

SULPHUR-CONTAINING METAL COMPLEXES

I. REACTIONS OF PENTACARBONYL(CARBENE) COMPLEXES WITH DIALKYL SULPHIDES

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Summary

The sulphides SR^1R^2 ($R^1 = C_2H_5$; $R^2 = C_2H_5, CH_2Ph$) react with the carbene complexes $[(CO)_5CrC(OC_2H_5)R]$ ($R = Bu, Ph$), to produce the neutral pentacarbonyl(thio)chromium(0) complexes $[(CO)_5CrSR^1R^2]$, which have been characterized by chemical analysis, IR, NMR and mass spectra. Confirmation of the structures of the new complexes comes from a single-crystal X-ray study of $(CO)_5CrS(C_2H_5)CH_2Ph$, the first such study of a pentacarbonyl(dialkylthio)-metal complex.

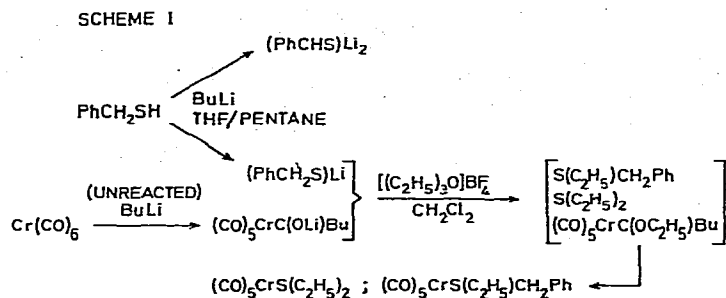
Introduction

During the course of a preliminary study [1] of the reactivity of the dilithium dianion, $Li_2(SCHC_6H_5)$ [2], towards hexacarbonylchromium, the compounds pentacarbonyl(butylethoxycarbene)chromium(0) [3], pentacarbonyl(ethylthioethyl)chromium(0) and pentacarbonyl(ethylbenzylthio)chromium(0) were isolated, pure but in low yield from the reaction mixture after alkylation with Meerwein's reagent, $[(C_2H_5)_3O]BF_4$. We suggest that these compounds are formed by reaction of carbene complexes with neutral sulphides present in the final solution, as set out in Scheme 1.

This scheme suggested the possibility of synthesizing neutral sulphur-donor-ligand complexes via carbene substitution, which was further investigated. Reactions of phosphines with pentacarbonyl(carbene)metal complexes are known. It can lead to either carbonyl or both carbonyl and carbene substitution, depending on the basicity of the phosphine [4–7]. At low temperatures, ylide complexes

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are formed [8]. There are no reports of reactions of carbene complexes with dialkyl sulphides. Furthermore, very little is known about pentacarbonyl sulphide complexes of Group VI metals and very few non-photochemical synthetic routes towards these complexes are available. Recently Fischer and Kreis [9] described an addition and rearrangement reaction of chromium and tungsten thiocarbenes leading to pentacarbonyl(1-bromoethyl) methyl sulphide complexes, but these were unstable oils at room temperature and so not suitable for crystal structure determinations. Although the method of Connor and Hudson [10] produced pentacarbonyl(thio)metal complexes, those containing chromium could generally not be isolated in pure form. The crystal structure of a pentacarbonylchromium phosphine sulphide complex, $(\text{CO})_5\text{CrSP}(\text{CH}_3)_3$, has been reported by Baker and Reay [11].

In this paper we wish to report the reaction and products obtained when diethyl sulphide or ethyl benzyl sulphide is treated with pentacarbonyl(butylethoxycarbene) or pentacarbonyl(phenylethoxycarbene)chromium(0), corresponding to the final step in the proposed scheme.

Experimental

General

All preparations were carried out under an atmosphere of purified nitrogen. Solvents were carefully dried and freshly distilled under nitrogen before use. Commercially available ligands were used without purification.

