Crystal Structure of Dicarbonyl(thiocarbonyl)bis(triphenylphosphine)-iridium(I) Hexafluorophosphate–Acetone †

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Crystals of the title compound are monoclinic with a = 15·199, b = 23·814, c = 13·383 Å, β = 119·07°, Z = 4 space group $P2_1/m$. 7113 visually estimated intensities were used, and the structure refined to R 9·83%. There are two crystallographically independent cations each possessing a mirror plane. The iridium atoms are at the centre of a trigonal bipyramid with the PPh_3 ligands at the apices and the CO and CS groups co-planar with the iridium atoms in the equatorial plane. Mean thiocarbonyl bonding parameters are: Ir–C(S) 1·867, C–S 1·511 Å; Ir–C–S = 178·2°. The σ and π bonding properties of the CO and CS groups are compared.

THE first transition-metal complexes containing a thiocarbonyl ligand were reported in 1966,[1] and in the same year the structure of $Rh(CS)Cl(PPh_3)_2$ was published.[2] No further structure determinations of transition-metal complexes containing a unidentate CS ligand have been described, and the prime interest of this work is thus the mode of bonding and bonding parameters of the thiocarbonyl ligand. It was observed [2] that the Rh–C bond length in $Rh(CS)Cl(PPh_3)_2$ (1·787 Å) was shorter than those in the related compounds $RhH(CO)(PPh_3)_3$ [3] (1·81 Å) and $Rh(CO)Cl(PPh_3)_2$ [2] (1·86 Å). This shortening was attributed to the increased amount of back-bonding possible with CS. In the present structure it is possible to compare Ir–C(S) and Ir–C(O) bond lengths within the same complex. Also of interest is the effect

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† Reprints not available.

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of the CS group on the geometry of the ligands around the metal atom.

EXPERIMENTAL

Crystal Data.—$C_{39}H_{24}F_6IrO_2P_3S,C_3H_6O$, $M = 1013{\cdot}2$, Monoclinic, $a = 15{\cdot}199(9)$, $b = 23{\cdot}814(12)$, $c = 13{\cdot}383(12)$ Å, $\beta = 119{\cdot}07(6)^\circ$, $U = 4233{\cdot}7$ Å^3, $D_m = 1{\cdot}61$, $Z = 4$, $D_c = 1{\cdot}589$ g cm^{-3}, $F(000) = 1992$. Space group $P2_1/m$ or $P2_1$ (from absences). Cu-K_α radiation, μ(Cu-K_α) $= 81{\cdot}9$ cm^{-1}.

Yellow crystals, approximately cubic in form, were prepared by the method of ref. 4. The compound was originally formulated as having no solvent of crystallization, but a significant difference between observed and calculated densities was noted ($D_m > D_c$). The acetone molecule was only revealed in the final stages of the structure solution. Densities were measured by flotation in carbon tetrachloride–ethyl iodide.

Initial cell-dimensions were obtained from oscillation and Weissenberg photographs about b and c ($\lambda = 1{\cdot}5418$ Å). More accurate values were obtained later by the α-doublet splitting method[5] [λ(Cu-$K_{\alpha1}$) 1·54051, and λ(Cu-$K_{\alpha2}$) 1·54433 Å]. Intensities were collected from equi-inclination Weissenberg photographs of the $h0$—20, l and $hk0$—3 layers, using Ni-filtered Cu-K_α radiation and the multiple-film technique. The same crystal was used for all photographs and for the preparation of a calibration strip which was used to estimate the intensities. Intensities were brought to a common scale by the method of Rae and Blake.[6] Absorption corrections were made by a method which approximates the crystal to a pseudo-ellipsoid.* 7113 independent reflexions were assigned non-zero intensity.

Structure Determination and Refinement.—The space group was assumed to be $P2_1/m$ and nothing emerged during the course of the analysis to suggest that this assumption is invalid. A three-dimensional Patterson synthesis revealed two crystallographically independent iridium atoms lying in the mirror plane at $y = \frac{1}{4}$. A Fourier synthesis phased on the iridium atoms showed the positions of the axial phosphorus atoms, and of the CO and CS groups which must lie in the mirror plane. Packing considerations and subsequent Fourier syntheses determined the positions of the phenyl rings and the hexafluorophosphate anion. The latter occupies a general position, and thus the asymmetric unit includes one half of each of the independent cations, plus the anion. At this stage, with U 0·05 Å^2 for all atoms, R was 15%.

