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SULPHUR-CONTAINING METAL COMPLEXES

II.* THE CRYSTAL AND MOLECULAR STRUCTURES OF cis-[1,3-DITHIAN-2-YLIDENE(HYDROXY)METHYL(ETHOXY)CARBENE-C,S]-TETRACARBONYLCHROMIUM(O) AND fac-{[1,3-DITHIAN-2-YLIDENE(ETHOXY)METHYL(ETHOXY)CARBENE-C,S] t-BUTYL ISOCYANIDE} TRICARBONYLCHROMIUM(O).

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SUMMARY

The structures of the title compounds
$\underline{cis}$-$\mathrm{\underline{Cr\{C(OEt)[C(OH)C}\overline{S(CH_2)_2S}]\}(CO)_4}$ (I) and
$\underline{fac}$-$\mathrm{\underline{Cr\{C(OEt)[C(OEt)C}\overline{S(CH_2)_3S}]\}(CNCMe_3)(CO)_3}$ (II) have been determined from three dimensional X-ray data and confirm that their formation can be rationalized in terms of pathways involving respectively carbonyl insertion and double carbonylation. Refinement of the structures converged to final R-indices of 5.8 and 4.0% for respectively 1473 and 2650 independent reflections.

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[*] For part I, see ref. 1.

The crystals of I are monoclinic, space group C2/c, with Z = 8 in a unit cell of dimensions : a 20.19(2), b 7.22(1), c 22.10(2) Å, β = 106.9(1)°. For II the crystal data are: triclinic, space group P$\bar{1}$, cell constants a 12.329(9), b 9.605(6), c 9.637(6) Å, α 105.6(1), β 95.0(1), γ 94.9(1)°, Z = 2. Although part of chelating ring systems, the carbene carbon-donor atoms have similar bonding characteristics to carbon donors in simpler alkoxycarbene complexes, and have Cr-C bond lengths comparable to the chromium-isonitrile linkage.

Introduction

We have recently [2,3] reported the synthesis of <u>cis</u>-[1,3-dithian-2-ylidene(hydroxy)methyl(ethoxy)carbene-C,S]-tetracarbonylchromium(O) (I) and <u>fac</u>-[[1,3-dithian-2-ylidene(ethoxy)methyl(ethoxy)carbene-C,S] t-butylisocyanide] tricarbonylchromium(O) (II), according to the following reactions:

$$\mathrm{Cr(CO)_6} \xrightarrow[\mathrm{(ii)\ (Et_3O)BF_4}]{\mathrm{(i)\ LiCH(SR^1)R^2}} \underline{\mathrm{Cr[C(OEt)[C(OH)C(S}}\mathrm{R^1)R^2]](CO)_4} \quad (1)$$

(for I, $R^1R^2 = (CH_2)_3S$)

$$\mathrm{CrS(CH_2R^2)R^1} \xrightarrow[\mathrm{(ii)\,2(Et_3O)BF_4}]{\mathrm{(i)\,2BuLi,\ R^3NC}}$$

$$\underline{\mathrm{Cr[C(OEt)[C(OEt)C(S}}\mathrm{R^1)R^2]](CNR^3)(CO)_4} \quad (2)$$

(for II, $R^1R^2 = (CH_2)_3S$, $R^3 = CMe_3$)

The compounds I and II represent the first examples of complexes obtained according to the two new classes of reactions which entail respectively so called carbonyl insertion (reaction (1) prior to alkylation) and the incorporation of two molecules of carbon monoxide (reaction (2) prior to alkylation). These synthetic routes can also be used with other metal carbonyl complexes, other groups R^1 and R^2, other donor atoms than sulphur and, in the case of reaction (2), with other Lewis bases than t-butyl isocyanide [4]. As far as we know, the X-ray structure of compound II also represents the first example of a zerovalent chromium complex containing the important isocyanide ligand.

Experimental

Well-shaped red and purple crystals of the compounds I (Mol. wt. 368, mass spec.) and II (Mol. wt. 451, mass spec.) respectively, were obtained from ether-pentane solution (-30°C).

