

## THE CRYSTAL AND MOLECULAR STRUCTURE OF $\eta^5$ -CYCLOPENTADIENYLIODOMETHYL(METHYLTHIO)CARBENE- (TRIPHENYLPHOSPHINE)IRIDIUM(III) IODIDE

G. BOMBIERI,

*Laboratorio di Chimica e Tecnologia dei Radioelementi del C.N.R., Padova (Italy)*

F. FARAONE, G. BRUNO and G. FARAONE

*Centro di Strutturistica diffrattometrica e Istituto di Chimica Generale dell'Università,  
 98100 Messina (Italy)*

(Received October 2nd, 1979)

### Summary

The crystal and molecular structure of  $\eta^5$ -cyclopentadienyliodomethyl(methylthio)carbene(triphenylphosphine)iridium(III) iodide  $[\text{Ir}\{\text{C}(\text{Me})\text{SMe}\}-(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)]\text{I}$  has been determined from three dimensional X-ray data in order to clarify the contribution of the  $\alpha$ -sulphur atom to the bonding in this carbenoid complex.

The compound crystallizes in space group  $Pbc2_1$  with four formula units in a cell of dimensions  $a$  9.745(6),  $b$  15.201(8) and  $c$  17.364(10) Å. Least-squares refinement of the structure has led to the final discrepancy index  $R = 0.047$  for the 1655 symmetry-independent observable reflections. The coordination geometry about the iridium atom is approximately tetrahedral; the coordination positions are occupied by the  $\eta^5\text{-C}_5\text{H}_5$  ring center, the phosphorus, the iodide I(1) and the carbon C(6) of the C(Me)SMe ligand (Ir–Rc 1.89, Ir–P 2.280(7), Ir–I(1) 2.651(2) and Ir–C(6) 2.03(3) Å).

The bonding of the C(Me)SMe group indicates that this complex must be formulated as a C(Me)=SMe complex of iridium(III).

### Introduction

It is well established that in oxidative addition reactions the products depend on the nature of the metal and the coordinated ligands [1].

The reactions between alkyl halides and the compound  $(\eta^5\text{-C}_5\text{H}_5)\text{MCO}(\text{PPh}_3)$  (M = Rh, Ir) give an acyl–metal complex for M = Rh whereas for M = Ir ionic products containing iridium–methyl  $\sigma$  bonds are formed [3]. On the other

hand we have found [4] that the rhodium(I) and iridium(I) thiocarbonyl complexes of the type  $[M(\eta^5-C_5H_5)(CS)(PPh_3)]$  react with methyl iodide at room temperature to give compounds which analyse for  $M(C_5H_5)(CS)(PPh_3)_2(MeI)_2$ . On the basis of conductivity measurements, IR and  $^1H$  NMR spectral data the complexes were formulated as methyl(methylthio)carbene derivatives  $[MI(\eta^5-C_5H_5)\{(CMe)SMe\}(PPh_3)]I$ . The X-ray studies reported for several types of carbene-complexes [5] provide useful information about the type and degree of carbenoid stabilization. In particular, for carbene ligands possessing  $\alpha$ -oxygen or  $\alpha$ -nitrogen atoms, the carbene atom interacts more strongly with these  $\alpha$ -heteroatoms than with the metal atom, and the carbon-to-metal bond order is often close to unity. The previously known complex containing a carbene ligand possessing an  $\alpha$ -sulphur, viz. pentacarbonyl[methyl(phenylthio)carbene]chromium(I) [6], provides further evidence for back donation of electrons from the heteroatom to the carbene carbon atom.

For a better understanding of the contribution of the  $\alpha$  sulphur atom of this carbene ligand to the bonding to the metal we undertook an X-ray analysis of the title compound.