Anisotropic temperature factors were assigned to the iridium atoms, individual isotropic temperature factors to the phosphorus atoms and to atoms in the CO and CS groups, and overall isotropic temperature factors to the phenyl carbon atoms and to the fluorine atoms. Only 9 variable positional parameters were included for each phenyl group, namely the atomic co-ordinates of 3 alternate carbon atoms. The position of the remaining 3 carbon atoms was determined from the known geometry of the benzene ring. Complex neutral scattering factors[7] were employed, and the weighting scheme was $w = 1/(14{\cdot}38 + F_o + 0{\cdot}0037F_o^2)$ with the constants chosen from an analysis of the variance. Several cycles of least-squares refinement, with the secondary extinction coefficient[8] as a refinable parameter, reduced R to 10·9%.

A difference-Fourier synthesis revealed two sets of 4 distinct peaks, lying in the mirror plane, and occupying holes in the structure. The peaks were attributed to two crystallographically independent acetone molecules. Individual isotropic temperature factors were assigned to the carbon and oxygen atoms of each acetone molecule. 3 cycles of full-matrix least-squares refinement (7113 reflexions) yielded a final R of 9·83%. A final difference Fourier synthesis showed no peak greater than 1·5 eÅ^{-3}.

RESULTS

The final fractional co-ordinates and thermal factors are listed in Tables 1 and 2. The temperature factors of the anion and the acetone molecules suggest little or no disorder. No correction for thermal motion has been applied to the bond lengths and angles. A Table of observed and calculated structure factors is published in Supplementary Publication No. SUP 20468 (43 pp., 1 microfiche).†

The crystal structure of $[Ir(CO)_2(CS)(PPh_3)_2][PF_6],Me_2CO$ consists of well separated monomeric ions with acetone molecules occupying holes. The closest contact between two independent iridium atoms is 7·94 Å, and between a fluorine atom and an iridium atom is 7·98 Å. The geometry of the cation approximates closely to a trigonal bipyramid, which is to be expected for five-co-ordinated complexes of the d^8 platinum metals.[9-20] The triphenylphosphine groups occupy the axial positions, and crystallographic symmetry constrains the iridium atom and the CO and CS groups to lie in the equatorial plane. The mode of bonding of the thiocarbonyl ligand is, as expected, through the carbon atom.[1,2] The CO and CS groups are staggered with respect to the phenyl rings, the latter being eclipsed due to the presence of the mirror plane. Figure 1 shows a projection down b of the asymmetric unit, giving the labelling of the atoms. Figure 2 shows a projection of the structure down c, parallel to the mirror planes. Atoms lying in the mirror plane overlap in the projection and, except for the iridium atoms, are shown as a single solid line of appropriate length. Bond lengths and angles are listed in Table 3.

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

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TABLE 1

Final fractional co-ordinates ($\times 10^4$) with estimated standard deviations in parentheses. The two independent cations are denoted A and B, and the two independent acetone molecules I and II. The phenyl groups are numbered 1—6