Data Collection and structure determination

Crystal data: $C_{12}H_{12}CrO_3S_2$ (I), M = 368.34. Monoclinic, a = 20.19(2), b = 7.22(1), c = 22.10(2) Å, β = 106.9(1); D_c = 1.59, D_m = 1.57 g cm^{-3}; Z = 8. Space group C2/c(hkl; h + k = 2n; h0l, l = 2n). μ(Mo-K_α) = 10.6 cm^{-1}. 1473 independent reflections with $\theta < 20^\circ$, 367 unobservable. Crystal size = 0.1 x 0.15 x 0.2 mm.

$C_{18}H_{25}CrO_5NS_2$(II), M = 451.52. Triclinic, a = 12.329(9), b = 9.605(6), c = 9.637(6) Å, α = 105.6(1), β = 95.0(1), γ = 94.9(1)°; D_c = 1.38, D_m = 1.37 g cm^{-3}, Z = 2. Space group $P\bar{1}$ (no systematic absences). μ(Mo-K_α) = 7.6 cm^{-1}. 2650 independent reflections with $\theta < 22^\circ$, 552 unobservable. Crystal size = 0.1 x 0.1 x 0.2 mm.

The experimental conditions were the same for both crystals. Accurate cell dimensions were obtained by least-squares refinement of 25 reflections measured on a diffractometer.

Intensity data were collected on a Philips PW 1100 single crystal diffractometer using graphite-monochromated Mo-K_α radiation. The $\omega - 2\theta$ scanning technique was employed with a scan width of $1.2^\circ\theta$ and a scan speed of $0.04^\circ s^{-1}$. Background was counted for half the total scanning time on each side of a reflection. Reflections were regarded as unobserved with $I < 2\sigma(I)$.

Both structures were determined by the heavy-atom method and refined by full-matrix least-squares, with anisotropic thermal parameters. The hydrogen atom positions could not be located for (I) but in the case of (II) all the hydrogen atom positions were found in a difference map and subsequently refined with isotropic temperature factors. The final conventional R-indices were 5.8 and 4.0% for the compounds I and II respectively. For the Cr atom the anomalous scattering factors of Cromer & Liberman [5] were applied. All the calculations were performed with the XRAY system of crystallographic computer programs [6]. Final positional and thermal parameters are given in Tables 1, 2 and 3 and bond lengths and angles in Table 4. Lists of the observed and calculated structure factors are available from the authors on request (G.J.K.). The values of the thermal parameters of the hydrogen atoms for II varied between U = 6(1) and 12(1) $Å^2$. Details of least-square planes and lines are given in Table 5.

Results and Discussion

The conformations of the two structures are illustrated by the perspective drawings in Figs. 1 and 2. The numbering systems are also shown.

(Continued on p. 256)

TABLE 1 FINAL FRACTIONAL COORDINATES ($\times 10^4$) AND THERMAL PARAMETERS ($\times 10^3$) FOR *cis*-$Cr[C(OEt)[C(OH)\overline{CS(CH_2)_3S}]](CO)_4$ ‡