## Experimental

Dark purple, air-stable crystals of  $[IrI\{C(Me)SMe\}(\eta^5-C_5H_5)(PPh_3)]I$  were obtained by recrystallization from methyl iodide/pentane. Preliminary Weissenberg and precession photographs showed Laue symmetry characteristic of the orthorhombic system. The systematic absences observed were consistent with the space groups  $Pbcm$  or  $Pbc2_1$ . Lattice constants were determined at room temperature from a least-squares refinement of the setting angles of strong reflections centered on a four-circle automatic diffractometer using  $Mo-K_\alpha$  radiation ( $\lambda$  0.7107 Å). They are  $a$  9.745(6),  $b$  15.201(8) and  $c$  17.364(10) Å. The density calculated for four formula weights per unit cell is 2.188 g/cm<sup>3</sup> which agrees well with the experimental value of 2.17 g/cm<sup>3</sup>. With four formula weights in the unit cell either a mirror plane, twofold axis or a centre of symmetry is imposed on the ions if the centrosymmetric space group  $Pbcm$  is chosen, no symmetry is imposed to the ions with the noncentrosymmetric space group  $Pbc2_1$ . The intensity data were collected with the  $\theta/2\theta$  scan mode: scan width 1° scan speed 0.025°/sec and two background counts of 10 sec at each end of the scan, in a  $\theta$  interval varying between 3 and 25°, with the  $Mo-K_\alpha$  radiation monochromatized by a graphite crystal.

Of the 2346 unique reflections thus considered, the 1655 having a net intensity greater than  $3\sigma$  ( $\sigma$  = standard error based on counting statistics) were used in the structure determination and refinement. During the collection, two standard reflections were measured every hour to check the stability of the crystals and of the instrument; only statistic fluctuations were observed. The values of  $I$  and  $\sigma(I)$  were corrected for Lorentz and polarization effects and an absorption correction was applied as proposed by North et al. [7].

## Structure determination and refinement

Geometrical considerations associated with the possible molecular symmetry of the cation ruled out the centric space group  $Pbcm$ , which imposes on the

compound either a center of symmetry, or a mirror plane, or a twofold axis. Hence the non centric space group  $Pbc2_1$  was assumed.

The iridium and iodine atoms were located from a three-dimensional origin-removed sharpened Patterson map, and the remaining non hydrogen atoms were located from subsequent difference Fourier syntheses completed with least-squares refinement. The function minimized was  $\sum w(|F_o| - |F_c|)^2$ , where  $|F_o|$  and  $|F_c|$  are the observed and calculated structure amplitudes and  $w = 1$ . The atomic scattering factors for iridium and iodine were taken from ref. [8], for the other non-hydrogen atoms from ref. [9] and for the hydrogen atoms from ref. [10]. The anomalous dispersion terms used for iridium were those given by of Cromer and Liberman [11]. The phenyl rings of the phenylphosphine were refined as rigid groups (symmetry  $D_{6h}$ ; C—C 1.395 Å) with individual isotropic thermal parameters. With all of the isotropic non hydrogen atoms present, the structure was refined to  $R = 0.158$ . Anisotropic temperature factors were then assigned to the non group atoms. Few cycles of least-squares

TABLE 1

FRACTIONAL COORDINATES ( $\times 10^4$ ) WITH e.s.d.'s IN PARENTHESES AND ISOTROPIC  $U(\times 10^3)$ 

