Carbon Compounds of the Transition Metals. Part XXIV.[1] The Crystal and Molecular Structure of Pentacarbonyl[methyl(phenylthio)carbene]-chromium

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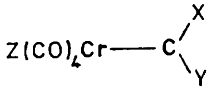
The crystal structure of the title compound, the first reported of a carbene complex with sulphur as hetero-substituent, shows an octahedral molecule similar to other carbene complexes of chromium. The crystals are monoclinic, space-group $P2_1/c$, with $Z = 4$ in a unit cell of dimensions: $a = 10{\cdot}236(4)$, $b = 6{\cdot}152(3)$, $c = 23{\cdot}340(6)$ Å, and $\beta = 103{\cdot}00(2)°$. After refinement with anisotropic temperature parameters, the Cr–C(carbene), S–C(carbene), and S–C(Ph) distances are 2·020(3), 1·690(3), and 1·781(3) Å respectively.

THE structures of a number of carbene complexes of chromium, (II)—(V), in which the carbene ligand contained oxygen or nitrogen substituents have been reported. The variations in the Cr–C(carbene) bond length have been interpreted [2-5] in terms of a metal–carbene double-bond weakened by p_π–p_π donation of electrons from the heteroatom to the carbene carbon atom.



	X	Y	Z	Ref.
(I)	SPh	Me	CO	This work
(II)	OMe	Ph	CO	2
(III)	OMe	Me	PPh_3	3
(IV)	NHMe	Me	CO	4
(V)	NEt_2	Me	CO	5

We now report the structure of pentacarbonyl[methyl(phenylthio)carbene]chromium (I), in which the carbene carbon atom is bonded to sulphur, for consideration in the light of this interpretation.

EXPERIMENTAL

Crystal Data.—$C_{13}H_8CrO_5S$, $M = 328{\cdot}3$, Monoclinic, $a = 10{\cdot}236(4)$, $b = 6{\cdot}152(3)$, $c = 23{\cdot}340(6)$ Å, $\beta = 103{\cdot}00(2)°$, $U = 1432{\cdot}9$ Å^3, $D_m = 1{\cdot}49(2)$, $Z = 4$, $D_c = 1{\cdot}52$, $F(000) = 664$. Space-group $P2_1/c$ (C^5_{2h}, No. 14) by systematic absences. Mo-K_α radiation, $\lambda = 0{\cdot}7107$; μ(Mo-K_α) = 9·9 cm.$^{-1}$.

Black crystals of (I) were coated with Shellac for *X*-ray photography. Data were collected on a Hilger and Watts computer-controlled, four-circle diffractometer [6] as far as $\theta = 28°$ with Mo-K_α radiation. 2327 unique reflections with intensities $>3\sigma(F^2)$ were obtained in five shells which were scaled together by comparison of counting times. 146 reflections were remeasured with attenuation of the primary beam to correct for dead-time losses. Corrections were applied for Lorentz and polarisation factors but not for absorption.

Solution and Refinement.—The positions of the chromium and sulphur atoms were obtained from a Patterson synthesis and the complete structure from three successive Fourier syntheses. When the structure had been refined, by full-matrix least-squares methods, to *R* 10·4%, a difference Fourier synthesis showed peaks at likely hydrogen positions together with indications of anisotropic motion, especially of the phenyl group within its own plane. Methyl proton co-ordinates, taken initially from the map, were improved geometrically and other hydrogen atoms placed at normal phenyl positions. Further refinement, with anisotropic motion allowed to all non-hydrogen atoms, was performed with the large block-diagonal method (see Chart). The hydrogen atoms were re-positioned from a difference synthesis which showed no other peak $>0{\cdot}5$ eÅ^{-3}. In the refinement, the function minimised was $\Sigma w(F_o - k|F_c|)^2$ with $w^{-1} = 0{\cdot}000745F_o^2 + 0{\cdot}0735F_o - 1{\cdot}4$ for $F_o \geq 24$ and $w^{-1} = 0{\cdot}00683F_o^2 - 0{\cdot}2198F_o + 2{\cdot}37$ for $F_o < 24$. The two strongest reflections, 102 and $\bar{1}17$, were omitted on the grounds of likely extinction and, for the final rounds of refinement, seven weak reflections with

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[1] Part XXIII, M. J. Barrow and O. S. Mills, *J. Chem. Soc.* (*A*), 1971, 1982.