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cr	3407(1)	-1397(3)	1170(1)	56(1)	47(1)	44(1)	-2(1)	21(1)	-1(1)
S(1)	3064(1)	-1138(4)	2112(1)	56(2)	54(2)	50(2)	-3(2)	24(2)	-3(2)
S(2)	3618(2)	1227(5)	3280(2)	93(3)	75(3)	59(2)	-8(2)	35(2)	-15(2)
O(1)	2129(5)	667(13)	403(4)	96(7)	79(7)	71(6)	22(6)	23(6)	-5(6)
O(2)	2721(5)	-5167(14)	953(5)	109(8)	63(7)	92(7)	-30(7)	41(6)	-20(6)
O(3)	3757(4)	-1853(14)	-48(4)	112(8)	92(8)	69(6)	15(6)	49(6)	10(6)
O(4)	4204(4)	2298(12)	1269(4)	77(6)	62(6)	77(6)	-18(5)	29(5)	9(5)
O(5)	4253(5)	3289(12)	2378(4)	92(7)	57(6)	83(6)	-31(6)	29(5)	-16(5)
O(14)	4779(5)	-3223(14)	1759(5)	70(7)	92(8)	102(8)	4(6)	29(6)	2(6)
C(1)	2611(7)	-172(19)	707(6)	68(9)	57(9)	55(9)	3(8)	22(7)	-3(7)
C(2)	2967(7)	-3736(22)	1035(6)	62(9)	80(11)	50(8)	3(9)	27(6)	-16(8)
C(3)	3619(6)	-1608(18)	433(6)	71(9)	60(9)	56(8)	4(8)	19(7)	8(8)
C(4)	3856(5)	1019(16)	1502(5)	36(7)	45(8)	69(9)	15(6)	16(6)	9(7)
C(5)	3904(6)	1680(18)	2150(6)	53(8)	59(9)	56(9)	13(7)	21(7)	4(8)
C(6)	3611(6)	669(17)	2513(6)	69(8)	59(9)	50(8)	-13(7)	20(7)	-14(7)
C(7)	3785(7)	-1066(19)	3664(5)	94(10)	73(10)	48(8)	17(9)	24(7)	12(8)
C(8)	3298(7)	-2586(19)	3321(6)	98(10)	71(9)	47(8)	-18(9)	39(7)	-10(8)
C(9)	3385(7)	-3069(18)	2660(5)	88(10)	69(9)	48(8)	9(8)	32(7)	13(7)
C(10)	4299(8)	2038(22)	630(6)	143(14)	104(13)	58(9)	-33(11)	62(10)	3(8)
C11	4713(9)	3655(14)	527(8)	132(14)	110(13)	122(13)	-25(12)	78(12)	11(12)
C(14)	4228(7)	-2518(20)	1551(6)	59(9)	75(10)	55(8)	-14(8)	30(8)	-7(8)

‡ The U_{ij} coefficients are from the expression $T = \exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + \ell^2b^{*2}U_{33} + hka^*b^*U_{12} + h\ell a^*c^*U_{13} + k\ell b^*c^*U_{23})]$

TABLE 2

FINAL FRACTIONAL COORDINATES ($\times 10^4$) AND THERMAL PARAMETERS ($\times 10^3$) FOR $\underline{fac}\text{-Cr}[\text{C(OEt)}[\text{C(OEt)}\overline{\text{CS(CH}_2)_3\text{S}}]](\overset{CN}{\wedge}\text{CMe}_3)(\text{CO})_4$ NON-HYDROGEN ATOMS

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cr	7337(1)	6524(1)	-812(1)	56(1)	49(1)	29(1)	15(1)	4(1)	11(1)
S(1)	8959(1)	8141(1)	61(1)	54(1)	60(1)	42(1)	14(1)	14(1)	18(1)
S(2)	9586(1)	10375(2)	3004(2)	48(1)	61(1)	73(1)	5(1)	1(1)	-2(1)
O(1)	6688(4)	7918(5)	-3162(4)	142(4)	116(3)	51(2)	57(3)	14(2)	44(2)
O(2)	8587(3)	4421(4)	-2814(4)	105(3)	91(3)	59(2)	50(3)	23(2)	11(2)
O(3)	5390(4)	4306(4)	-2068(5)	88(3)	71(3)	101(3)	2(2)	-30(2)	8(2)
O(4)	5764(2)	8600(3)	775(3)	41(2)	62(2)	53(2)	9(2)	4(2)	6(2)
O(5)	7176(3)	10273(3)	2847(3)	52(2)	53(2)	55(2)	6(2)	16(2)	0(2)
N	7789(3)	5333(4)	1912(4)	70(3)	58(2)	36(2)	6(2)	-6(2)	17(2)
C(1)	6963(5)	7379(6)	-2269(5)	83(4)	72(4)	38(3)	27(3)	12(3)	14(3)
C(2)	8113(4)	5227(6)	-2016(5)	63(3)	65(3)	39(3)	17(3)	-1(2)	18(2)
C(3)	6125(5)	5214(6)	-1530(5)	70(4)	62(3)	52(3)	19(3)	-2(3)	16(3)