	x	y	z	U		x	y	z
Ir	1282(1)	1443(1)	4935(0)	—				
I(1)	-323(2)	38(1)	4859(2)	—				
I(2)	5779(2)	2645(2)	4443(2)	—				
P	1229(8)	1563(5)	6243(4)	—				
S	4173(8)	679(5)	5456(5)	—				
C(1)	424(35)	2801(17)	4781(17)	—	H(10)	28	3115	5199
C(2)	-272(36)	2246(25)	4260(20)	—	H(20)	-1229	2131	4232
C(3)	791(38)	1900(20)	3758(21)	—	H(30)	660	1463	3373
C(4)	1994(36)	2269(27)	3946(20)	—	H(40)	2823	2203	3664
C(5)	1818(32)	2772(20)	4559(22)	—	H(50)	2536	3068	4823
C(6)	2974(27)	671(18)	4862(20)	—				
C(7)	3074(39)	159(26)	4134(25)	—	H(70)	2401	182	3739
					H(71)	3744	602	4047
					H(72)	3503	-402	4131
C(8)	5668(29)	139(20)	5072(24)		H(80)	6118	11	5545
					H(81)	5107	-346	4929
					H(82)	6334	240	4683
C(10)	1180(14)	3288(11)	6797(11)	43(7)	H(100)	217	3212	6852
C(11)	1783(14)	4094(11)	6980(11)	31(6)	H(110)	1231	4566	7161
C(12)	3197(14)	4205(11)	6900(11)	58(9)	H(120)	3608	4754	7025
C(13)	4007(14)	3512(11)	6635(11)	78(11)	H(130)	4969	3588	6580
C(14)	3403(14)	2707(11)	6451(11)	62(9)	H(140)	3955	2234	6270
C(9)	1990(14)	2595(11)	6532(11)	44(7)				
C(16)	-1611(18)	1748(12)	6190(8)	48(8)	H(160)	-1501	1805	5649
C(17)	-2912(18)	1826(12)	6518(8)	61(9)	H(170)	-3687	1937	6201
C(18)	-3075(18)	1742(12)	7313(8)	48(8)	H(180)	-3961	1796	7537
C(19)	-1937(18)	1579(12)	7779(8)	60(9)	H(190)	-2048	1522	8321
C(20)	-637(18)	1501(12)	7451(8)	42(7)	H(200)	138	1390	7768
C(15)	-474(18)	1585(12)	6656(8)	25(5)				
C(22)	1826(19)	9867(12)	6720(9)	45(8)	H(220)	1302	-307	6284
C(23)	2372(19)	9231(12)	7211(9)	45(7)	H(230)	2221	-1376	7110
C(24)	3141(19)	9486(12)	7851(9)	66(10)	H(240)	3514	-947	8186
C(25)	3363(19)	376(12)	7999(9)	75(12)	H(250)	3887	550	8435
C(26)	2816(19)	1012(12)	7508(9)	48(8)	H(260)	2967	1619	7609
C(21)	2047(19)	757(12)	6868(9)	34(6)				

TABLE 2

ANISOTROPIC THERMAL PARAMETERS ( $\times 10^3$ ) IN THE FORM  $\exp[-2\pi^2 \sum U_{ij} a_i^* a_j^* h_i h_j]$ 

	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
Ir	33.5(5)	30.7(4)	33.5(4)	3.6(5)	2.6(9)	-1.5(9)
I(1)	65(1)	42(1)	70(2)	-13(1)	-8(2)	-5(2)
I(2)	54(1)	62(2)	87(2)	3(1)	21(1)	18(2)
P	32(4)	20(3)	33(4)	5(3)	3(4)	-2(3)
S	40(4)	59(5)	50(5)	11(4)	-2(4)	-15(4)
C(1)	75(22)	22(14)	37(23)	14(15)	9(15)	-5(12)
C(2)	51(21)	83(28)	57(23)	1(20)	-16(18)	14(20)
C(3)	93(25)	19(17)	66(23)	28(17)	-3(20)	14(16)
C(4)	51(21)	131(31)	41(2)	-45(21)	-21(17)	44(21)
C(5)	61(20)	44(18)	67(24)	-55(16)	-16(14)	33(17)
C(6)	41(15)	55(16)	20(17)	1(13)	22(16)	22(16)
C(7)	68(25)	66(25)	130(38)	49(21)	-31(27)	-42(26)
C(8)	38(16)	68(20)	64(30)	0(14)	3(18)	-15(21)

refinement lowered the discrepancy factor to  $R = 0.058$ . The positions of the hydrogen atoms were idealized ( $d(\text{C-H}) 0.95 \text{ \AA}$ ) and each hydrogen atom was assigned an isotropic temperature factor equal to that of the attached carbon atom (for the anisotropic carbon—the isotropic equivalent).