Microanalyses were carried out by F. Pascher and E. Pascher, Microanalytical Laboratory, Bonn. Infrared spectra were recorded on a Perkin-Elmer 257 instrument. Each spectrum was calibrated using the band at 1871 cm^{-1} of polystyrene film. ^1H NMR spectra were recorded on either a Varian HA100 spectrometer operating at 100 MHz, or a Varian T60 at 60 MHz. Mass spectra were recorded on a Varian CH4 instrument and electronic spectra on a calibrated Shimadzu double-beam spectrophotometer.

Reaction of diethyl sulphide with pentacarbonyl(butylethoxycarbene)chromium(0)

1.5 g (5 mmol) $(\text{CO})_5\text{CrC}(\text{OC}_2\text{H}_5)\text{Bu}$ [3] and 0.9 g (10 mmol) $\text{S}(\text{C}_2\text{H}_5)_2$ were dissolved in 20 ml hexane and the solution was refluxed for 15 h. Volatile material was then removed in vacuo (40°C) and the residue chromatographed on a silica gel column. Elution with hexane (-10°C) gave firstly the unreacted carbene complex, and, secondly, a yellow zone which was concentrated and stripped of solvent under high vacuum (0°C) to give 0.63 g (2.2 mmol, 44%)

of a yellow oil, pentacarbonyl(ethylthioethyl)chromium(0). The compound is soluble in a variety of polar and non-polar organic solvents. It is stable under nitrogen at -30°C , but unstable in air. (Found: C, 38.43; H, 3.51; Cr, 18.21; O, 28.55; S, 11.23. Mol. wt. 282 (mass spec.). $\text{C}_9\text{H}_{10}\text{CrO}_5\text{S}$ calcd.: C, 38.30; H, 3.57; Cr, 18.42; O, 28.34; S, 11.36%. Mol. wt. 282.23). In addition to the molecular-ion peak, the mass spectrum shows fragment ions at m/e -values corresponding to consecutive losses of five CO groups.

Reaction of ethyl benzyl sulphide with pentacarbonyl(phenylethoxycarbene)-chromium(0)

3.3 g (10 mmol) $(\text{CO})_5\text{CrC}(\text{OC}_2\text{H}_5)\text{Ph}$ [12] and 3.0 g (20 mmol) $\text{S}(\text{C}_2\text{H}_5)\text{CH}_2\text{Ph}$ dissolved in pentane, were magnetically stirred at room temperature for 20 h. Volatile material was removed in vacuo (90°C) and the viscous residue chromatographed on a silica gel packed column. Elution with pentane (-10°C) gave first a red zone containing unreacted carbene complex and then a yellow zone which was concentrated and further purified by preparative TLC ($\text{CH}_2\text{Cl}_2/\text{pentane}$, 1 : 4). Removal of the solvent under high vacuum gave 0.56 g (1.9 mmol, 19%) analytically pure yellow crystals of pentacarbonyl(ethylbenzylthio)chromium(0), m.p. $64-66^{\circ}\text{C}$. The compound is soluble in all the common organic solvents. It is stable in air. (Found: C, 48.87; H, 3.45; Cr, 14.89; O, 23.30; S, 9.26. Mol. wt. 344 (mass spec.). $\text{C}_{14}\text{H}_{12}\text{CrO}_5\text{S}$ calcd.: C, 48.83; H, 3.52; Cr, 15.10; O, 23.23; S, 9.29%. Mol. wt. 344.3). In addition to the molecular ion peak, the mass spectrum showed fragment ions at m/e -values corresponding to consecutive losses of five CO groups.

Structure determination

Well-shaped single crystals of $(\text{CO})_5\text{CrS}(\text{C}_2\text{H}_5)\text{CH}_2\text{Ph}$, suitable for diffraction studies, were obtained from pentane solution (-30°C). Weissenberg and precession photographs of a crystal mounted along [010], yielded the space group and approximate cell constants. Improved cell constants were obtained from measurements on a Stoe two-circle diffractometer with Mo-K_α radiation from a graphite-crystal incident-beam monochromator.

