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THE CRYSTAL AND MOLECULAR STRUCTURE OF THE TETRAPHENYLPHOSPHONIUM SALT OF THE ANION BROMOTRI-μ-CARBONYLOCTACARBONYL-*tetrahedro*-TETRAIRIDATE(—1)

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Summary

Crystals of $[Ir_4Br(CO)_{11}](PPh_4)$ are orthorhombic, space group $P2_12_12_1$, with *a* 13.276(3), *b* 18.347(4), *c* 16.041(4) Å. The structure has been elucidated by the analysis of 2876 observed intensities recorded on an automatic diffractometer, and refined by the least-squares method to R = 0.043. The anion contains a tetrahedral cluster of iridium atoms (mean Ir—Ir 2.710 Å). The carbonyl arrangement differs from that of the parent $Ir_4(CO)_{12}$, and is similar to that known for $Co_4(CO)_{12}$ and $Rh_4(CO)_{12}$, with one terminal CO group in the basal $M_3(CO)_9$ moiety replaced by the bromide ligand; two of the bridging CO groups become markedly asymmetric.

Introduction

Reactions of $Ir_4(CO)_{12}$ with various nucleophiles leading to monosubstituted anionic species have recently been studied [1]. The reaction with a large excess of $(PPh_4)Br$ produces a yellow-orange compound of formula $[Ir_4Br(CO)_{11}]$-(PPh_4). We have carried out an X-ray structural analysis of this species in order to elucidate the stereochemistry of these new compounds, which was expected, on the basis of the IR spectra, to be similar to that of $M_4(CO)_{12}$ species (M = Co, Rh) [2]. A brief account of this study has appeared previously [1].

Experimental

Crystal data. $C_{35}H_{20}O_{11}PBrIr_4$, mol. wt. 1505.2, orthorhombic, *a* 13.276(3), *b* 18.347(4), *c* 16.041(4) Å, U 3907.2 Å^3, D_m 2.53(2) (by flotation), D_c 2.56 g cm^{-3} for Z = 4, $F(000)$ = 3424. Space group $P2_12_12_1$ (No. 19) from systematic

TABLE 1

POSITIONAL AND THERMAL PARAMETERS WITHIN $[Ir_4Br(CO)_{11}](PPh_4)$ [a, b]