In the subsequent structure factor calculations the contributions of these hydrogen atoms were taken into account. After three additional cycles the refinement converged to give the  $R$  factor = 0.047. For the acentric space group  $Pbc2_1$  two possible enantiomeric configurations of the asymmetric unit exist, viz. the structure A, determined above, and its enantiomer, B, the mirror image of A reflected across a plane at  $Z = 1/4$ . In order to test the possibility that B might be the correct structure the signs of the  $Z$  coordinates for all the atoms were inverted and the resulting structure B was refined by least-squares. This converged to give an  $R$  factor of 0.053, which is significantly higher than that obtained from the refinement of enantiomer A. Thus it was concluded that our original arbitrary choice of the enantiomer A was correct. In the final cycle of the refinement the ratios of the parameter shifts to standard deviations were  $< 0.1$ . A final difference Fourier showed few peaks ranging from 0.5 to 1.1  $e/\text{\AA}^3$  in the proximity of the Iridium and I(2) atoms. The residual electron density around the iridium was not located along the direction of any bond and so no chemical meaning is to be attributed to it. Also some very low residual peaks of 0.2–0.3  $e/\text{\AA}^3$  are present in proximity of the cyclopentadienyl ring, suggesting some degree of rotational disordering in the ring. All data processing and computations were carried out using the SHELX 76 [12] and X-Ray 72 [13] program package.

Tables of structure factors are available from the authors.

## Results and discussion

The separate molecules of  $[\text{IrI}(\eta^5\text{-C}_5\text{H}_5)\{\text{C}(\text{Me})\text{SMe}\}(\text{PPh}_3)]\text{I}$  occupy general positions in the unit cell. The compound is formed by discrete ionic units in the ratio 1/1 with the  $[\text{IrI}(\eta^5\text{-C}_5\text{H}_5)\{\text{C}(\text{Me})\text{SMe}\}(\text{P}(\text{Ph})_3)]$  group as the cation

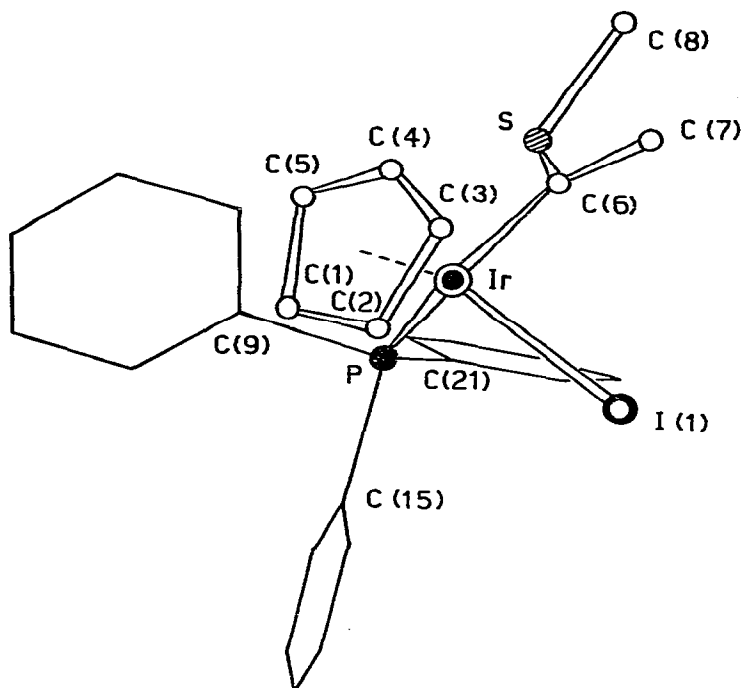


Fig. 1. Perspective view of the cation.

