Crystal Structure of Carbonylchloro(tetracyanoethylene)bis(triphenylarsine)iridium

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The crystal structure of the title complex has been determined from diffractometer data by the heavy-atom method and refined by least-squares techniques to R 7·8 for 4837 independent reflections. The crystals are monoclinic, space-group $P2_1/n$, with $a = 11{\cdot}644(4)$, $b = 18{\cdot}847(5)$, $c = 17{\cdot}748(5)$ Å, $\beta = 96{\cdot}37(2)°$, $Z = 4$. The co-ordination geometry is trigonal bipyramidal, with carbonyl and chlorine at the apices. The central C–C bond of the tetracyanoethylene ligand is almost parallel to the equatorial plane, and this group is greatly distorted from planarity. The Ir–C bonds and the central C–C bond are probably very slightly shorter than in the analogous bromo-(triphenylphosphine)-complex.

METAL complexes similar to carbonyl(chloro)bis(triphenylphosphine)iridium, $IrCl(CO)(PPh_3)_2$, reversibly or irreversibly add a variety of simple ligands and serve as oxygen carriers or homogeneous catalysts.[1] We have studied the crystal structure of the tetracyanoethylene (tcne) adduct carbonyl(chloro)(tetracyanoethylene)bis(triphenylarsine)iridium, $IrCl(CO)(tcne)(AsPh_3)_2$, in order to clarify the mode of binding of the adduct to the metal in complexes of this type. Since tcne adducts are among the most stable known where the adduct remains intact, the question of possible metal–carbon sigmoid bonding[2] is of interest. Finally, the comparison of the arsine and an isomorphous phosphine complex[3-5] provides the opportunity to see whether the general increased stability of arsine relative to phosphine complexes[6] is paralleled by structural change.

EXPERIMENTAL

A multifaced crystal, with maximum and minimum dimensions *ca.* 0·40 and 0·25 mm, was used for measurement of unit-cell parameters and data collection. The space group was determined from Weissenberg and precession photographs. Unit-cell dimensions were determined from a least-squares fit of $\sin^2\theta$ values by use of 47 reflections measured with Mo-K_α radiation on the diffractometer.

Crystal Data.—$C_{43}H_{30}As_2ClIrN_4O$, $M = 996{\cdot}2$, Monoclinic $a = 11{\cdot}644(4)$, $b = 18{\cdot}847(5)$, $c = 17{\cdot}748(5)$ Å, $\beta = 96{\cdot}37(2)°$, $U = 3871$ Å^3, $D_m = 1{\cdot}71(1)$ (by flotation), $Z = 4$, $D_c = 1{\cdot}711(4)$, $F(000) = 1936$. Space group $P2_1/n$ from systematic absence: $h0l$ for $h + l \neq 2n$ and $0k0$ for $k \neq 2n$. Mo-K_α radiation, $\lambda = 0{\cdot}7107$ Å; μ(Mo-K_α) $= 55{\cdot}44$ cm^{-1}.

All independent reflections to a sin θ value of 0·481 were scanned on a Picker four-circle card-controlled diffractometer using zirconium filtered Mo-K_α radiation and a Na(Tl)I scintillation detector set to accept *ca.* 90% of the K_α pulse distribution. In this range 4392 reflections were scanned over a range in 2θ of 2° at a rate of 1° min^{-1}. Background was measured for 20 s at each end of the scan. Based on an observational threshold of 2σ, 2857 reflections were classed as observed. After the structure was solved, all independent reflections in the sinθ region from 0·481 to 0·632 which had $|F_c| > 27{\cdot}0$ were scanned under the same conditions as for the initial data set. In this region, 2422 reflections were scanned and 1980 were considered observed, giving a total of 4837 observed reflections. Approximately 4280 additional accessible reflections in this region were not scanned. Several standard reflections were repeatedly measured as a check on instrument and crystal stability. A slow overall increase of *ca.* 5% was detected with a scatter of *ca.* 2% between the various standards. All net intensities were corrected for this increase. At the end of data collection, the crystal had yellowed but showed no other change. Each reflection was assigned a standard deviation $\sigma_I = [C + \left(\frac{t_c}{2t_B}\right)^2 (B_1 + B_2)^2]^{\frac{1}{2}}$, and the standard deviation in F_o was chosen as the greater of $\sigma_I/2|F_o|LP$ or $p|F_o|$, where C = total scan count, B_1 and B_2 = background counts, $t_C = 120$ s, $t_B = 20$ s, L and P are the Lorentz and polarization corrections, and p was set equal to 0·025. Before final refinement of the structure, absorption corrections were applied to both $|F_o|$ and σ_F with the use of the Busing program ORABS. The transmission factors ranged between 0·11 and 0·29.