C(4)	6751(4)	8162(5)	620(5)	49(3)	46(3)	42(3)	7(2)	3(2)	18(2)
C(5)	7523(4)	9198(5)	1763(5)	49(3)	47(3)	46(3)	9(2)	9(2)	9(2)
C(6)	8613(4)	9195(5)	1713(5)	43(3)	42(3)	49(3)	7(2)	5(2)	13(2)
C(7)	10747(5)	9324(8)	2966(7)	44(3)	83(4)	90(5)	5(3)	-6(3)	16(4)
C(8)	11029(5)	8521(7)	1495(7)	44(3)	81(4)	85(4)	15(3)	10(3)	21(3)
C(9)	10135(5)	7345(7)	665(7)	57(3)	78(4)	65(4)	26(3)	18(3)	17(3)
C(10)	4818(4)	7798(6)	-213(6)	44(3)	88(4)	68(4)	2(3)	-2(3)	10(3)
C(11)	3818(5)	8315(8)	438(8)	53(4)	76(5)	76(4)	14(3)	7(3)	15(4)
C(12)	6616(6)	9797(7)	3903(7)	89(5)	74(4)	60(4)	5(4)	29(3)	4(3)
C(13)	6374(8)	11082(9)	5032(9)	101(6)	104(6)	73(5)	2(5)	38(5)	-12(4)
C(14)	7619(4)	5701(5)	866(5)	52(3)	45(3)	43(2)	6(2)	1(2)	4(2)
C(15)	7957(4)	5089(5)	3342(5)	61(3)	50(3)	39(3)	6(2)	-2(2)	16(2)
C(16)	8649(6)	6448(7)	4330(6)	93(5)	71(4)	45(3)	1(4)	-9(3)	10(3)
C(17)	8558(7)	3764(7)	3215(7)	91(5)	76(4)	58(4)	26(4)	-1(3)	23(3)
C(18)	6838(5)	4871(9)	3842(7)	73(4)	113(6)	61(4)	5(4)	10(3)	41(4)

The U_{ij} coefficients as defined in Table 1.

TABLE 3

FINAL POSITIONAL PARAMETERS ($\times 10^3$) OF THE HYDROGEN ATOMS IN COMPLEX II

Atom	x	y	z
H(1)	1062(4)	855(6)	363(6)
H(2)	1128(4)	999(6)	336(5)
H(3)	1125(5)	930(7)	86(7)
H(4)	1168(4)	805(5)	172(5)
H(5)	1040(4)	680(5)	−23(5)
H(6)	990(4)	674(5)	130(5)
H(7)	485(4)	809(5)	−117(5)
H(8)	485(4)	674(5)	−27(5)
H(9)	315(5)	777(6)	−22(7)
H(10)	376(4)	807(5)	134(6)
H(11)	377(5)	931(7)	65(6)
H(12)	596(5)	908(6)	347(6)
H(13)	710(6)	912(8)	429(7)
H(14)	577(6)	1139(7)	435(7)
H(15)	702(4)	1170(6)	534(6)
H(16)	603(5)	1080(7)	579(7)
H(17)	871(4)	631(5)	533(6)
H(18)	821(5)	727(7)	441(6)
H(19)	946(5)	653(6)	392(6)
H(20)	807(5)	287(6)	250(7)
H(21)	863(4)	358(5)	422(6)
H(22)	925(4)	393(6)	295(6)
H(23)	692(4)	460(5)	477(6)
H(24)	653(5)	575(7)	385(7)
H(25)	643(5)	389(6)	315(6)