Crystallographic data: monoclinic, space group $P2_1/c$; unit cell dimensions, $a = 9.70(1)$, $b = 19.11(1)$, $c = 9.92(1)$ Å; $\beta = 122.9(1)^{\circ}$, $V = 1545$ Å³. Four molecules in the unit cell ($Z = 4$); $D_{\text{calcd}} = 1.480$ g cm⁻³; $D_{\text{obs}} = 1.482$ g cm⁻³. Mo-K_α radiation, $\lambda = 0.71069$ Å; $\mu(\text{Mo-K}_\alpha) = 8.27$.

The intensities of 1128 independent reflections ($2\theta < 55^{\circ}$) were measured on the Stoe instrument at an ω -scan rate of 1 sec per 0.02° . Standard reflections measured at regular intervals gave no indication of crystal deterioration.

The atomic coordinates of the chromium and sulphur atoms were obtained from a three-dimensional Patterson synthesis. The structure was solved (for non-hydrogen atoms) by successive difference Fourier syntheses and refined by full matrix anisotropic least-squares. At the termination of refinement when all parameter shifts were less than 0.1 e.s.d., R 0.082.

To eliminate any possible errors arising from layer-line scaling, another crystal was mounted along [100] and 615 independent reflections were recorded. The two sets of data were merged and the structure refined as before, R 0.097. The two refinements yielded similar results and only those structural parameters

obtained with the larger data set, are considered.

Most of the crystallographic calculations were carried out with the SHELX set of programs written by Dr. G.M. Sheldrick on an IBM 370/115 computer. Thermal ellipsoids and stereo pairs were drawn by ORTEP [13] on an IBM 370/165 machine.

Results and discussion

The two complexes $(\text{CO})_5\text{CrS}(\text{C}_2\text{H}_5)_2$ and $(\text{CO})_5\text{CrS}(\text{C}_2\text{H}_5)\text{CH}_2\text{Ph}$ produced by the substitution of two different carbene ligands, were obtained in fairly low yields (44 and 19% respectively). We are at present investigating the effects of the carbene ligand, sulphide ligand, temperature and possible carbonyl labilization on the substitution rate in this class of reaction.

The number, position and intensity of the IR bands of the two sulphide complexes (Table 1) indicate octahedral structures. The frequencies are much the same as those reported for $(\text{CO})_5\text{CrS}(\text{CH}_3)\text{CHBrCH}_3$ [9]. Different force constants, calculated by means of the Cotton-Kraihanzel force-field technique [14] and presented in Table 1 as well as qualitative σ and π bonding parameters derived therefrom according to Graham's approach [15] in Table 2, suggest a $\sigma(\text{donor})/\pi(\text{acceptor})$ ratio for dialkyl sulphides between that for phosphines (such as $\text{P}(\text{Ph})_3$ [3,14]) and amines (such as $\text{NH}_2\text{C}_6\text{H}_{11}$ [3]). This is also supported by an interpretation of the electronic spectra, *vide infra*. The different constants and parameters obtained from published IR frequencies for the phosphine sulphide complex, $(\text{CO})_5\text{CrSP}(\text{CH}_3)_3$ [16], reveal an insignificant π interaction for the ligand $\text{SP}(\text{CH}_3)_3$ which is in line with previous findings of Cotton and Zingales [17] concerning the smaller tendency of bivalent sulphur ligands compared to dialkyl sulphides to function as π acceptors.

Three regions of electronic absorption were observed for each of the two sulphide complexes (Table 1) at ca 33000 cm^{-1} , 32500 cm^{-1} and 25300 cm^{-1} . The latter, practically free from ligand interference, can be assigned to a $d-d(x^2-y^2 \leftarrow xy, yz)$ transition and is sensitive to the bonding characteristics of the non-carbonyl ligand, L, in $(\text{CO})_5\text{CrL}$ complexes [18]. The energy of this transition should increase with an increasing $\sigma(\text{donor})/\pi(\text{acceptor})$ ratio of L. According to the position of their absorption maxima, the two sulphide ligands fit in between phosphines and amines ($\nu(d-d)$ $(\text{CO})_5\text{Cr}(\text{phosphine}) > 27000\text{ cm}^{-1}$; $\nu(d-d)$ $(\text{CO})_5\text{Cr}(\text{amine}) < 24000\text{ cm}^{-1}$ [18]).