Solution and Refinement.—The structure was solved by the heavy-atom and difference-Fourier methods. As in the isomorphous crystal $IrBr(CO)(tcne)(PPh_3)_2$,[3] evidence for disorder in the positions of the carbonyl and halogen ligands appeared during early stages of least-squares refinement. However, to establish the existence and nature of the disorder beyond doubt, an ordered mode first was refined to convergence resulting in R 8·7% with the iridium, arsenic, and chlorine atoms anisotropic. The C=O distance was 0·81 Å and temperature factors were 2·4 and 6·2 Å^2 for the carbon and oxygen atoms of the carbonyl group. The short C=O distance, vastly different temperature factors, and Fourier and difference maps clearly established that disorder existed and differed considerably from equal populations of the two orientations. Three cycles each of least-squares calculations were then run with two models having disordered carbonyl and chlorine ligands, but with fixed occupancy factors of 0·8 and 0·7 for the preferred orientation. In each case, the Ir–Cl, Ir–C, and C–O distances of the two disorder sites were required to be equal, and only the parameters of the major sites were refined. Minor-site parameters were rederived after each cycle by expressions of the type $x' = 2x_{Ir} - x$, *etc.*, which required both atoms of a disordered pair to be equidistant

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[1] L. Vaska, *Accounts Chem. Res.*, 1968, **1**, 335; J. P. Collman, *Adv. Organometallic Chem.*, 1968, **7**, 53.

[2] G. W. Parshall and F. N. Jones, *J. Amer. Chem. Soc.*, 1965, **87**, 5356; W. H. Baddley, *ibid.*, 1966, **88**, 4545; 1968, **90**, 3705.

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[4] L. Manojlovic-Muir, K. W. Muir, and J. A. Ibers, *Discuss. Faraday Soc.*, 1969, 84.

[5] J. K. Stalick and J. A. Ibers, *J. Amer. Chem. Soc.*, 1970, **92**, 5533.

[6] J. T. Mague and G. Wilkinson, *J. Chem. Soc.* (*A*), 1966, 1736.

from the iridium atom. Major-site isotropic thermal parameters were permitted to refine, and minor-site values reset accordingly.

