.93; N, 3.41. $CrC_{16}H_{21}NO_6S_2$ calcd.: C, 43.73; H, 4.82; N, 3.19%.

X. Yield: 0.27 g (26%). M.p. 130°C (dec.). Anal. Found: C, 42.56; H, 4.67; N, 3.50. $CrC_{15}H_{19}NO_6S_2$ calcd.: C, 42.35; H, 4.50; N, 3.29%.

Repeating the reaction at $-80°C$ yielded only compound IX (50%)

(d) Structure determinations

The crystal structures were determined by the heavy-atom method. No absorption corrections were applied to either data set. Details of the crystal data, data collection, and structure refinement are listed in Table 5. All non-hydrogen atoms were refined anisotropically. In compound VIII all hydrogens, except H(15), were refined individually, but in IX all hydrogens were placed and refined in calculated positions. All calculations were carried out with the SHELX-76 [24] program. The atomic coordinates for non-hydrogen atoms are shown in Tables 6 and 7.

TABLE 6

FRACTIONAL COORDINATES ($\times 10^4$) FOR THE NON-HYDROGEN ATOMS IN COMPLEX VIII

Atom	x	y	z	U_{11}
Cr	8341(1)	2393(1)	2128(1)	392(7)
S(1)	7176(2)	3221(2)	4340(2)	434(11)
S(2)	7367(2)	238(2)	2498(2)	495(11)
O(1)	9616(6)	1179(6)	−697(6)	990(47)
O(2)	10999(5)	2366(7)	3745(7)	470(36)
O(3)	6264(5)	2716(5)	−164(6)	602(35)
O(4)	9398(5)	5227(6)	2101(7)	649(37)
C(1)	9139(7)	1626(7)	404(9)	590(52)
C(2)	9960(7)	2337(8)	3180(8)	420(47)
C(3)	6981(6)	2583(6)	791(8)	334(40)
C(4)	6987(6)	4127(8)	2083(8)	330(41)
O(5)	4056(4)	3109(4)	2458(4)	468(28)
O(6)	4998(4)	2205(4)	5364(4)	550(29)
C(5)	5724(6)	581(7)	3165(7)	440(41)
C(6)	5601(6)	2083(6)	4031(6)	478(41)
C(7)	4700(6)	2066(7)	2679(7)	342(38)
C(8)	3147(8)	2710(8)	1126(8)	463(47)
C(9)	2476(9)	3944(9)	1016(10)	595(58)
C(10)	4411(9)	3471(8)	5928(8)	687(60)
C(11)	3932(10)	3545(9)	7426(9)	843(70)
C(12)	4742(6)	765(7)	1983(7)	386(41)
C(13)	7782(9)	1085(9)	5652(9)	627(62)
C(14)	8192(8)	127(8)	4277(9)	569(54)
C(15)	7957(8)	2643(8)	5861(8)	584(55)

TABLE 7

FRACTIONAL COORDINATES ($\times 10^4$) FOR THE NON-HYDROGEN ATOMS IN COMPLEX IX

Atom	x	y	z	U_{11}
Cr	−1200(2)	5425(2)	3284(1)	445(13)
S(1)	1265(3)	6077(3)	3805(2)	413(21)
S(2)	2897(4)	8281(4)	4481(2)	397(21)
O(5)	−2755(9)	9244(8)	3511(4)	482(58)
O(6)	−2466(8)	7859(9)	4660(4)	337(52)
O(1)	−276(11)	2740(9)	3353(5)	1064(86)
O(2)	−4184(10)	4462(10)	2728(5)	571(67)
O(3)	−465(11)	5126(9)	1979(4)	1293(95)
O(4)	−2108(13)	4798(10)	4516(5)	1524(108)
N(1)	−1944(10)	7333(9)	3188(5)	381(63)
C(1)	−696(13)	5304(13)	2480(6)	491(85)
C(2)	−3011(15)	4868(11)	2937(6)	652(102)
C(3)	−1751(17)	5211(17)	4083(7)	753(115)
C(4)	−579(16)	3790(13)	3340(7)	747(112)
C(13)	1138(12)	7713(12)	4080(6)	343(74)
C(6)	−2011(13)	8172(13)	3641(7)	330(83)
C(8)	−3413(16)	11344(13)	3622(7)	975(130)
C(7)	−2427(15)	10314(13)	3912(6)	964(119)
C(5)	−2601(14)	7786(12)	2551(5)	719(95)
C(9)	−1394(14)	7918(12)	4301(6)	396(83)
C(10)	−2011(14)	7702(14)	5313(6)	627(99)
C(12)	74(16)	7743(13)	4498(6)	647(106)
C(14)	3866(13)	8202(14)	3843(7)	400(88)
C(15)	3939(13)	6917(15)	3568(6)	422(92)
C(16)	2448(14)	6381(14)	3249(6)	743(109)
C(11)	−3311(15)	7682(20)	5621(7)	676(119)

ORTEP [25] representations of the structures are shown in Figs. 1 and 2. Lists of thermal parameters and observed and calculated structure factors are available from the authors (G.J.K.) on request.

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