TABLE 3

SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) WITH e.s.d.'s IN PARENTHESES

## Bond distances

Ir—I(1)	2.651(2)	Ir—C(6)	2.03(3)
Ir—P	2.280(7)	C(6)—S	1.56(3)
Ir—RC	1.89	C(6)—C(7)	1.49(5)
Ir—C(1)	2.24(3)	S—C(8)	1.80(3)
Ir—C(2)	2.27(3)	C(1)—C(2)	1.41(4)
Ir—C(3)	2.21(3)	C(2)—C(3)	1.45(5)
Ir—C(4)	2.24(3)	C(3)—C(4)	1.34(4)
Ir—C(5)	2.19(3)	C(4)—C(5)	1.32(5)
		C(5)—C(1)	1.41(4)
Av of 5 Ir—C (Cp)	2.23	Av of 5 C—C in 1 Cp ring	1.39
P—C(9)	1.81(2)	P—C(21)	1.82(2)
P—C(15)	1.81(2)	S—I(2)	3.80(1)

## Angles

RC—Ir—P	123.5(2)	Ir—P—C(9)	109.6(7)
RC—Ir—C(6)	122.9(9)	Ir—P—C(15)	114.7(6)
RC—Ir—I(1)	119.1(1)	Ir—P—C(21)	122.0(7)
I(1)—Ir—P	95.8(2)	C(9)—P—C(15)	104.5(8)
I(1)—Ir—C(6)	90.6(8)	C(9)—P—C(21)	103.8(8)
P—Ir—C(6)	97(1)	C(15)—P—C(21)	100.3(9)
Ir—C(6)—S	124(2)	C(1)—C(2)—C(3)	105(3)
Ir—C(6)—C(7)	114(2)	C(2)—C(3)—C(4)	109(3)
S—C(6)—C(7)	121(2)	C(3)—C(4)—C(5)	109(4)
C(6)—S—C(8)	111(2)	C(4)—C(5)—C(1)	111(3)
		C(5)—C(1)—C(2)	106(3)