TABLE 1

Final positional co-ordinates with estimated standard deviations in parentheses

	x	*y*	*z*
Ir	0·07901(5)	0·16688(3)	0·80145(3)
As(1)	0·1063(2)	0·2898(1)	0·8487(1)
As(2)	−0·1291(1)	0·1517(1)	0·7577(1)
Cl	0·1096(5)	0·2039(3)	0·6786(3)
Cl′	0·0484	0·1298	0·9243
C(CO)	0·620(19)	0·1424(11)	0·8992(12)
C′(CO)	0·0966	0·1913	0·7038
O(CO)	0·0446(15)	0·1266(9)	0·9622(8)
O′(CO)	0·1137	0·2071	0·6407
C(1)	0·2428(12)	0·1182(8)	0·8164(7)
C(2)	0·1585(14)	0·0702(7)	0·7785(9)
C(3)	0·3315(14)	0·1490(9)	0·7715(10)
C(4)	0·2964(15)	0·1031(9)	0·8917(9)
C(5)	0·1265(16)	0·0106(8)	0·8218(10)
C(6)	0·1693(16)	0·477(10)	0·7016(10)
N(1)	0·3998(13)	0·1714(10)	0·7378(9)
N(2)	0·3367(14)	0·0894(8)	0·9516(8)
N(3)	0·0980(14)	−0·0387(9)	0·8552(10)
N(4)	0·1782(16)	0·0319(10)	0·6401(9)
C(111)	0·2664(14)	0·2983(8)	0·8901(11)
C(112)	0·3002(17)	0·2651(11)	0·9603(11)
C(113)	0·4217(23)	0·2683(15)	0·9931(15)
C(114)	0·4936(22)	0·3048(15)	0·9594(17)
C(115)	0·4658(23)	0·3414(14)	0·8909(18)
C(116)	0·3423(19)	0·3363(13)	0·8534(18)
C(121)	0·0777(17)	0·3720(9)	0·7824(10)
C(122)	0·0164(23)	0·4258(13)	0·8027(15)
C(123)	−0·0081(23)	0·4871(14)	0·7512(16)
C(124)	0·0316(22)	0·4862(13)	0·6860(15)
C(125)	0·1111(28)	0·4267(15)	0·6651(16)
C(126)	0·1380(24)	0·3685(12)	0·7178(13)
C(131)	0·0215(16)	0·3169(9)	0·9343(8)
C(132)	−0·0842(16)	0·2843(11)	0·9411(10)
C(133)	−0·1469(19)	0·3052(13)	1·0009(12)
C(134)	−0·1006(22)	0·3617(15)	1·0504(12)
C(135)	0·0002(24)	0·3938(13)	1·0397(11)
C(136)	0·0653(20)	0·3709(11)	0·9816(11)
C(211)	−0·2212(13)	0·2278(8)	0·7096(9)
C(212)	−0·3308(17)	0·2179(11)	0·6799(13)
C(213)	−0·3939(18)	0·2733(12)	0·6455(13)
C(214)	−0·3495(17)	0·3378(10)	0·6416(12)
C(215)	−0·2308(25)	0·3473(12)	0·6148(17)
C(216)	−0·1704(19)	0·2931(10)	0·7027(12)
C(221)	−0·2188(13)	0·1192(9)	0·8392(8)
C(222)	0·3108(15)	0·1589(10)	0·8577(10)
C(223)	−0·3691(18)	0·1331(12)	0·9175(12)
C(224)	−0·3306(23)	0·0703(13)	0·9562(12)
C(225)	−0·2368(18)	0·0327(12)	0·9341(11)
C(226)	−0·1792(16)	0·0561(10)	0·8769(10)
C(231)	−0·1533(13)	0·0754(8)	0·6810(9)
C(232)	−0·2049(20)	0·0127(11)	0·6472(13)
C(233)	−0·2261(25)	−0·0345(12)	0·6342(14)
C(234)	−0·1919(20)	−0·0219(12)	0·5657(13)
C(235)	−0·1378(17)	0·0403(10)	0·5523(10)
C(236)	−0·1148(18)	0·0876(10)	0·6105(9)

Primed atomic co-ordinates are derived from those of the major (unprimed) disorder sites by $x'_{\mathrm{Cl}} = 2x_{\mathrm{Ir}} - x_{\mathrm{Cl}}$, *etc.*

The refined C–O distance was used to choose the most reasonable model. This distance appeared to be converging toward values of 1·01 and 1·16 Å for occupancy factors of 0·8 and 0·7. Since the latter value is approximately that found in similar structures, this model was chosen and further refinement proceeded with a fixed occupancy factor of 0·7. All atoms except carbon and oxygen were permitted to refine anisotropically. The disordered atoms were refined with temperature factors and interatomic distances of the two sites required to be equal, as already described. The final atomic parameters, corresponding to *R* 7·8%, appear in Tables 1 and 2.