In both complexes, which contain the group $C(OEt)[C(OR)\overline{CS(CH_2)_3S}]$ (R = H in I and R = Et in II) functioning as a bidentate ligand with carbene-carbon and sulphur donor atoms, the metal is in an approximate octahedral environment of ligands. In complex I the other co-ordination positions are occupied by carbonyl groups

whereas compound II is a complex of the fac-$(CO)_3ML_1L_2L_3$-type where a carbonyl cis to the above mentioned chelate ring, has been substituted by t-butyl isocyanide.
It follows from Table 5 that the co-ordinating atoms of the chelate ring in both complexes, conform well to the best plane through themselves, the central metal atom and the two trans carbonyl groups. Some displacement of the two cis carbon donor atoms occurs from their ideal octahedral positions which is also shown by the C(1)-Cr-C(14) angles of 173.5(I) and 174.2^o(II). The most obvious distortion of the octahedra occurs within the above mentioned plane with regard to the position of the carbene-carbon atoms. This is illustrated for both complexes by the angles C(4)-Cr-S(1) (I : 79.6, II : 80.1^o), C(3)-Cr-C(4) (I : 101.7, II : 103.1^o) and C(2)-Cr-C(4) (I : 167.6, II : 169.7^o).

The chromium-C(carbene) distances of 2.004 and 2.025 Å in the two complexes, are comparable to the Cr-C(carbene) bond lengths in $Cr[C(OMe)Ph](CO)_5$ (2.04 Å) [7] and cis-$Cr[C(OMe)Me]PPh_3(CO)_4$ (2.00 Å) [8]. Also in agreement with these reported structure determinations, are the expected single bond lengths for C(carbene)-C(5) (respectively 1.486 and 1.473 Å for I and II) and the C(carbene)-oxygen distances of 1.348 and 1.329 Å, which are again comparable to the typical $C(sp^2)$-OR separation (1.36 Å) in organic esters which possesses considerable double bond character.
In both complexes, C(5) and C(10) carbon atoms are disposed "trans" around the C(carbene)-O bond, in contrast to cis-$Cr[C(OMe)Me]PPh_3(CO)_4$ where the two CH_3 groups are "cis" disposed [8]. The C(5)-C(6) bond lengths of 1.344 and 1.350 Å are normal $C(sp^2)$-$C(sp^2)$ double bond lengths.
No significant double bond delocalization is cognisable in

(Continued on p. 260)

TABLE 4

BOND LENGTHS AND ANGLES FOR THE TWO COMPLEXES I AND II

Bond lengths (Å)	I	II
Cr – C(1)	1.859(13)	1.853(6)
Cr – C(2)	1.891(16)	1.853(5)
Cr – C(3)	1.805(15)	1.822(5)
Cr – C(14)	1.817(13)	1.999(5)
Cr – C(4)	2.004(12)	2.025(4)
Cr – S(1)	2.384(4)	2.365(2)
C(1) – O(1)	1.177(15)	1.158(8)
C(2) – O(2)	1.137(19)	1.170(6)
C(3) – O(3)	1.189(18)	1.178(6)
C(14) – O(14)	1.187(17)	
C(4) – O(4)	1.348(16)	1.329(6)
O(4) – C(10)	1.492(18)	1.458(5)
C(10) – C(11)	1.491(25)	1.490(8)
C(4) – C(5)	1.486(18)	1.473(5)
C(5) – C(6)	1.344(19)	1.350(6)
C(5) – O(5)	1.376(15)	1.383(5)
S(1) – C(6)	1.771(12)	1.751(5)
S(1) – C(9)	1.838(12)	1.819(6)
S(2) – C(6)	1.737(13)	1.737(4)
S(2) – C(7)	1.846(14)	1.818(7)
C(7) – C(8)	1.521(18)	1.506(9)
C(8) – C(9)	1.560(19)	1.509(7)
O(5) – C(12)		1.429(8)
C(12) – C(13)		1.480(10)
C(14) – N		1.162(6)
N – C(15)		1.460(6)
C(15) – C(16)		1.528(7)
C(15) – C(17)		1.509(9)
C(15) – C(18)		1.517(9)