RC is the point at the center of the Cp ring

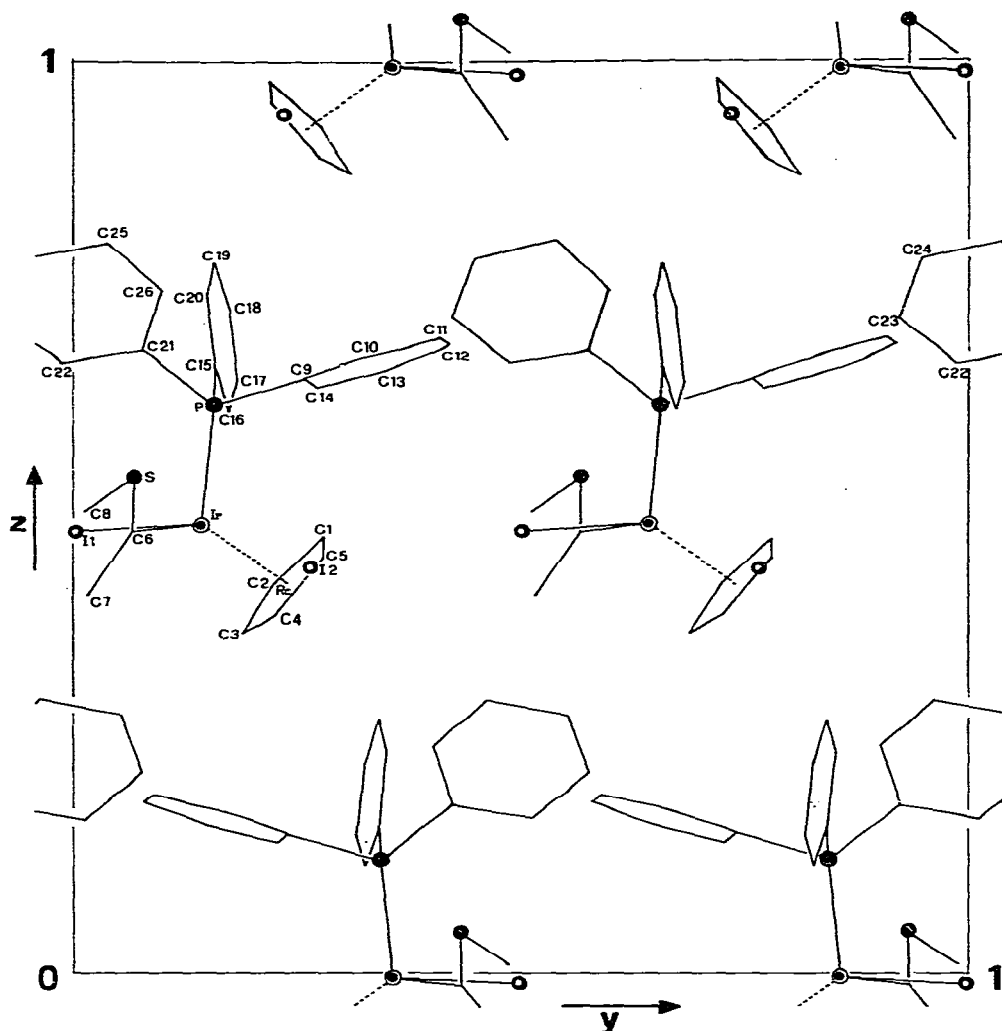


Fig. 2. Unit cell content as seen down [100].

and iodine as the anion. The cation is shown in Fig. 1 and a view of the unit cell content along [100] together with the atom numbering scheme is shown in Fig. 2. Selected interatomic distances and angles are given in Table 3.

The coordination about the iridium atoms can be considered either as distorted tetrahedral, the coordination positions being occupied by the cyclopentadienyl ring center, the phosphorus, the iodine I(1) and the carbon atom C(6) of the SMeSMe ligand, or as distorted octahedral with the  $\eta^5\text{-C}_5\text{H}_5$  bonded ring occupying three coordination sites. The data in Table 3 for interligand bond angles subtended at the iridium atom show for the first case a rather distorted tetrahedron with the phosphine, the CMeSMe group and the coordinated iodine atom bent away from the Ir—Rc vector by 123.5(2), 122.9(2) and 119.1(1)°, respectively, as a consequence of the steric hindrance of the coordinated bulky  $\eta^5\text{-C}_5\text{H}_5$  and  $\text{PPh}_3$  ligands. For the second case, a distorted octahedron, the

angles between the coordinated C(6), I(1) and P atoms are not far from the ideal value of  $90^\circ$  ranging between 91 and 97 degrees, the other three coordination sites being occupied by the  $\eta^5\text{-C}_5\text{H}_5$  ligand.

The triphenylphosphine iridium bond distance 2.280(7) Å is comparable with the values reported in  $\text{Cu}_4\text{Ir}_2(\text{PPh}_3)(\text{C}\equiv\text{CPh})_8$  [14] (averaged value 2.258(14) Å) and larger than the value of 2.216(9) Å reported for  $\text{Ir}(\text{PPh}_3)(\text{CH}_2)_4(\eta^5\text{-C}_5\text{Me}_5)$  [15], in general it lies among the shorter distances previously reported for iridium phosphorous distances [14], indicating some  $d_\pi\text{-}d_\pi$  back donation from iridium to phosphorus. The Ir—I(1) bond 2.651(2) Å is comparable to values reported for the terminal Ir—I bonds, viz. 2.68(1) and 2.69(1) Å, in the cation  $\text{Ir}_2\text{I}_5[\text{PMePh}_2]_4$  [16], and to the values 2.672(2) and 2.684(2) reported for  $\text{IrI}_2(\text{CO})(\text{C}_{10}\text{H}_8\text{N}_2)(\text{C}_2\text{H}_3\text{O}_2)$  [17].