Anisotropic atoms

Atom	x	y	z	b_{11}	b_{12}	b_{13}	b_{22}	b_{23}	b_{33}
Ir(1)	−1119(1)	−1738(1)	−556(1)	32(1)	2(1)	−3(1)	24(1)	2(1)	25(1)
Ir(2)	−2001(1)	−2359(1)	−1879(1)	33(1)	0(1)	2(1)	20(1)	−2(1)	25(1)
Ir(3)	−3040(1)	−1373(1)	−931(1)	29(1)	4(1)	5(1)	29(1)	−6(1)	29(1)
Ir(4)	−1520(1)	−904(1)	−1907(1)	35(1)	0(1)	0(1)	21(1)	4(1)	29(1)
Br	−3138(2)	−2472(1)	−3174(1)	51(1)	0(2)	−22(2)	32(1)	−9(1)	35(1)
C(1)	−1383(23)	−2525(15)	179(14)	85(19)	−48(22)	−15(23)	37(8)	42(16)	24(9)
O(1)	−1546(24)	−3002(14)	593(16)	146(24)	−35(27)	−33(32)	56(9)	43(18)	62(12)
C(2)	218(21)	−1921(16)	−880(14)	66(17)	−6(23)	16(22)	42(10)	23(16)	17(8)
O(2)	1048(16)	−1996(14)	−1120(15)	54(12)	37(20)	−4(21)	67(10)	13(19)	60(11)
C(3)	−852(22)	−1023(16)	229(15)	77(20)	0(25)	−9(23)	39(10)	−12(17)	20(8)
O(3)	−681(20)	−605(12)	747(17)	111(19)	−16(21)	−39(29)	38(7)	−14(18)	77(13)
C(4)	−1499(25)	−3289(13)	−1822(15)	124(23)	−36(24)	31(26)	23(7)	3(16)	20(8)
O(4)	−1102(17)	−3847(11)	−1745(16)	86(14)	66(16)	3(26)	34(6)	24(16)	84(13)
C(5)	−3625(23)	−1319(16)	127(17)	70(19)	19(25)	13(26)	34(9)	−2(19)	35(11)
O(5)	−3957(18)	−1259(14)	776(12)	91(15)	25(23)	42(19)	67(10)	−6(15)	31(8)
C(6)	−4190(26)	−1093(20)	−1581(22)	78(22)	34(29)	25(32)	48(12)	7(25)	55(15)
O(6)	−4907(17)	−1008(18)	−1973(16)	78(14)	46(25)	−95(20)	104(14)	38(23)	71(11)
C(7)	−267(25)	−356(17)	−1969(21)	89(21)	17(25)	−65(33)	31(9)	−27(22)	62(14)
O(7)	439(16)	−84(13)	−1991(19)	66(12)	−76(17)	59(26)	54(8)	−2(22)	111(17)
C(8)	−2121(21)	−524(12)	−2900(19)	57(16)	14(18)	−3(28)	15(6)	5(17)	60(14)
O(8)	−2431(22)	−338(14)	−3513(15)	160(24)	47(27)	−76(27)	53(9)	14(18)	48(9)
C(9)	−943(16)	−1891(13)	−2530(13)	36(12)	−18(16)	31(16)	24(7)	−1(13)	22(7)
O(9)	−269(16)	−1987(11)	−3023(13)	83(14)	0(18)	25(21)	43(7)	9(14)	41(8)
C(10)	−3163(22)	−2557(18)	−1094(14)	70(18)	−7(27)	32(21)	52(11)	−5(17)	15(8)
O(10)	−3738(14)	−3007(10)	−861(13)	67(12)	−41(15)	49(18)	34(6)	−16(13)	53(9)
C(11)	−2447(23)	−332(14)	−1025(14)	81(18)	18(22)	−25(23)	30(8)	−15(15)	18(8)
O(11)	−2532(14)	234(10)	−821(14)	54(11)	23(15)	−11(21)	29(6)	−28(14)	71(11)
P	−2881(4)	3641(3)	−1287(3)	34(3)	2(4)	7(4)	18(1)	0(3)	25(2)

Phenyl atoms

Atom	x	y	z	B (Å^2)
CT(11)	−3035(17)	4336(8)	−2050(9)	2.9(4)
CT(12)	−2799(15)	4198(7)	−2880(10)	3.7(5)
CT(13)	−2894(11)	4749(9)	−3472(8)	5.6(7)
CT(14)	−3225(17)	5439(8)	−3232(9)	5.3(7)
CT(15)	−3460(15)	5577(7)	−2402(10)	4.6(5)
CT(16)	−3366(11)	5026(9)	−1810(8)	4.1(5)
CT(21)	−1684(10)	3746(10)	−787(11)	3.4(4)
CT(22)	−1140(12)	4389(8)	−888(11)	4.1(5)
CT(23)	−196(13)	4462(7)	−520(12)	5.4(7)
CT(24)	204(10)	3893(10)	−52(11)	5.0(6)
CT(25)	−339(12)	3250(8)	48(11)	4.1(5)
CT(26)	−1283(13)	3176(7)	−319(12)	3.9(5)
H(112)	−2541	3662	−3066	3.7
H(113)	−2710	4642	−4118	5.6
H(114)	−3298	5868	−3692	5.3
H(115)	−3717	6114	−2215	4.6
H(116)	−3549	5134	−1163	4.1
H(122)	−1452	4832	−1253	4.1
H(123)	226	4964	−598	5.4
H(124)	939	3951	234	5.0
H(125)	−27	2808	414	4.1
H(126)	−1706	2676	−240	3.9