TABLE 2

Final anisotropic temperature factors ($\times 10^4$) [a] with estimated standard deviations in parentheses

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ir	39·0(3)	20·0(1)	20·9(1)	−1·8(6)	−3·0(4)	0·0(4)
As(1)	45·0(13)	22·1(5)	31·6(6)	−6·9(14)	−5·9(15)	−9·0(10)
As(2)	34·6(12)	20·9(5)	28·0(5)	−5·9(13)	−7·4(14)	2·0(8)
Cl	71(5)	36(2)	23(2)	2(5)	4(5)	3(8)
C	3·12(41) [b]					
O	4·56(36) [b]					
C(1)	31(10)	36(5)	24(4)	34(12)	−21(12)	−9(8)
C(2)	68(13)	16(4)	39(6)	31(12)	−1(15)	−15(8)
C(3)	44(12)	34(6)	52(7)	−20(14)	15(16)	8(11)
C(4)	78(15)	34(6)	29(5)	17(16)	1(15)	10(10)
C(5)	100(17)	17(5)	52(7)	0(15)	−21(19)	3(10)
C(6)	74(16)	38(6)	53(7)	8(18)	12(19)	−23(12)
N(1)	59(12)	67(8)	55(6)	−31(18)	22(15)	5(13)
N(2)	102(15)	33(5)	47(6)	24(15)	−25(16)	20(9)
N(3)	86(15)	36(6)	83(9)	−7(16)	−29(20)	21(12)
N(4)	145(21)	67(8)	45(6)	17(22)	27(14)	−43(12)
C(111)	43(13)	20(5)	80(9)	−8(14)	−20(19)	−33(11)
C(112)	92(18)	52(7)	29(7)	55(19)	−84(19)	−58(12)
C(113)	117(25)	78(11)	108(13)	57(28)	−69(32)	−97(19)
C(114)	97(23)	59(11)	117(16)	28(26)	15(33)	−11(23)
C(115)	120(25)	58(11)	129(17)	−41(29)	51(35)	−36(23)
C(116)	54(16)	49(9)	145(18)	−29(23)	−16(30)	−21(22)
C(121)	107(18)	21(5)	49(7)	−28(16)	9(20)	12(10)
C(122)	139(25)	36(8)	103(14)	34(24)	−77(31)	8(18)
C(123)	137(29)	62(10)	114(14)	14(30)	2(34)	87(20)
C(124)	169(26)	51(8)	106(13)	126(21)	−62(32)	64(17)
C(125)	247(38)	72(11)	76(12)	−139(31)	−37(37)	34(20)
C(126)	240(30)	62(8)	59(10)	−167(23)	−27(30)	30(18)
C(131)	99(15)	36(6)	21(4)	42(16)	25(14)	−10(8)
C(132)	73(16)	54(8)	46(7)	41(19)	42(17)	18(13)
C(133)	102(19)	77(10)	50(8)	101(22)	8(22)	27(16)
C(134)	168(24)	103(12)	44(8)	169(25)	56(23)	30(17)
C(135)	216(32)	75(10)	34(7)	124(28)	−37(25)	−37(14)
C(136)	145(20)	47(7)	41(7)	71(22)	−27(22)	−31(13)
C(211)	43(12)	19(4)	41(6)	8(12)	−23(14)	4(9)
C(212)	67(16)	37(7)	96(11)	7(18)	−81(22)	33(15)
C(213)	72(18)	53(9)	73(10)	−15(21)	−51(23)	31(16)
C(214)	98(17)	24(5)	75(9)	25(18)	−63(21)	−4(13)
C(215)	199(30)	37(9)	126(15)	50(25)	−183(32)	−15(19)
C(216)	119(20)	22(5)	77(9)	−9(18)	−96(22)	−6(13)
C(221)	49(11)	30(5)	33(5)	−9(13)	30(13)	8(9)
C(222)	67(13)	39(6)	46(6)	−20(17)	41(15)	−28(11)
C(223)	95(19)	51(8)	59(8)	−22(21)	57(20)	−8(15)
C(224)	132(23)	65(10)	54(8)	−71(24)	50(23)	0(16)
C(225)	116(20)	65(9)	44(7)	−93(21)	−1(21)	13(14)
C(226)	87(16)	36(16)	41(6)	−41(17)	4(18)	16(11)
C(231)	51(12)	21(4)	35(5)	3(13)	−18(14)	−17(8)
C(232)	164(24)	31(6)	85(10)	−76(20)	93(25)	−45(14)
C(233)	301(35)	41(8)	78(10)	−121(26)	155(29)	−37(16)
C(234)	109(22)	43(8)	72(10)	−2(23)	10(25)	−30(15)
C(235)	120(20)	32(6)	36(6)	23(19)	−44(19)	−13(11)
C(236)	104(19)	47(7)	29(6)	−14(20)	4(18)	−14(11)

[a] The thermal expression has the form $\exp-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)$. [b] These are isotropic parameters *B* in Å^2.