The Ir—C(6) bond distance 2.03(2) Å is consistent with the calculated value of 2.06 Å based on the covalent radius of an  $sp^2$ -hybridized carbon ( $r_c$  0.74 Å) and the  $r_{\text{Ir}}$  1.32 Å for the iridium(III). This value is obtained by assuming the Ir—I(1) bond to be a pure  $\sigma$  bond, and assuming a covalent radius of 1.33 Å for the iodine. A bond order of unity may also be attributed to the Ir—C(6) bond and comparison with some selected Ir—C bonds in Table 4 shows that the present distance lies at the lower limit.

Turning to the carbenoid C(Me)SMe ligand we note that the iridium is not perfectly coplanar with S—C(6)—C(7) ( $\Delta_{\text{Ir}}$  0.22 Å), also the angles involving C(6) (Ir—C(6)—C(7)  $114^\circ$ , Ir—C(6)—S  $124^\circ$  and S—C(6)—C(7)  $121^\circ$ ) suggest for C(6) may a slightly distorted  $sp^2$ -hybridization state; the C(6)—C(7) distance 1.49 Å corresponds to the value expected for a  $\text{C}(sp^2)\text{-C}(sp^3)$  bond

TABLE 4  
SELECTED Ir—C BOND DISTANCE

Complex	Dist. (Å)	Ref.
$\text{Cu}_4\text{Ir}(\text{PPh}_3)_2(\text{C}\equiv\text{CPh})_8$	2.018(27)	[14]
	2.067(29)	
	1.982(26)	
	2.055(23)	
	2.109(21)	
	2.015(25)	
	2.039(22)	
	2.064(34)	
	2.044(39) <sup>a</sup>	
Ir—C(av)		
$\text{Ir}(\text{PPh}_3)(\text{CH}_2)_4(\eta^5\text{-C}_5\text{Me}_5)$	2.10(4)	[15]
	2.14(4)	
$[\text{Ir}(\text{C}_3\text{Ph}_3)\text{Cl}(\text{CO})(\text{PMe}_3)_2][\text{BF}_4] \cdot \text{CH}_2\text{Cl}_2$	2.099(15)	[19]
	1.990(15)	
$(\text{PhCHCH}_2\text{COPh})\text{IrCl}_2[(\text{Me})_2\text{SO}]_2$	2.16(2)	[20]
$\text{Ir}[\text{Me}]\text{I}(\text{NO})(\text{PPh}_3)_2$	2.05(4)	[21]
$(\text{bipy})(\text{CO})\text{Ir}(\text{CO}_2\text{Me})\text{I}_2$	2.05(4)	[17]

<sup>a</sup> e.s.d.'s on average bond lengths are calculated from the expression

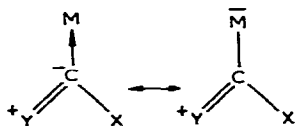
$$\sigma = \left\{ \left[ \sum_{N=1}^{i=N} (X_i - \bar{X})^2 / (N-1) \right]^{1/2} \right.$$

where  $X_i$  is the  $i_{\text{th}}$  bond length and  $\bar{X}$  is the mean of  $N$  equivalent bond lengths.

1.51 Å, while the S—C(6) bond, 1.56(3), and S—C(8) bond, 1.80(3) Å, compare favourably with the values reported for a typical C=S double bond (1.61 Å) and C—S single bond (1.81 Å), respectively, as in derivatives of thiourea and thiocarbazono [18].

A comparison of the present C(6)—S—C(8) skeleton with that in pentacarbonyl(phenylthio)carbenechromium [6] shows that while the S—C(8) distance 1.80(3) Å is comparable with that of 1.78(3) found in the latter compound, the S—C(6) distance 1.56(3) is 0.13 Å shorter than that in the analogous methyl phenylthiocarbene derivative, and is closer to the values of 1.592(8) and 1.587(7) observed for bridging CS groups in *cis*[CpFe(CS)CO]<sub>2</sub> [22] than to the value for bridging CS—Et group (C<sub>bridge</sub>—S 1.666(11)) in [Cp<sub>2</sub>Fe<sub>2</sub>(CO)<sub>3</sub>(CS—Et)]BF<sub>4</sub> [23]. In terms of the Fischer's interpretation of the bonding in transition metal—carbene complexes [24], this suggests strong *p*<sub>π</sub>—*p*<sub>π</sub> interaction between one of the lone pairs of the sulphur atom and the unused *p*-orbital of the carbene carbon, and indicates, in addition, that the carbene carbon atom interacts more strongly with this α-sulphur than with the iridium, and more strongly than with an α nitrogen or α-oxygen atom.