Phenyl atoms

Atom	x	y	z	B (Å^2)
CT(31)	−3869(10)	3694(11)	−525(9)	3.5(4)
CT(32)	−3646(9)	3547(10)	304(10)	2.9(4)
CT(33)	−4407(12)	3563(7)	901(7)	4.5(5)
CT(34)	−5391(10)	3726(11)	667(9)	4.1(5)
CT(35)	−5615(9)	3873(10)	−163(10)	4.5(6)
CT(36)	−4854(12)	3858(7)	−759(7)	3.8(5)
CT(41)	−2972(15)	2763(7)	−1782(10)	3.1(4)
CT(42)	−2093(11)	2413(9)	−2035(12)	4.8(6)
CT(43)	−2148(11)	1749(9)	−2453(12)	5.5(7)
CT(44)	−3082(15)	1435(7)	−2618(10)	5.0(6)
CT(45)	−3961(11)	1786(9)	−2365(12)	5.5(7)
CT(46)	−3906(11)	2450(9)	−1947(12)	3.6(4)
H(132)	−2879	3420	487	2.9
H(133)	−4233	3449	1549	4.5
H(134)	−5983	3739	1132	4.1
H(135)	−6381	4001	−344	4.5
H(136)	−5027	3973	−1406	3.8
H(142)	−1365	2657	−1906	4.8
H(143)	−1464	1477	−2650	5.5
H(144)	−8125	919	−2944	5.0
H(145)	−4688	1542	−2493	5.5
H(146)	−4589	2723	−1750	3.6

[a] All parameters × 10^4, except for the isotropic B factors. [b] The b_{ij} values are the coefficients of $\exp - (h^2b_{11} + k^2b_{22} + l^2b_{33} + hkb_{12} + hlb_{13} + klb_{23})$.

absences ($h00$: $h = 2n + 1$; $0k0$: $k = 2n + 1$; $00l$: $l = 2n + 1$). Mo-K_α radiation (λ 0.7107 Å); μ(Mo-K_α) 156.0 cm^{-1}.

Intensity measurements. A crystal of dimensions 0.34 × 0.39 × 0.43 mm. was mounted on the automatic BASIC diffractometer * and 4018 intensities, corresponding to the $+h$, $+k$, $+l$ octant in the 2ϑ range 7—50°, were collected using graphite-monochromatized Mo-K_α radiation and the ω-scan technique, with a total scan width of 1.0° and a scan speed of 0.05°/sec. The background was measured on both sides of each reflection for half of the peak-scanning time. One standard intensity was measured at periodic intervals and no decay was detected. Integrated intensities were reduced to F_0 values by correction for Lorentz, polarization, and absorption effects, the transmission factors being in the range 0.035—0.074 [3]. 2876 reflections were significantly above background ($\sigma(I)/I < 0.40$) and were used in the structure determination and refinement.

Determination and refinement of the structure. The structure was solved by deconvolution of the Patterson map and, after a preliminary refinement of the iridium atoms parameters, a difference-Fourier synthesis showed the locations of all the non-hydrogen atoms. The refinement was carried out by the least-squares method in the block-diagonal approximation. The phenyl groups of the cation were treated as rigid bodies (D_{6h} symmetry, C—C 1.392 Å) with individual carbon temperature factors. The hydrogen atoms were introduced in the computation of the structure factors but not refined (C—H 1.08 Å, temperature factors equal to those of the corresponding carbon atom). Anisotropic thermal factors were assigned to the phosphorous atom and to all the anion atoms. During the refinements the anomalous dispersion was taken into account for iridium, bromine and phosphorus [4] and the absolute configuration was determined. This, however, is not chemically relevant because the anion has an idealized C_s symmetry. The observations were weighted according to the formula $w = 1/(A + BF_0 + CF_0^2)$, where in final cycles, A, B and C had values 133.1, —1.86 and 8.1 × 10^{-3} respectively and were chosen on the basis of an analysis of $\Sigma w(F_0 - k|F_c|)^2$. Atomic scattering factors were taken from ref. 5 for all the non-hydrogen atoms and from ref. 6 for hydrogen. The final values of the reliability indices were $R = 0.043$ and $R_w = 0.052$. The final difference-Fourier synthesis was flat except for some residual peaks not exceeding 0.8 e/Å^3 near to the metal atoms. The results of the refinement are reported in Table 1. The final list of observed and calculated structure factor moduli can be obtained by application to the authors.