All the bands in the proton NMR spectra are completely resolved for the free and coordinated ligands (Table 3). The electron loss on coordination is clearly shown and may even be reflected in the downfield shift for the phenyl ring-proton singlet of the coordinated ethyl benzyl sulphide ligand compared to the free ligand.

The formation of sulphide complexes is confirmed by the single-crystal structure determination of the air-stable compound. The crystals are built up from discrete $(\text{CO})_5\text{CrS}(\text{C}_2\text{H}_5)\text{CH}_2\text{Ph}$ molecules. Fig. 1 shows the molecular structure and the atom labelling scheme. Fig. 2 gives a stereoscopic view. The final atomic and thermal parameters are given in Table 4 and calculated bond lengths and bond angles in Table 5. Copies of a list of structure factors may be obtained from the authors.

(continued on p. 151)

TABLE 1
INFRARED AND ELECTRONIC SPECTROSCOPIC DATA ^a

Compound	$\nu(\text{CO})$ (cm^{-1})	Infrared force constants			Electronic	
		k_1	k_2	k_i ^c	ν (cm^{-1})	$10^{-3} \times \epsilon_{\text{max}}$ ^d
$(\text{CO})_5\text{CrS}(\text{C}_2\text{H}_5)_2$	2070 m (A_1^1)	15.28	15.81	0.32	32637	1.70
	1978 w (B)				32258	
	1938 (vs) (E_2)				25407	
	1930 (sh) (A_1^2)					
$(\text{CO})_5\text{CrS}(\text{C}_2\text{H}_5)\text{CH}_2\text{Ph}$	2068 m (A_1^1)	15.29	15.84	0.31	33389	1.50
	1986 w (B)				32841	
	1941 vs (E_2)				25253	
	1933 sh (A_1^2)					
$(\text{CO})_5\text{CrSP}(\text{CH}_3)_3$	2062 m ^b	15.17	15.85	0.29		
	1984 m					
	1944 s					
	1927 s					

^a Measured in hexane unless otherwise noted. ^b IR frequencies measured in cyclohexane, were taken from [16]. An "anomalous" band at 1909 cm^{-1} was ignored in the calculations. ^c $\text{mdyn } \text{\AA}^{-1}$. ^d $\text{mol}^{-1} \text{cm}^{-1}$.

TABLE 2
 σ - AND π -BONDING PARAMETERS FOR $(\text{CO})_5\text{Cr}$ (SULPHIDE) COMPLEXES

Compound	Δk_1	Δk_2	σ	π
$(\text{CO})_5\text{CrS}(\text{C}_2\text{H}_5)_2$	0.20	0.04	-0.12	0.16
$(\text{CO})_5\text{CrS}(\text{C}_2\text{H}_5)\text{CH}_2\text{Ph}$	0.21	0.07	-0.07	0.14
$(\text{CO})_5\text{CrSP}(\text{CH}_3)_3$	0.09	0.08	0.07	0.01
$(\text{CO})_5\text{CrNH}_2(\text{C}_6\text{H}_{11})$ ^a	0.00	0.00	0.00	0.00

^a Reference compound. Force constants of $k_1 = 15.08$ and $k_2 = 15.77$ taken from [3].