[2] O. S. Mills and A. D. Redhouse, *J. Chem. Soc.* (*A*), 1968, 642.

[3] O. S. Mills and A. D. Redhouse, *J. Chem. Soc.* (*A*), 1969, 1274.

[4] (*a*) P. E. Baikie, E. O. Fischer, and O. S. Mills, *Chem. Comm.*, 1967, 1199, and unpublished work; (*b*) R. L. Beddoes, R. J. Hoare, and O. S. Mills, unpublished work.

[5] J. A. Connor and O. S. Mills, *J. Chem. Soc.* (*A*), 1969, 334.

[6] D. B. G. Edwards, K. Bowden, J. Standeven, and O. S. Mills, *Computer Bulletin*, 1966, **10**, 54.

$F_o < 2k|F_c|$, were omitted. Scattering factors[7,8] were corrected, where appropriate, for the real part of anomalous dispersion.[9]

CHART

Matrix (1):	(2 × 2)	Overall scale and temperature factors
Matrix (2):	(39 × 39)	Cr all parameters; C(1)—(6) and O(1)—(4) positional parameters
Matrix (3):	(33 × 33)	S all parameters; C(7)—(13) and O(5) positional parameters
Matrix (4):	(54 × 54)	C(1)—(4) and O(1)—(5) thermal parameters
Matrix (5):	(54 × 54)	C(5)—(13) thermal parameters

Refinement of the non-hydrogen atom parameters converged at R 4·48% (13 observations per parameter refined). Subsequent refinement of all the hydrogen-atom parameters as well resulted in a general improvement of bond lengths. The temperature factors of the phenyl hydrogen atoms reflected well the vibrations of the carbon atoms to which they were attached, although one methyl proton had a rather high temperature factor (*ca.* B 9 Å^2). The final R was 4·35% at convergence (11 observations per parameter). The phenyl protons had a root-mean-square displacement of 0·04 Å^2 from the plane of the carbon atoms.

RESULTS

The final atomic parameters are given in Table 1. Table 2 shows the agreement analysis after the final structure-factor calculation. Table 3 contains some of the results of molecular geometry calculations and the atom numbering scheme is shown in Figure 1. Closest intermolecular approaches are listed in Table 4 and a molecular packing diagram shown in Figure 2. Observed and calculated