All the computations were carried out on a UNIVAC 1108 computer with local programs.

Discussion

The structure consists of discrete $[\mathrm{Ir_4Br(CO)_{11}}]^-$ anions and $\mathrm{PPh_4^+}$ cations in the ratio 1/1, as shown in Fig. 1 (packing down the a axis).

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* Basic stands for "Basic Siemens Controlled" diffractometer. It was assembed by Prof. P.L. Bellon with a Siemens—Hoppe four circle goniometer and a 16 K Helwlet and Packard computer, partly programmed in the Basic language.

TABLE 2

BOND DISTANCES AND ANGLES WITHIN $[Ir_4Br(CO)_{11}](PPh_4)$

Distances (Å)		Angles (deg.)	
Ir(1)—Ir(2)	2.678(1)	Ir(1)—C(1)—O(1)	178(2)
Ir(1)—Ir(3)	2.704(1)	Ir(1)—C(2)—O(2)	175(2)
Ir(1)—Ir(4)	2.706(1)	Ir(1)—C(3)—O(3)	177(3)
Ir(2)—Ir(3)	2.735(1)	Ir(2)—C(4)—O(4)	173(3)
Ir(2)—Ir(4)	2.745(1)	Ir(3)—C(5)—O(5)	177(3)
Ir(3)—Ir(4)	2.695(1)	Ir(3)—C(6)—O(6)	172(3)
Ir(2)—Br	2.576(3)	Ir(4)—C(7)—O(7)	177(3)
Ir(1)—C(1)	1.90(3)	Ir(4)—C(8)—O(8)	175(3)
Ir(1)—C(2)	1.88(3)	Ir(2)—C(9)—O(9)	145(2)
Ir(1)—C(3)	1.85(3)	Ir(4)—C(9)—O(9)	132(2)
Ir(2)—C(4)	1.83(3)	Ir(2)—C(10)—O(10)	144(2)
Ir(3)—C(5)	1.87(3)	Ir(3)—C(10)—O(10)	134(2)
Ir(3)—C(6)	1.92(3)	Ir(3)—C(11)—O(11)	144(2)
Ir(4)—C(7)	1.95(3)	Ir(4)—C(11)—O(11)	136(2)
Ir(4)—C(8)	1.91(3)	Ir(2)—C(9)—Ir(4)	82(1)
Ir(2)—C(9)	1.95(2)	Ir(2)—C(10)—Ir(3)	81(1)
Ir(4)—C(9)	2.21(2)	Ir(3)—C(11)—Ir(4)	79(1)
Ir(2)—C(10)	2.02(3)	Ir(1)—Ir(2)—Br	158.4(1)
Ir(3)—C(10)	2.19(3)	Ir(3)—Ir(2)—Br	101.9(1)
Ir(3)—C(11)	2.07(3)	Ir(4)—Ir(2)—Br	101.6(1)
Ir(4)—C(11)	2.15(3)	Ir—Ir(1)—C(*cis*)	97 [a]
C(1)—O(1)	1.12(4)	Ir—Ir(1)—C(*trans*)	154 [a]
C(2)—O(2)	1.18(4)	Ir(1)—Ir—C(*cis*)	101 [a]
C(3)—O(3)	1.15(4)	Ir(1)—Ir(3,4)—C(*trans*)	161 [a]
C(4)—O(4)	1.16(4)	C—Ir(1)—C	100 [a]
C(5)—O(5)	1.13(4)	Br—Ir(2)—C(4)	100(1)
C(6)—O(6)	1.15(4)	C(5)—Ir(3)—C(6)	99(1)
C(7)—O(7)	1.06(4)	C(7)—Ir(4)—C(8)	97(1)
C(8)—O(8)	1.12(4)		
C(9)—O(9)	1.21(3)		
C(10)—O(10)	1.18(3)		
C(11)—O(11)	1.10(3)		
P—CT(11)	1.78(2)		
P—CT(21)	1.79(2)		
P—CT(31)	1.80(2)		
P—CT(41)	1.80(2)		

[a] Mean value.