Atom	*x/a*	*y/b*	*z/c*
Ir(A)	1553(1)	2500	2837(1)
P(A)	1514(2)	1507(2)	2875(3)
C(A1)	2810(18)	2500	2785(20)
O(A1)	3610(15)	2500	2900(16)
C(A2)	410(17)	2500	1345(19)
O(A2)	−361(15)	2500	430(17)
C(AS)	1492(18)	2500	4194(21)
S(A)	1470(7)	2500	5312(8)
C(11)	2707(18)	1198(10)	3915(20)
C(12)	2917(18)	638(10)	3813(20)
C(13)	3803(18)	393(10)	4638(20)
C(14)	4479(18)	707(10)	5563(20)
C(15)	4268(18)	1267(10)	5665(20)
C(16)	3383(18)	1512(10)	4841(20)
C(21)	1260(18)	1211(10)	1501(20)
C(22)	350(18)	969(10)	768(20)
C(23)	164(18)	775(10)	−304(20)
C(24)	887(18)	823(10)	−642(20)
C(25)	1798(18)	1064(10)	91(20)
C(26)	1984(18)	1258(10)	1163(20)
C(31)	553(18)	1218(10)	3164(20)
C(32)	574(16)	673(10)	3445(18)
C(33)	−190(18)	450(10)	3642(20)
C(34)	−975(18)	772(10)	3557(20)
C(35)	−995(16)	1317(10)	3276(19)
C(36)	−232(18)	1540(10)	3080(20)
Ir(B)	4981(1)	2500	−425(1)
P(B)	5011(2)	1505(1)	−310(2)
C(B1)	3982(15)	2500	111(17)
O(B1)	3455(12)	2500	547(14)
C(B2)	4315(14)	2500	−2074(17)
O(B2)	3881(13)	2500	−3067(15)
C(BS)	6389(17)	2500	407(19)
S(B)	7525(7)	2500	1034(8)
C(41)	6091(16)	1171(10)	−307(20)
C(42)	6334(16)	1314(10)	−1145(20)
C(43)	7075(17)	1015(10)	−1249(18)
C(44)	7573(16)	571(10)	−514(20)
C(45)	7329(17)	428(10)	324(20)
C(46)	6588(18)	728(10)	427(18)
C(51)	5030(18)	1266(10)	984(20)
C(52)	4438(18)	824(10)	973(20)
C(53)	4487(17)	635(10)	1978(20)
C(54)	5129(18)	887(10)	2993(20)
C(55)	5721(18)	1329(10)	3004(20)
C(56)	5672(17)	1518(10)	2000(20)
C(61)	3924(18)	1164(10)	−1483(20)
C(62)	4050(18)	650(10)	−1913(20)
C(63)	3219(18)	378(10)	−2800(20)
C(64)	2264(18)	622(10)	−3257(20)
C(65)	2139(18)	1137(10)	−2827(20)
C(66)	2969(18)	1408(10)	−1940(20)
P(3)	8187(3)	953(2)	6176(4)
F(1)	8020(10)	1409(6)	5274(11)
F(2)	8543(10)	1390(6)	7169(11)
F(3)	9308(10)	811(6)	6407(11)
F(4)	7091(10)	1001(6)	5918(11)
F(5)	7851(10)	479(6)	5205(11)
F(6)	8386(10)	492(6)	7085(11)
O(I)	5775(20)	2500	6954(23)
C(I1)	6529(19)	2500	6829(22)
C(I2)	7608(26)	2500	7848(30)
C(I3)	6399(28)	2500	5647(33)
O(II)	1564(16)	2500	7795(18)
C(II1)	629(20)	2500	7569(23)
C(II2)	−218(33)	2500	6371(37)
C(II3)	501(28)	2500	8620(33)

The P–Ir–P′ angles for the two independent cations are similar (175·8 and 173·2°) and close to the ideal value. Ideally the angles in the mirror plane should be 120° for a trigonal bipyramidal iridium atom. This is not the case, the C(1)–Ir–C(2) angles (111·9 and 110·3°) being considerably smaller for both cations. Moreover cations A and B have significantly different values for the remaining C(1)–Ir–C(S) (123·4 and 130·1°) and C(2)–Ir–C(S) (124·7 and 119·5°) angles. The Ir–P bond lengths (2·367 and 2·372 Å) compare well with values found in related complexes, *e.g.* 2·34

TABLE 2

(*a*) Anisotropic vibrational amplitudes (Å^2 $\times 10^4$) *

Atom	U_{11}	U_{22}	U_{33}	U_{13}
Ir(A)	448(4)	446(5)	443(4)	194(3)
Ir(B)	370(4)	430(4)	307(3)	105(3)

(*b*) Isotropic vibrational amplitudes (Å^2 $\times 10^4$)

Atom	*U*	Atom	*U*	Atom	*U*
P(A)	531(8)	P(B)	456(7)	P(3)	803(12)
C(A1)	719(56)	C(B1)	587(44)	O(I)	1366(84)
O(A1)	940(51)	O(B1)	777(41)	C(I1)	769(61)
C(A2)	677(52)	C(B2)	552(42)	C(I2)	1109(98)
O(A2)	936(51)	O(B2)	851(45)	C(I3)	1222(122)
C(AS)	748(59)	C(BS)	668(51)	O(II)	1093(63)
S(A)	1127(25)	S(B)	1091(24)	C(II1)	798(64)
F(1)—(6)	1209(17)			C(II2)	1423(139)
C(Ph)	735(7)			C(II3)	1239(114)

* In the form $\exp[-2\pi^2(h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12} + \ldots)]$ $(U_{12} = U_{23} = 0)$.