TABLE 3
PROTON NMR SPECTRA OF SULPHIDE COMPLEXES AND FREE LIGANDS ^a

Compound	$\tau(\text{SCH}_2\text{CH}_3)$	$\tau(\text{SCH}_2\text{CH}_3)$	$\tau(\text{SCH}_2\text{C}_6\text{H}_5)$	$\tau(\text{C}_6\text{H}_5)$
$\text{S}(\text{C}_2\text{H}_5)_2$	7.44 (q, 2)	8.73 (t, 3)		
$(\text{CO})_5\text{CrS}(\text{C}_2\text{H}_5)_2$	7.36 (q, 2)	8.67 (t, 3)		
$\text{S}(\text{C}_2\text{H}_5)\text{CH}_2\text{C}_6\text{H}_5$	7.71 (q, 2)	8.90 (t, 3)	6.42 (s, 2)	2.83 (s, 5)
$(\text{CO})_5\text{CrS}(\text{C}_2\text{H}_5)\text{CH}_2\text{C}_6\text{H}_5$	7.40 (q, 2)	8.71 (t, 3)	6.18 (s, 2)	2.66 (s, 5)

^a CDCl_3 solutions. τ values relative to internal TMS. Abbreviations: s, singlet; t, triplet; q, quartet. Number of protons in brackets.

TABLE 4

FINAL REFINED ATOMIC COORDINATES AND THERMAL PARAMETERS^a FOR (CO)₅CHS(C₂H₅)CH₂Ph

The atomic coordinates have been multiplied by 10⁴. The u_{ij} coefficients are from the expression $T = \exp[-2\pi^2(h^2a^*u_{11} + k^2b^*u_{22} + l^2c^*u_{33} + hka^*b^*u_{12} + hla^*c^*u_{13} + klb^*c^*u_{23})]$.

Atom	x/a	y/b	z/c	u ₁₁	u ₂₂	u ₃₃	u ₂₃	u ₁₃	u ₁₂
Cr	1628(3)	1596(1)	1778(3)	530	447	478	-23	337	4
S	2229(4)	1526(2)	9673(4)	375	310	347	12	206	26
C(1)	3932(19)	1570(9)	3352(17)	349	422	346	-134	153	-74
C(2)	9359(25)	1606(9)	281(22)	778	455	652	-96	560	-125
C(3)	1735(26)	2973(11)	1778(24)	1143	215	749	93	741	82
C(4)	1478(24)	628(11)	1907(21)	1064	283	644	6	671	-90
C(5)	1172(20)	1654(9)	3368(19)	522	573	408	33	268	158
C(6)	313(21)	1513(9)	7613(18)	616	395	336	98	176	105
C(7)	9588(22)	2234(10)	7156(21)	473	573	536	-60	65	-16
C(8)	2990(20)	649(9)	9783(19)	650	410	599	24	482	114
C(9)	3186(20)	480(9)	8421(18)	588	281	429	-17	325	148
C(10)	4400(19)	828(10)	8275(19)	436	799	574	354	363	197
C(11)	4612(22)	633(9)	7025(20)	666	243	515	-91	380	-143
C(12)	3705(21)	119(11)	6020(22)	437	789	589	333	343	326
C(13)	2480(24)	-233(10)	6090(22)	759	399	632	-377	260	-96
C(14)	2233(20)	-60(10)	7351(20)	395	745	551	-203	267	-144
O(1)	5317(15)	1557(7)	4333(15)	440	710	612	-50	188	-59
O(2)	7953(15)	1593(7)	9416(17)	371	753	982	-161	290	-36
O(3)	1743(20)	3134(9)	1828(18)	1235	461	880	170	552	188
O(4)	1281(17)	59(7)	1916(16)	1152	231	878	63	776	-31
O(5)	937(15)	1687(7)	4384(15)	791	1052	676	-65	567	109

^a Numbers in parentheses here and in the other table are standard deviations of the last significant figures.