The structure of the anion is depicted in Fig. 2. It contains a tetrahedral cluster bearing eight terminal and three edge-bridging carbonyl groups; the bromine atom is terminally bonded to the basal Ir(2) atom. The ligand stereochemistry is of the type present in $Co_4(CO)_{12}$ [2a] and in $Rh_4(CO)_{12}$ [2b], where a terminal CO group (nearly *trans* with respect to the apical metal atom) in the basal $M_3(\mu\text{-}CO)_3(CO)_6$ moiety, is substituted by the bromide ligand. The overall idealized symmetry of the anion is C_s. The more interesting bond parameters are reported in Table 2.

In the classes of compounds $Ir_4(CO)_{12-n}L_n$ and $[Ir_4(CO)_{12-n}X_n]^{n-}$ a stereochemistry derived from that of $M_4(CO)_{12}$ (M = Co, Rh) is preferred with substituent ligands having poorer π-acceptor ability than CO, such as L = PPh_3 (n = 1, 2, 3) [7,8], LL = 1,2-bis(dimethylarsino)benzene (diars) [9], and X = Cl, Br, I, CN, SCN (n = 1) [1] and X = H (n = 2) [10]. With ligands as L = CN(t-Bu) (n =

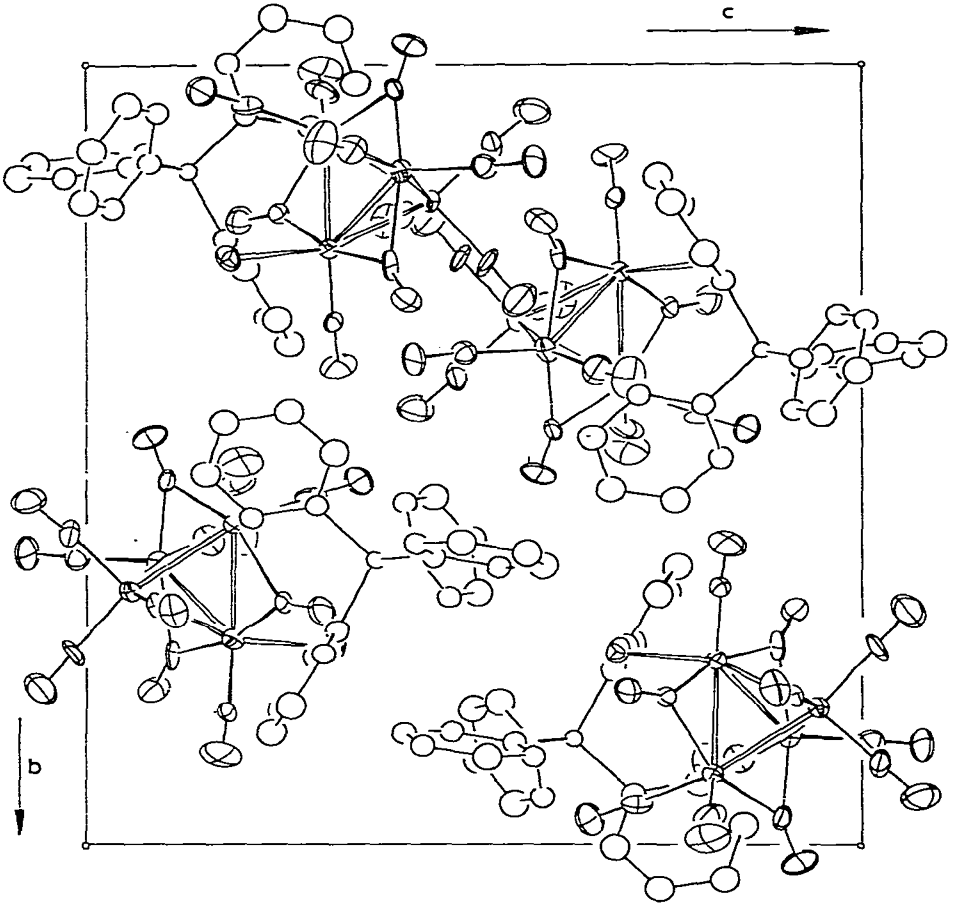


Fig. 1. Projection of the cell content down the *a* axis.