TABLE 1

Final atomic co-ordinates (×10^4) and anisotropic temperature parameters * (×10^4), with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c	b_{11}	b_{22}	b_{33}	b_{12}	b_{31}	b_{23}
Cr	1978(1)	2371(1)	4310(0)	88(1)	225(1)	14(0)	−4(1)	13(0)	2(0)
C(1)	2985(4)	4589(6)	4791(2)	109(4)	325(11)	19(1)	−11(6)	13(1)	8(2)
O(1)	3560(3)	5872(6)	5090(2)	174(4)	474(12)	32(1)	−66(6)	14(2)	−50(3)
C(2)	929(4)	152(6)	3859(2)	122(4)	267(10)	20(1)	−18(6)	17(1)	4(2)
O(2)	292(3)	−1154(5)	3586(2)	192(5)	337(10)	36(1)	−90(6)	19(2)	−26(2)
C(3)	3618(4)	887(6)	4307(1)	111(4)	272(10)	16(1)	−11(5)	13(1)	4(2)
O(3)	4594(3)	37(5)	4297(1)	121(3)	399(10)	31(1)	60(5)	19(1)	−2(2)
C(4)	376(3)	3987(6)	4300(1)	105(4)	283(10)	17(1)	−14(5)	14(1)	−4(2)
O(4)	−563(3)	4948(5)	4299(1)	116(3)	431(10)	29(1)	60(5)	17(1)	−3(2)
C(5)	1798(4)	877(7)	5000(2)	124(4)	353(12)	18(1)	22(6)	18(1)	18(2)
O(5)	1670(4)	2(6)	5409(1)	194(5)	576(14)	28(1)	44(7)	31(2)	62(3)
C(6)	2071(3)	3867(5)	3550(1)	89(3)	207(8)	14(1)	5(4)	11(1)	−2(2)
C(7)	970(3)	3901(7)	3010(1)	92(3)	373(12)	16(1)	−44(6)	4(1)	14(2)
S	3497(1)	5200(2)	3517(0)	90(1)	380(3)	16(0)	−49(1)	6(0)	14(1)
C(8)	3345(3)	6204(6)	2790(1)	76(3)	294(10)	16(1)	−21(5)	11(1)	5(2)
C(9)	3744(4)	4893(6)	2377(2)	95(3)	329(12)	21(1)	−1(5)	14(1)	0(2)
C(10)	3634(4)	5649(8)	1808(2)	124(5)	463(16)	20(1)	−7(7)	17(2)	−12(3)
C(11)	3136(4)	7689(8)	1657(2)	110(4)	534(18)	17(1)	−53(7)	7(1)	24(3)
C(12)	2742(4)	9010(7)	2070(2)	115(4)	329(12)	25(1)	−17(6)	9(2)	21(3)
C(13)	2860(4)	8276(7)	2643(3)	103(4)	297(10)	22(1)	−9(5)	15(1)	0(2)

* Defined in the expression exp − $(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + 2b_{23}kl + 2b_{31}lh + 2b_{12}hk)$.

Hydrogen atom co-ordinates (×10^3) and temperature factors

Atom	x/a	y/b	z/c	B/Å^2	Atom	x/a	y/b	z/c	B/Å^2
H(71)	118(4)	352(8)	268(2)	5·8(9)	H(10)	382(4)	478(6)	152(2)	5·9(9)
H(72)	19(4)	312(7)	308(2)	5·5(9)	H(11)	304(4)	820(7)	130(2)	6·1(9)
H(73)	78(5)	523(9)	280(2)	9·0(14)	H(12)	237(4)	1047(6)	198(2)	5·5(9)
H(9)	411(4)	343(7)	247(2)	5·6(8)	H(13)	251(3)	913(6)	291(1)	4·6(7)

TABLE 2

Agreement distribution as a function of (sin θ/λ)^2 and F_o

Range of (sin θ/λ)^2	No. of reflections (n)	$\Sigma w\Delta^2/n$
0·00—0·04	92	1·42
0·04—0·08	161	0·91
0·08—0·12	214	0·76
0·12—0·16	235	0·51
0·16—0·20	273	0·36
0·20—0·24	253	0·35
0·24—0·28	270	0·47
0·28—0·32	251	0·51
0·32—0·36	244	0·62
0·36—0·40	184	1·02
0·40—0·44	143	1·09

Range of F_o	No. of reflections (n)	$\Sigma w\Delta^2/n$
2—4	21	0·49
4—8	600	0·66
8—16	878	0·65
16—32	536	0·57
32—64	217	0·67
Over 64	68	1·05

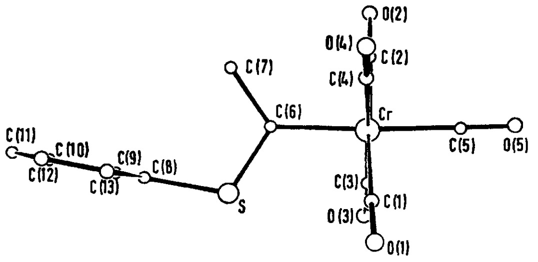

FIGURE 1 View of the molecule projected onto the carbene plane [plane (4), Table 3*c*], showing the atomic numbering

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[7] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

[8] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

[9] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.