Bond angles (degrees)	I	II
S(1)-Cr-C(1)	91.0(5)	92.9(2)
S(1)-Cr-C(2)	88.0(4)	90.1(2)
S(1)-Cr-C(3)	177.0(4)	177.3(5)
S(1)-Cr-C(4)	80.1(4)	79.6(1)
S(1)-Cr-C(14)	95.0(5)	88.7(1)
C(1)-Cr-C(2)	92.7(6)	91.6(2)
C(1)-Cr-C(3)	86.5(6)	87.5(3)
C(1)-Cr-C(4)	90.8(5)	89.1(2)

Bond angles (degrees)	I	II
C(1)-Cr-C(14)	173.5(7)	174.2(2)
C(2)-Cr-C(3)	90.4(6)	87.2(2)
C(2)-Cr-C(4)	167.6(5)	169.7(1)
C(2)-Cr-C(14)	90.0(6)	94.1(2)
C(3)-Cr-C(4)	101.7(6)	103.1(2)
C(3)-Cr-C(14)	87.5(6)	91.2(2)
C(4)-Cr-C(14)	87.9(5)	85.6(2)
Cr-C(1)-O(1)	176.4(13)	177.2(5)
Cr-C(2)-O(2)	177.8(13)	177.8(6)
Cr-C(3)-O(3)	176.3(11)	174.9(5)
Cr-C(14)-O(14)	175.0(13)	-
Cr-C(14)-N	-	174.6(4)
Cr-C(4)-O(4)	133.4(9)	134.1(3)
Cr-C(4)-C(5)	121.9(9)	119.0(3)
Cr-S(1)-C(6)	101.5(5)	101.1(2)
Cr-S(1)-C(9)	112.4(5)	115.6(2)
O(4)-C(4)-C(5)	104.6(9)	106.8(3)
C(4)-O(4)-C(10)	119.9(10)	120.2(3)
O(4)-C(10)-C(11)	106.1(12)	107.4(4)
C(4)-C(5)-O(5)	120.5(11)	122.3(4)
C(4)-C(5)-C(6)	119.0(11)	120.1(4)
O(5)-C(5)-C(6)	120.5(11)	117.4(4)
C(5)-C(6)-S(1)	114.8(9)	113.6(3)
C(5)-C(6)-S(2)	125.2(10)	123.5(3)
S(1)-C(6)-S(2)	119.2(8)	121.9(3)
C(6)-S(2)-C(7)	100.9(6)	102.6(2)
S(2)-C(7)-C(8)	114.4(8)	116.9(5)
C(7)-C(8)-C(9)	113.3(12)	112.6(5)
C(8)-C(9)-S(1)	109.5(9)	110.5(4)
C(9)-S(1)-C(6)	100.3(5)	101.4(3)
C(5)-O(5)-C(12)	-	116.4(4)
O(5)-C(12)-C(13)	-	109.3(6)
C(14)-N-C(15)	-	171.2(4)
N-C(15)-C(16)	-	106.4(4)
N-C(15)-C(17)	-	108.5(4)
N-C(15)-C(18)	-	107.6(4)
C(16)-C(15)-C(17)	-	110.8(5)
C(16)-C(15)-C(18)	-	111.8(5)
C(17)-C(15)-C(18)	-	115.6(6)

the chelate ring. The O(5) ... O(5) separation between two molecules of I (2.921 Å), indicates so called "long" intermolecular hydrogen bonding [9] accross the twofold axis. The chromium-sulphur bond lengths of 2.384 and 2.365 Å respectively in I and II however, are significantly shorter than the Cr-S distance (2.459 Å) in $Cr[S(C_2H_5)Ch_2Ph](CO)_5$ [1]. Nevertheless, this does not lead to any bond lengthning of the trans-Cr-C linkages. On the contrary, in both complexes I and II, the shortest Cr-CO bond distances (1.805

TABLE 5

DISTANCES (Å) FROM LEAST-SQUARES PLANES AND LINES

Plane	I	II
Cr*	-0.005	-0.004
S(1)*	-0.044	0.002
C(2)*	0.049	-0.001
C(3)*	-0.047	0.003
C(4)*	0.046	-0.001
O(4)	-0.005	-0.362
C(5)	0.270	0.434
O(5)	0.381	0.564
C(6)	0.397	0.620
S(2)	0.668	1.126
C(9)	1.393	1.269
Line	**I**	**II**
Cr*	0.070	0.065
C(1)*	0.035	0.034
C(14)*	0.035	0.032
O(1)	0.166	0.149
O(14), N	0.206	0.176
C(15)		0.582
Angle◆	1.1°	2.4°

* Atoms contributing to plane or line

◆ Angle between line and normal to plane.