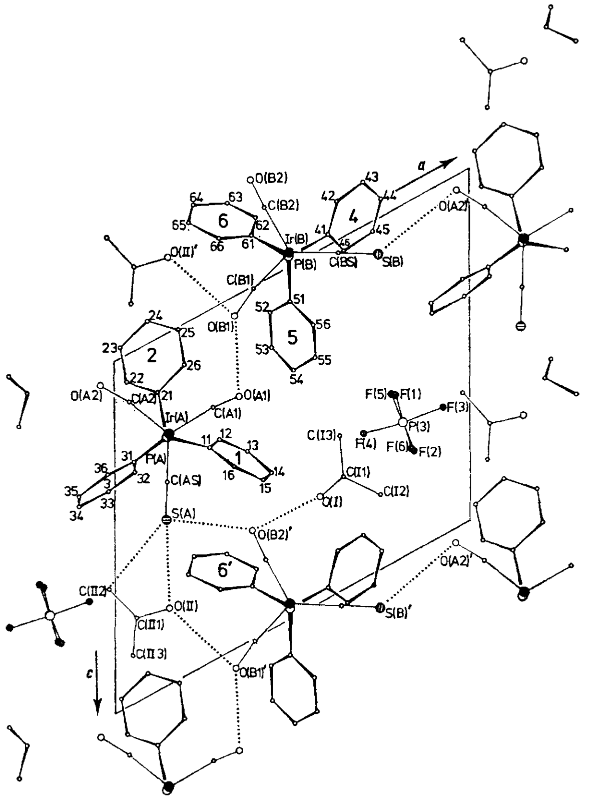

FIGURE 1 Projection down *b* of the asymmetric unit giving the labelling of the atoms and the phenyl groups. Symmetry related atoms are primed. Important intermolecular contacts between atoms lying in the mirror plane are shown by dotted lines

TABLE 3

(*a*) Bond lengths (Å) and angles (°) around the two crystallographically independent iridium atoms. P(A′) and P(B′) are the mirror images of P(A) and P(B)

Cation A		Cation B	
Ir(A)–P(A)	2·367(5)	Ir(B)–P(B)	2·372(4)
Ir(A)–C(A1)	1·945(25)	Ir(B)–C(B1)	1·969(21)
Ir(A)–C(A2)	1·907(25)	Ir(B)–C(B2)	1·930(21)
Mean Ir–CO	1·926	Mean Ir–CO	1·949
Ir(A)–C(AS)	1·863(27)	Ir(B)–C(BS)	1·871(24)
C(A1)–O(A1)	1·150(28)	C(B1)–O(B1)	1·198(25)
C(A2)–O(A2)	1·215(27)	C(B2)–O(B2)	1·161(24)
Mean C–O	1·182	Mean C–O	1·179
C(AS)–S(A)	1·512(26)	C(BS)–S(B)	1·509(24)
P(A)–Ir(A)–C(A1)	92·1(1)	P(B)–Ir(B)–C(B1)	88·3(1)
P(A)–Ir(A)–C(A2)	90·2(1)	P(B)–Ir(B)–C(B2)	93·3(1)
P(A)–Ir(A)–C(AS)	88·0(1)	P(B)–Ir(B)–C(BS)	88·9(1)
P(A)–Ir(A)–P(A′)	175·8(2)	P(B)–Ir(B)–P(B′)	173·2(2)
C(A1)–Ir(A)–C(A2)	111·9(10)	C(B1)–Ir(B)–C(B2)	110·3(9)
C(A1)–Ir(A)–C(AS)	123·4(11)	C(B1)–Ir(B)–C(BS)	130·1(10)
C(A2)–Ir(A)–C(AS)	124·7(11)	C(B2)–Ir(B)–C(BS)	119·5(10)
Ir(A)–C(A1)–O(A1)	171·4(21)	Ir(B)–C(B1)–O(B1)	173·4(17)
Ir(A)–C(A2)–O(A2)	175·4(19)	Ir(B)–C(B2)–O(B2)	177·5(17)
Ir(A)–C(AS)–S(A)	178·6(16)	Ir(B)–C(BS)–S(B)	177·8(15)

(*b*) Selected bond lengths (Å) and angles (°) for the triphenylphosphine ligands, the acetone molecules, and the hexafluorophosphate anion