Table 3

(*a*) Intramolecular distances (Å)

Cr–C(1)	1·914(4)	C(5)–O(5)	1·132(4)
Cr–C(2)	1·901(4)	C(6)–C(7)	1·490(4)
Cr–C(3)	1·912(4)	C(6)–S	1·690(3)
Cr–C(4)	1·914(4)	S–C(8)	1·781(3)
Cr–C(5)	1·899(3)	C(8)–C(13)	1·384(5)
Cr–C(6)	2·020(3)	C(8)–C(9)	1·386(5)
C(1)–O(1)	1·129(4)	C(9)–C(10)	1·388(5)
C(2)–O(2)	1·137(4)	C(10)–C(11)	1·370(6)
C(3)–O(3)	1·134(4)	C(11)–C(12)	1·390(6)
C(4)–O(4)	1·128(4)	C(12)–C(13)	1·391(5)
C(7)–H(71)	0·88(4)	C(10)–H(10)	0·91(4)
C(7)–H(72)	0·98(4)	C(11)–H(11)	0·87(4)
C(7)–H(73)	0·95(5)	C(12)–H(12)	0·98(4)
C(9)–H(9)	0·98(4)	C(13)–H(13)	0·95(3)

(*b*) Bond angles (°)

C(1)–Cr–C(2)	177·3(2)	Cr–C(1)–O(1)	177·6(3)
C(1)–Cr–C(3)	89·2(2)	Cr–C(2)–O(2)	179·1(4)
C(1)–Cr–C(4)	89·0(2)	Cr–C(3)–O(3)	178·6(3)
C(1)–Cr–C(5)	89·5(2)	Cr–C(4)–O(4)	179·4(3)
C(1)–Cr–C(6)	93·7(1)	Cr–C(5)–O(5)	178·8(4)
C(2)–Cr–C(3)	92·4(2)	Cr–C(6)–C(7)	125·0(2)
C(2)–Cr–C(4)	89·5(2)	Cr–C(6)–S	118·2(2)
C(2)–Cr–C(5)	88·4(2)	C(6)–S–C(8)	108·7(1)
C(2)–Cr–C(6)	88·5(1)	S–C(8)–C(13)	120·4(3)
C(3)–Cr–C(4)	177·1(2)	C(13)–C(8)–C(9)	120·6(3)
C(3)–Cr–C(5)	91·4(2)	C(8)–C(9)–C(10)	119·8(4)
C(3)–Cr–C(6)	89·9(1)	C(9)–C(10)–C(11)	120·0(4)
C(4)–Cr–C(5)	90·9(2)	C(10)–C(11)–C(12)	120·4(3)
C(4)–Cr–C(6)	87·9(1)	C(11)–C(12)–C(13)	120·1(4)
C(5)–Cr–C(6)	176·6(2)	C(12)–C(13)–C(8)	119·1(4)
C(6)–C(7)–H(71)	116(3)	C(8)–C(9)–H(9)	123(2)
C(6)–C(7)–H(72)	110(2)	C(9)–C(10)–H(10)	121(2)
C(6)–C(7)–H(73)	119(3)	C(10)–C(11)–H(11)	122(3)
H(71)–C(7)–H(72)	113(3)	C(11)–C(12)–H(12)	123(2)
H(71)–C(7)–H(73)	81(4)	C(12)–C(13)–H(13)	119(2)
H(72)–C(7)–H(73)	115(4)		

(*c*) Equations of least-squares planes in the form $l(x + z \,.\, \cos\beta) + m \,.\, y + n \,.\, z \,.\, \sin\beta = d$ where x, y, and z are atomic co-ordinates in Å, and in square brackets deviations (Å) of atoms from the planes