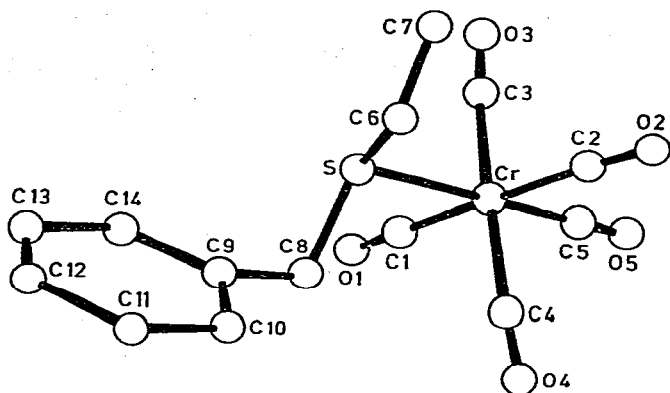


Fig. 1. A general view of the molecular structure of $(\text{CO})_5\text{CrS}(\text{C}_2\text{H}_5)\text{CH}_2\text{Ph}$, showing the numbering scheme adopted. Hydrogen atoms are not shown.

The chromium atoms, surrounded by five carbonyl groups and one sulphur atom, are in an approximate octahedral environment. Some distortion occurs and deviations from linearity are: $\text{C}(5)\text{—Cr—S}$ $179.6(2)$, $\text{C}(1)\text{—Cr—C}(2)$ $178.2(3)$, $\text{C}(3)\text{—Cr—C}(4)$ $175.2(3)$.

The chromium—sulphur bond distance is $2.459(2)$ Å which is significantly shorter than the Cr—S bond length of $2.510(2)$ Å in pentacarbonyl(trimethylphosphinethio)chromium(0), indicating a smaller σ (donor)/ π (acceptor) ratio for $\text{S}(\text{C}_2\text{H}_5)\text{CH}_2\text{Ph}$ compared to the phosphine sulphide ligand for which practically no π interaction has been assumed [11]. This result also fits in with the IR spectroscopic data for the two complexes as discussed above.

The conclusion that π -bonding plays a role in the dialkyl sulphide complexes, is supported by a comparison of Cr—C bond lengths in some pentacarbonylchromium complexes (See the discussion by Baker and Reay [11]). The four *cis* Cr—C bonds in $(\text{CO})_5\text{CrS}(\text{C}_2\text{H}_5)\text{CH}_2\text{Ph}$ average 1.879 Å compared to the 1.909 Å distance in $\text{Cr}(\text{CO})_6$ [19]. The shorter *trans* distance of $1.859(7)$ Å is comparable to those in analogous complexes with the π -bonding ligands $\text{P}(\text{Ph})_3$ and $\text{PO}(\text{Ph})_3$ ($1.845(4)$ and $1.861(4)$ Å respectively) [20], and significant-

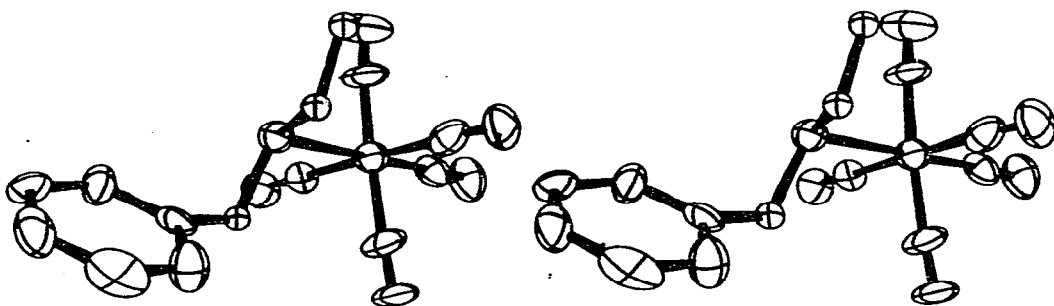


Fig. 2. Stereoscopic view of $(\text{CO})_5\text{CrS}(\text{C}_2\text{H}_5)\text{CH}_2\text{Ph}$.