Cation A		Cation B	
P(A)–C(11)	1·821(25)	P(B)–C(41)	1·823(25)
P(A)–C(21)	1·827(25)	P(B)–C(51)	1·810(25)
P(A)–C(31)	1·819(25)	P(B)–C(61)	1·825(25)
Mean P–C	1·822	Mean P–C	1·819
Ir(A)–P(A)–C(11)	113·2(8)	Ir(B)–P(B)–C(41)	115·2(8)
Ir(A)–P(A)–C(21)	111·1(8)	Ir(B)–P(B)–C(51)	111·6(8)
Ir(A)–P(A)–C(31)	114·5(8)	Ir(B)–P(B)–C(61)	114·1(8)
Mean Ir–P–C	112·9	Mean Ir–P–C	113·6
C(11)–P(A)–C(21)	104·9(12)	C(41)–P(B)–C(51)	105·3(10)
C(11)–P(A)–C(31)	106·8(12)	C(41)–P(B)–C(61)	104·2(12)
C(21)–P(A)–C(31)	105·7(12)	C(51)–P(B)–C(61)	105·6(12)
Mean C–P–C	105·8	Mean C–P–C	105·0

Acetone I		Acetone II	
C(I1)–O(I)	1·236(33)	C(II1)–O(II)	1·301(31)
C(I1)–C(I2)	1·541(42)	C(II1)–C(II2)	1·491(49)
C(I1)–C(I3)	1·495(44)	C(II1)–C(II3)	1·511(45)
C(I2)–C(I1)–O(I)	122·5(27)	C(II2)–C(II1)–O(II)	121·7(28)
C(I3)–C(I1)–O(I)	119·2(28)	C(II3)–C(II1)–O(II)	113·8(26)
C(I2)–C(I1)–C(I3)	118·3(27)	C(II2)–C(II1)–C(II3)	124·5(29)

Anion

P(3)–F(1)	1·551(15)	F(4)–P(3)–F(2)	91·7(8)
P(3)–F(2)	1·563(15)	F(4)–P(3)–F(3)	177·6(8)
P(3)–F(3)	1·585(15)	F(5)–P(3)–F(1)	89·7(8)
P(3)–F(4)	1·532(15)	F(5)–P(3)–F(2)	177·0(8)
P(3)–F(5)	1·605(15)	F(5)–P(3)–F(3)	88·4(8)
P(3)–F(6)	1·555(15)	F(5)–P(3)–F(4)	89·2(8)
Mean P–F	1·565	F(6)–P(3)–F(1)	178·3(8)
F(2)–P(3)–F(1)	93·1(9)	F(6)–P(3)–F(3)	89·4(7)
F(3)–P(3)–F(1)	88·9(7)	F(6)–P(3)–F(4)	90·4(7)
F(3)–P(3)–F(2)	90·6(8)	F(6)–P(3)–F(5)	90·1(9)
F(4)–P(3)–F(1)	91·3(7)		

in $[IrH(NO)(PPh_3)_3][ClO_4]$ [11] and 2·36 Å in $[IrI(CO)(NO)(PPh_3)_2][BF_4],C_6H_6$.[12] The Ir–C(O) lengths (mean 1·926 and 1·949 Å) fall within the range (1·81—2·08 Å) quoted for M–C distances of second- and third-row transition-metal carbonyls.[12] These Ir–C(S) bond lengths (1·863 and 1·871 Å) are the first to be reported.

The mean C–O bond lengths (1·182 and 1·179 Å) are similar to those found in carbonyl derivatives of transition metals.[13,20] The Ir–C(1)–O(1) angles (171·4 and 173·4°) are significantly less than 180°. The values of the C–S bond lengths (1·512 and 1·509 Å) and Ir–C–S angles (178·6 and 177·8°) agree closely with those found in $Rh(CS)Cl(PPh_3)_2$.[2] Mean bond lengths and angles for the triphenylphosphine ligands are: P–C 1·822 and 1·819 Å; Ir–P–C 112·9 and 113·6°; C–P–C 105·8 and 105·0°. Thus the Ir–P–C angles are larger than tetrahedral and the C–P–C angles correspondingly smaller. The values of all these parameters are consistent with those found in the co-ordinated ligand and in triphenylphosphine itself.[21] Bond lengths for the two acetone molecules have high standard deviations ($\sigma >$ 0·03 Å), but are in agreement with the values normally quoted.[22] The carbon and oxygen atoms of acetone I approximate more closely to the ideal *mm* symmetry [C(I3)–C(I1)–O(I) 119·2° and C(I2)–C(I1)–O(I) 122·5°] than in acetone II [C(II3)–C(II1)–O(II) 113·8° and C(II2)–C(II1)–O(II) 124·5°]. The geometry of the hexafluorophosphate anion is typically octahedral with P–F lengths (mean 1·565 Å) in agreement with the standard value (1·58 Å).[23]