	l	*m*	*n*	*d*
Plane (1):				
Cr, C(1)—(4), O(1)—(4)	−0·2789	−0·4863	0·8281	−7·4765
[Cr 0·000, C(1) 0·025, O(1) 0·084, C(2) 0·048, O(2) 0·066, C(3) −0·031, O(3) −0·076, C(4) −0·047, O(4) −0·069]				
Plane (2):				
Cr, C(1), C(2), C(5), C(6), O(1), O(2), O(5)	0·8624	−0·5063	−0·0039	−1·0169
[Cr 0·031, C(1) 0·006, O(1) −0·024, C(2) 0·005, O(2) −0·024, C(5) 0·019, O(5) −0·011, C(6) −0·001]				
Plane (3):				
Cr, C(3)—(6), O(3)—(5)	−0·4136	−0·7225	−0·5540	−6·3888
[Cr 0·004, C(3) −0·028, O(3) −0·052, C(4) −0·027, O(4) −0·055, C(5) 0·025, O(5) 0·042, C(6) 0·091]				
Plane (4):				
Cr, C(6), C(7), S	0·4466	−0·8360	−0·3188	−4·4528
[Cr −0·001, C(5) 0·024, O(5) 0·022, C(6) 0·002, C(7) −0·001, S −0·001, C(8) 0·112, C(11) 0·340]				
Plane (5):				
S, C(8)—(13)	−0·8896	−0·3731	−0·2633	−4·8409
[S 0·002, C(8) 0·005, C(9) −0·003, C(10) −0·002, C(11) 0·003, C(12) 0·005, C(13) −0·010]				

structure factors are listed in Supplementary Publication No. SUP 20292, (16 pp. 1 microfiche).*

Table 4

Intermolecular contacts <3 Å

O(2) · · · H(73$^{\mathrm{I}}$)	2·99	H(71) · · · H(12$^{\mathrm{I}}$)	2·93
O(3) · · · H(10$^{\mathrm{II}}$)	2·78	H(72) · · · H(73$^{\mathrm{III}}$)	2·73
O(4) · · · H(11$^{\mathrm{III}}$)	2·82	H(72) · · · H(12$^{\mathrm{III}}$)	2·97
H(71) · · · H(73$^{\mathrm{III}}$)	2·90	H(9) · · · H(12$^{\mathrm{I}}$)	2·62

Superscripts refer to the following positions:

I $x, y - 1, z$

II $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$

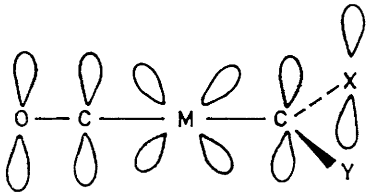
III $-x, y - \frac{1}{2}, -z + \frac{1}{2}$

DISCUSSION

The structure of (I) is in accord with those described earlier (II)—(V). The chromium atom has octahedral co-ordination and lies in the plane of the carbene ligand, the normal to which is inclined at 36° with one of the octahedral axes. Whilst the thiophenyl group is planar, it is perpendicular to the plane of the carbene ligand. The methyl and phenyl groups are *cis* to one another relative to the S–C(carbene) bond. Within the phenyl group the C–C distances lie within the normal range of 1·37—1·40 Å and the C–H distances, all of which were refined, range between 0·87 and 0·98 Å and thus reflect the shift of the bonded electrons away from the nuclear positions of the hydrogen atoms.

The molecule provides further evidence for back-donation of electrons from the heteroatom to the carbene carbon atom in these complexes. The S–C(carbene) distance 1·69 Å is markedly shorter than the S–C(Ph) value, 1·78 Å, although both involve formally sp^2-hybridised carbon atoms. This thiophenyl complex thus involves double bonding as do (II)—(V). Both the S–C(Ph) and Me–C(carbene) distances are normal.

The angle subtended at the carbene carbon atom by its organic substituents is 116·7°, slightly larger than shown in complexes (III)—(V) where a *cis*-arrangement holds; (II) contains a *trans*-arrangement and the angle is much smaller (104°).