TABLE 5

BOND LENGTHS AND ANGLES FOR $(\text{CO})_5\text{CrS}(\text{C}_2\text{H}_5)\text{CH}_2\text{Ph}$

Bond lengths (Å)		Bond angles (degrees)	
S—Cr	2.458(2)	C(1)—Cr—S	88.9(2)
C(1)—Cr	1.910(8)	C(2)—Cr—S	92.7(2)
C(2)—Cr	1.871(10)	C(2)—Cr—C(1)	178.2(3)
C(3)—Cr	1.870(10)	C(3)—Cr—S	90.9(2)
C(4)—Cr	1.864(10)	C(3)—Cr—C(1)	89.2(4)
C(5)—Cr	1.859(7)	C(3)—Cr—C(2)	91.7(4)
C(6)—S	1.872(8)	C(4)—Cr—S	93.9(2)
C(8)—S	1.810(8)	C(4)—Cr—C(1)	91.0(4)
O(1)—C(1)	1.155(8)	C(4)—Cr—C(2)	87.9(4)
O(2)—C(2)	1.152(9)	C(4)—Cr—C(3)	175.2(3)
O(3)—C(3)	1.073(9)	C(5)—Cr—S	179.6(2)
O(4)—C(4)	1.105(9)	C(5)—Cr—C(1)	91.2(3)
O(5)—C(5)	1.149(8)	C(5)—Cr—C(2)	87.3(3)
C(7)—C(6)	1.502(12)	C(5)—Cr—C(3)	88.8(4)
C(9)—C(8)	1.498(10)	C(5)—Cr—C(4)	86.5(4)
C(10)—C(9)	1.428(10)	C(6)—S—Cr	112.0(3)
C(14)—C(9)	1.408(11)	C(8)—S—Cr	106.0(2)
C(11)—C(10)	1.412(10)	C(8)—S—C(6)	100.6(4)
C(12)—C(11)	1.335(11)	O(1)—C(1)—Cr	178.3(6)
C(13)—C(12)	1.399(12)	O(2)—C(2)—Cr	176.4(7)
C(14)—C(13)	1.433(11)	O(3)—C(3)—Cr	175.2(8)
		O(4)—C(4)—Cr	175.4(9)
		O(5)—C(5)—Cr	178.0(7)
		C(7)—C(6)—S	110.0(6)
		C(9)—C(8)—S	113.2(5)
		C(10)—C(9)—C(8)	120.4(8)
		C(14)—C(9)—C(8)	119.1(7)
		C(14)—C(9)—C(10)	120.3(7)
		C(11)—C(10)—C(9)	119.2(8)
		C(12)—C(11)—C(10)	119.9(7)
		C(13)—C(12)—C(11)	123.4(8)
		C(14)—C(13)—C(12)	118.8(8)
		C(13)—C(14)—C(9)	118.3(7)

ly longer than the corresponding bonds in complexes with sulphur and nitrogen ligands without π -bonding ability, i.e. $(\text{CO})_5\text{CrSP}(\text{CH}_3)_3$ 1.815(8) Å [11] and $(\text{CO})_3\text{Cr}(\text{diethylenetriamine})$ 1.816(5) Å [21].

Conclusions drawn from the C—O bond lengths should be treated with caution, especially since two of the *cis* distances (C(3)—O(3) 1.073(9) and C(4)—O(4) 1.105(9)) are significantly shorter than the other two (C(2)—O(2) 1.152(9) and C(5)—O(5) 1.149(8)). An analogous result was obtained for $(\text{CO})_5\text{CrSP}(\text{CH}_3)_3$ [11]. In the related phosphine complex $(\text{CO})_5\text{CrPPh}_3$, these bond lengths are more or less identical to one another [20]. Nevertheless, the *trans* C—O distance 1.149(8) Å is markedly longer than the mean of the *cis* distances (1.121 Å), which is the expected behaviour. Differences in the carbonyl infrared frequencies of carbonyl-phosphines, -amines and -sulphides of chromium(0) are not consistent with the differences in experimental (coordinated) C—O bond lengths with regard to the π -bonding model. In the coordinated ligand $\text{S}(\text{C}_2\text{H}_5)\text{CH}_2\text{Ph}$, all the sulphur bonds have some s-character. The bond angles vary from 100.6(0.4) to 112.0(0.3)°.

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