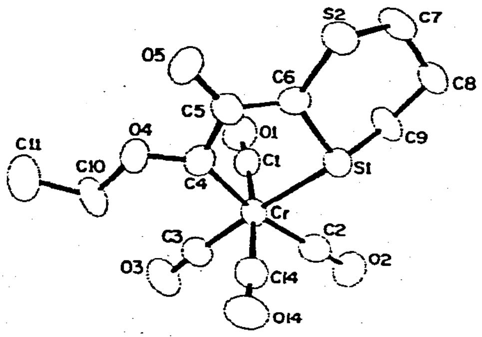

Fig. 1. Perspective view of the $\underline{\text{cis}}$-$\mathrm{\underline{Cr[C(OEt)[C(OH)}\overline{CS(CH_2)_3S}]](CO)_4}$ molecule, showing the numbering scheme adopted.

and 1.822 Å) occur *trans* to the sulphur donor atoms. Generally, it seems that no significant bonding changes in the $\mathrm{CrL_1L_2(CO)_3}$ moiety result from the substitution of a third carbonyl group by an isocyanide ligand.

The similarity of Cr-carbene (2.025 Å separation) and Cr-C(isonitrile) bonding (1.999 Å separation) is also substantiated by the identical Cr-C distances of 1.853 Å

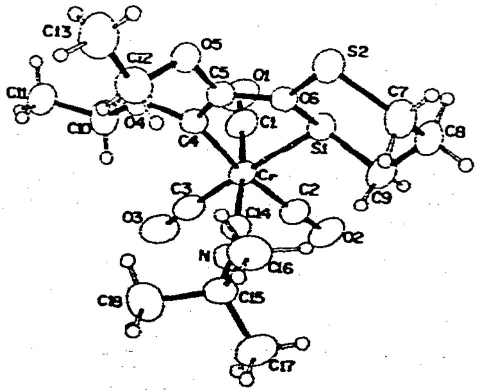

Fig. 2. Perspective view of the $\underline{\text{fac}}$-$\mathrm{\underline{Cr[C(OEt)[C(OEt)}\overline{CS(CH_2)_3S}]](CNCMe_3)(CO)_3}$ molecule, showing the numbering scheme adopted.

exhibited in complex II for the carbonyl ligands trans to the C(carbene) and C(isocyanide) donor atoms. In contrast to the comparable bond lengths of carbonyl and isocyanide ligands in $(\pi\text{-}C_5H_5)Mo(CO)_2I(CNPh)$ reported by Sim et al [10], a comparison of the Cr-C(isocyanide) bond length in II (1.999 Å) with the cis-Cr-C(carbonyl) bond lengths in I (av. 1.838 Å), indicates a markedly stronger metal-carbonyl bond. The isocyanide ligand is described as linear although deviations from linearity occur at both the coordinating C(14) atom (174.6°) and the N atom (171.2°). The distances calculated for the 1,3-dithian ring systems (in chair conformations) are similar for the structures of I and II and in approximate agreement with the values reported previously by Cotton et al in $(cyclo\text{-}1,3\text{-}C_4H_8S_2)Fe(CO)_4$ [11], except for the C(8) - C(9) bond lengths which were now found significantly shorter, similar to the C(7) - C(8) bond lengths and comparable to analogous distances in other related heterocycles [12,13]. The S-C-S angles in I and II are typical for sp^2 hybridized carbon atoms (respectively 119.2 and 121.9°).

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