The bonding in metal–carbene complexes has been interpreted in terms of a metal–carbon double-bond which is weakened by competitive π donation from a hetero-atom, X, attached to the carbene carbon atom. The formally empty p_z orbital on the carbene carbon may receive electrons both from the filled *d* orbital of the metal *via* back-donation and also from the hetero-substituent, X. As the effect of the latter increases, so must the former effect decrease. Thus an enhanced effect from the hetero-substituent should strengthen

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* For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20.

back-donation from the metal to the carbonyl groups, in particular to that *trans* to the carbene ligand. In Table 5 we list some properties of pentacarbonyl-(methylcarbene)chromium compounds. Whilst the Cr–C(carbene) distances and the dipole moments show pronounced and systematic variations, the Cr–C(*trans*) distances, not listed in Table 5, are more constant.

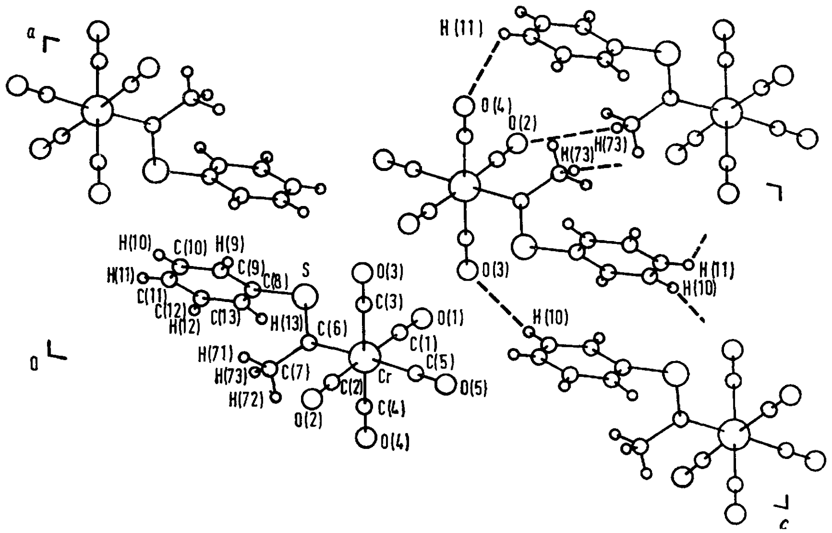

FIGURE 2 Projection of the unit cell along *b*, showing some close intermolecular contacts

TABLE 5

Properties of methylcarbene- and other chromium complexes

Compound	ν(CO) A_1'/cm^{-1}	μ[D]	r(M–C)/Å
$Cr(CO)_6$			1·92[a]
(III) X = OMe	1966[b]	3·61[c]	2·00[d]
(I) X = SPh	1960[e]	4·93[c]	2·02[f]
(IV) X = NHMe	1940[g]	6·20[g]	2·10[h]
(V) X = NEt_2	1929[g]	7·05[c]	2·16[i]
Estimated Cr–C(sp^2)			2·21[i]

[a] A. Whitaker and J. W. Jeffrey, *Acta Cryst.*, 1967, **23**, 977. [b] C. G. Kreiter and E. O. Fischer, *Chem. Ber.*, 1970, **103**, 1561. [c] J. A. Connor and E. O. Fischer, unpublished results. [d] Ref. 3. [e] U. Klabunde and E. O. Fischer, *J. Amer. Chem. Soc.*, 1967, **89**, 7141. [f] This work. [g] J. A. Connor and E. O. Fischer, *J. Chem. Soc.* (*A*), 1969, 578. [h] Ref. 4(*b*). [i] Ref. 5.

Measurements of the CO stretching frequency of the *trans* carbonyl group [ν(CO)A_1'] do show such a systematic variation. The changes in the Cr–C(carbene) bond length and C–O stretching frequency can readily be interpreted in terms of the net electron shift within the molecule (as shown by the dipole moment) and the expected electron-releasing power of the group X. The possible shortening of the Cr–C(*trans*) bond length has been noted[5] in various carbene complexes and this is again just possible in (I) although at the limit of statistical significance. Both the Cr–C and Cr–O distances are 0·01 Å shorter than the mean equatorial values. When this is taken together with the earlier results, the view is strengthened that a slight *trans* bond shortening does occur in these complexes.

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