1, 2) [11], having a π-acceptor ability more similar to that of a carbonyl group, a stereochemistry like that of the parent $Ir_4(CO)_{12}$ [12] is present. This behaviour may be rationalized taking into account (i) the supposed higher π-acidity of the bridging with respect to the terminal carbonyls (inferred from the lowering of the CO stretching frequencies and from the lengthening of the C—O bond distances) and, especially, (ii) the fact that bridging carbonyls can transfer charge from one metal to another by becoming asymmetric [1].

The Ir—Ir distances have an overall mean value, 2.710 Å, similar to the corresponding mean values in $Ir_4(CO)_{12}$ (2.693 Å) [12b] and in $Ir_4(CO)_{9-10}(PPh_3)_{3-2}$ (2.73 Å) [8]. However the two carbonyl-bridged edges involving Ir(2) are significantly longer (mean 2.740 Å) than the remaining ones (mean 2.696 Å). The presence of bridging carbonyls has either an insignificant or a moderate shortening effect on the metal—metal bond lengths [13]. We suggest that a shortening of the bridged metal—metal bond can be related to the σ-donor ability of the carbonyl groups and a lengthening to their π-acceptor ability, and the two opposing factors determine the actual metal—metal bond distance. This is illustrated in Scheme 1.

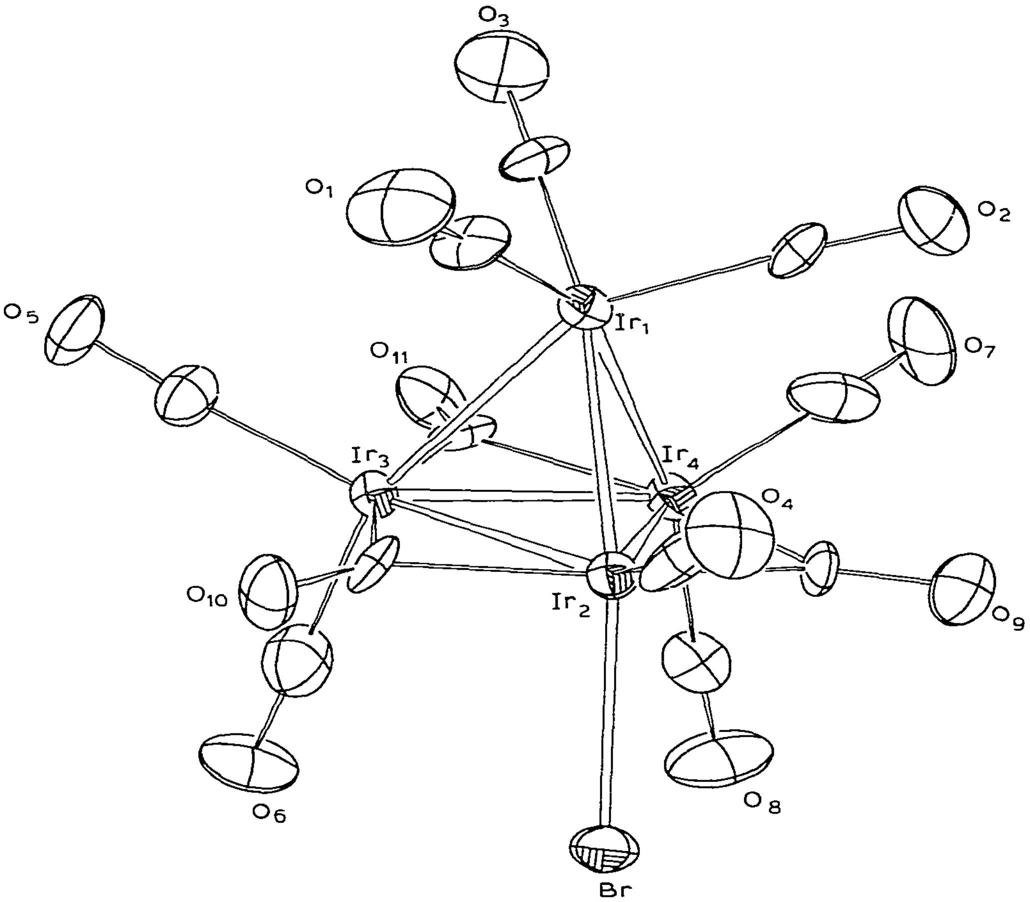
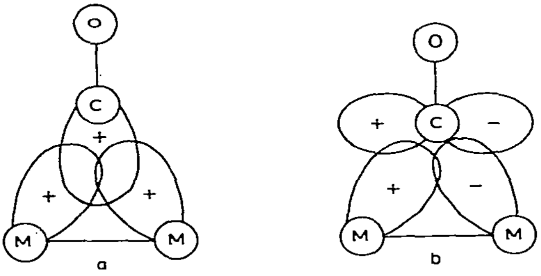