These observations also suggest that in terms of the extreme electronic configurations given by F.A. Cotton and C.M. Lukehart [5] for the bonding in a complexed carbene molecule of the type  $\begin{matrix} X \\ Y \end{matrix} > C$  our complex is best described by the following resonance:



where Y in our case is the sulphur.

### Acknowledgement

We thank Prof. M.F. Lappert for helpful comments.

### References

- 1 J.P. Collman and W.R. Roper, *Adv. Organometal. Chem.*, 7 (1968) 63; L. Vaska, *Acc. Chem. Res.*, 1 (1968) 335.
- 2 A.J. Oliver and W.A.G. Graham, *Inorg. Chem.*, 9 (1970) 243.
- 3 A.J. Oliver and W.A.G. Graham, *Inorg. Chem.*, 9 (1970) 2653.
- 4 F. Faraone, G. Tresoldi and G.A. Loprete, *J. Chem. Soc. Dalton*, (1979) 933.
- 5 F.A. Cotton and C.M. Lukehart, *Progress in Inorg. Chem.*, 16 (1972) 574.
- 6 R.J. Hoare and O.S. Mills, *J. Chem. Soc. Dalton*, (1972) 653.
- 7 A.C.T. North, D.C. Phillips and F.S. Mathews, *Acta Cryst. A*, 24 (1968) 351.
- 8 *International Tables for X-Ray Crystallography*, 2nd Edn., Vol. 4, p. 102, Kynoch Press, Birmingham.
- 9 D.T. Cromer and J.B. Mann, *Acta Cryst. A*, 24 (1968) 321.
- 10 R.F. Stewart, *J. Chem. Phys.*, 42 (1965) 3175.
- 11 D.T. Cromer and D. Liberman, *J. Chem. Phys.*, 53 (1970) 1891.
- 12 SHELX 76, G. Sheldrick, *Computing System*, University of Cambridge, 1976.
- 13 *The X-Ray 72 System*, Version of April 1973, TR 192, University of Maryland.
- 14 M.R. Churchill and S.A. Bezman, *Inorg. Chem.*, 13 (1974) 1418.
- 15 P. Diversi, G. Ingrosso, A. Lucherini, W. Porzio and M. Zocchi, *J. Chem. Soc. Chem. Commun.*, (1977) 811.



- 16 M.J. Nolte, E. Singleton and E. Van der Stock, *Acta Cryst. B*, **34** (1978) 1684.
- 17 V.G. Albano, P.L. Bellon and M. Sansoni, *Inorg. Chem.*, **8** (1969) 298.
- 18 F. Iwasaki, *Acta Cryst. B*, **30** (1974) 2503; C. Lecompte, A. Aubry, J. Protas, G. Bcussard and M. Marrand, *Acta Cryst. B*, **30** (1974) 1992.
- 19 R.M. Tuggle and D.L. Weaver, *Inorg. Chem.*, **11** (1972) 2237.
- 20 M. McPartlin and R. Mason, *Chem. Commun.*, (1967) 545.
- 21 D.M. Mingos, W.T. Robinson and J.A. Ibers, *Inorg. Chem.*, **10** (1971) 1043.
- 22 J.W. Dunker, J.S. Finer, J. Clardy and R.J. Angelici, *J. Organometal. Chem.*, **114** (1976) C49.
- 23 R.E. Wagner, R.A. Jacobson and R.J. Angelici, *J. Organometal. Chem.*, **148** (1978) C35.
- 24 E.O. Fischer, *Advances in Organometallic Chemistry Vol. 14*, Academic Press, New York, 1976, p. 6.