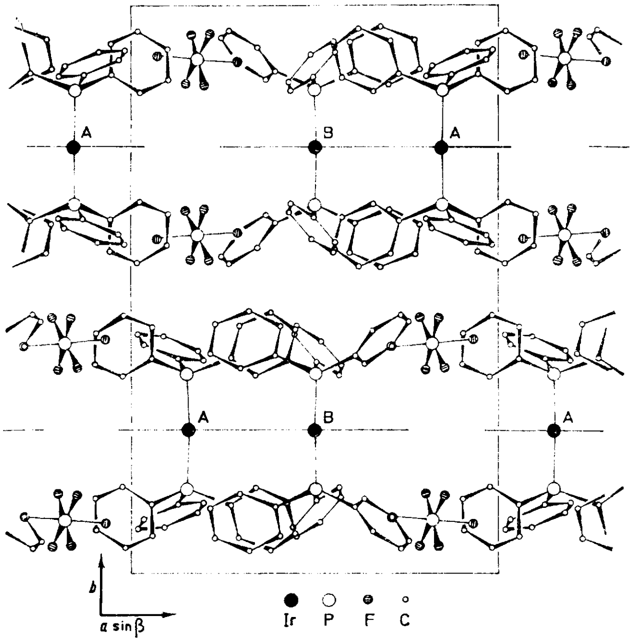

FIGURE 2 Projection of the contents of the unit cell dawn *c*

It can be seen from Figure 2 that the ions are arranged in layers normal to *b*, containing the sequence cation A, cation B, anion, cation A, cation B, anion . . . . An interesting feature is the closely parallel couples formed by overlapping phenyl rings [rings (1) and (6′)] within each layer. Packing within the mirror plane at $y = \frac{1}{4}$ is illustrated in Figure 1, dotted lines showing significant intermolecular contacts (Table 4). All other intermolecular contacts are

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TABLE 4

Values for intermolecular contacts (Å) shown in Figure 1

Atoms	Contact	Sum of van der Waals radii
O(A1) · · · O(B1)	3·041	2·80
O(A2′) · · · S(B)	3·676	3·25
S(A) · · · C(II2)	3·482	3·42
S(A) · · · O(II)	3·257	3·25
S(A) · · · O(B2′)	3·226	3·25
O(B1′) · · · O(II)	3·397	2·80
O(B2′) · · · O(I)	2·866	2·80

at least 0·4 Å greater than the sum of the van der Waals radii for the two atoms.[24]

DISCUSSION

In both cations the Ir–C(S) is shorter than the Ir–C(O) bond length. For A the shortening is significant at the 95% confidence level and for B at the 99% confidence level. This observation provides support for the original conclusion [1] that the CS ligand is both a better σ donor and π acceptor than CO. The C–S bond length (mean 1·511 Å) appears to be longer than the sum of the triple-bond covalent radii (1·47 Å) [24] but shorter than the value in carbon disulphide (1·554 Å).[25] The Ir–C–S angles are close to 180° consistent with the formulation of the CS ligand as a σ donor.

Recent work [11] has shown that electron-pair repulsions between M–X bonds in five-co-ordinated transition-metal complexes, $\mathrm{MH(X)(PPh_3)_3}$ (M = Co, X = $\mathrm{N_2}$; M = Rh, X = CO; and M = Ir, X = $\mathrm{NO^+}$) are responsible for deviations from ideal trigonal bipyramidal geometry. Certainly, in the present structure the S · · · O and O · · · O non-bonded contacts within each cation (5·20—6·53 Å) are too large to account for distortion from the ideal C–Ir–C angle of 120°. Moreover the small C(1)–Ir–C(2) angle found in the cations (111·9 and 110·3°) is consistent with the increased electron density associated with the Ir–C(S) bond. Remaining angular distortions such as the opening of the C(B1)–Ir(B)–C(BS) angle (130·1°), the bent Ir–C(1)–O(1) linkages, and the small C(II3)–C(II1)–O(II) angle (113·8°) in the acetone II molecule are probably the result of packing forces. The dotted lines in Figure 1 show intermolecular contacts which could be responsible for these distortions. Their values are given in Table 4, and it can be seen that some are close to the limit of the sum of the van der Waals radii.

We thank Dr. M. J. Mays and Dr. F. P. Stefanini for the crystals, Dr. G. M. Sheldrick for the use of his computer programmes, the University Computer Laboratory for their facilities, the Elsie Ballot Foundation for financial support (to J. S. F.), and the S.R.C. for the provision of equipment.

[2/1013 *Received, 8th May*, 1972]

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