Fig. 2. A view of the anion $[Ir_4Br(CO)_{11}]^-$ with the atom numbering.

SCHEME 1

The bonding mode of an edge-bridging carbonyl group can be described as the sum of a σ donation (a) and a π back-donation (b). The signs of the lobes of the interacting orbitals of the two metal atom are such that in the first case they can give a weak M—M bonding contribution, while in the second case their interaction can be M—M weakly antibonding.



In our compound the presence of a σ- and π-donor bromide ligand causes a large π-back-donation from Ir(2) toward the bridging carbonyl groups and this gives rise to a lengthening of the subtended Ir—Ir bonds. The species $Rh_4(CO)_8$-$[P(OPh)_3]_4$ [14] shows an analogous behaviour, while the anion $[Co_4I(CO)_{11}]^-$ [15], where the iodide ligand substitutes an apical carbonyl group and, therefore, the bridging CO groups are not involved in charge delocalization, shows exactly the opposite behaviour.

The Ir—Br bond length, 2.576(3) Å, is somewhat longer than the sum of the covalent radii (ca. 2.50 Å), but similar to that found, e.g., in $Ir_2Br_2(CO)_2$-$(PPh_3)_2(C_{10}H_4S_4)$ (mean value 2.549(2) Å) [16].

The Ir—C(terminal) bonds range from 1.83(3) to 1.95(3) Å (mean value 1.89 Å) and no significant differences are observed between the basal and the apical ones. The C—O(terminal) bonds are normal (mean value 1.13 Å) and, as expected, shorter than the C—O(bridging) bonds (mean value 1.16 Å). Two of the three edge bridging CO groups, bound to Ir(2), the metal bearing the bromide ligand, are markedly asymmetric. They show Ir(2)—C bonds (mean 1.98 Å) significantly shorter than the Ir(3, 4)—C bonds (mean 2.20 Å). The third CO bridge shows only a very small, though significant, asymmetry (Ir—C 2.07 and 2.15 Å). Asymmetric CO bridges have been found in many polynuclear carbonyl compounds such as, for instance, in $[Ir_4(CO)_{10}H_2]^{2-}$ [10], $[Rh_4(CO)_{11}]^{2-}$ [17], and in many others. The effect can be ascribed principally to charge equalization (see also above) and has been discussed in detail previously [1].

The P—C bond lengths (mean 1.79 Å) in the cation are, within the limits of errors, in close agreement with the literature data. The coordination around the phosphorus atom shows normal C—P—C angles, in the range 107.4(9)—110.6(9)°.

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