Observed and calculated structure factors corresponding to these parameters are noted in Supplementary Publication No. SUP 20390 (4 pp., 1 microfiche).*

Atomic form factors, corrected for real and imaginary components of anomalous dispersion, were taken from ref. 7. Major computing programs used were BLSA, a

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* See Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. supplied as full size copies).

[7] 'International Tables for *X*-Ray Crystallography,' vol. III, 1962, pp. 202, 215.

local version of UCLALSI by Gantzel, Sparks, and Trueblood, and FOUR by Fritchie.

DISCUSSION

A stereoscopic picture of the complex is given in Figure 1, the numbering scheme in Figure 2, and a view of the packing in Figure 3. The geometry is trigonal bipyramidal with axial carbonyl and chlorine ligands, if one considers the tcne group to occupy a single co-ordination site. The C=C bond of tcne is nearly in the $IrAs_2$ plane, with an angle of 3·6° between the $IrAs_2$ and IrC_2 planes. This compares with 0·7° for the isomorphous compound $IrBr(CO)(tcne)(PPh_3)_2$.[4]

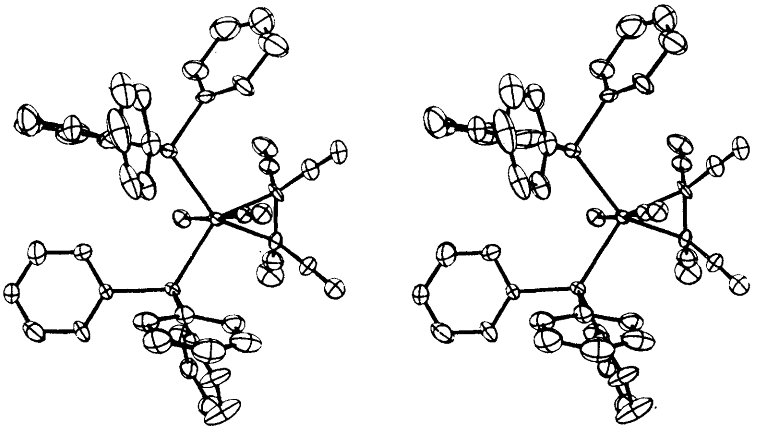

FIGURE 1 The molecular structure

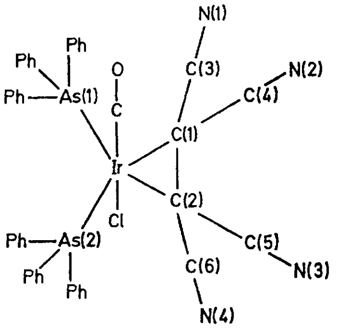

FIGURE 2 The phenyl carbon atoms are labelled C(*ijk*), where *i* designates the arsenic to which the phenyl is attached, *j* the phenyl ring, and *k* the carbon atom in the ring, with carbon 1 bound to arsenic and the others labelled sequentially

TABLE 3

Selected interatomic distances (Å) with estimated standard deviations in parentheses

Ir–As(1)	2·478(2)	C(2)–C(6)	1·45(2)
Ir–As(2)	2·481(2)	C(3)–N(1)	1·13(3) [c]
Ir–Cl [b]	2·354(5)	C(4)–N(2)	1·13(3)
Ir–C(CO)	1·826(14)	C(5)–N(3)	1·17(3)
Ir–C(1)	2·110(18)	C(6)–N(4)	1·15(3)
Ir–C(2)	2·104(15)	As(1)–C(111)	1·93(3)
C(CO)–O(CO)	1·20(2)	As(1)–C(121)	1·96(3)
C(1)–C(2)	1·447(23) [a]	As(1)–C(131)	1·95(2)
C(1)–C(3)	1·44(2) [b]	As(2)–C(211)	1·93(2)
C(1)–C(4)	1·49(2)	As(2)–C(221)	1·97(2)
C(2)–C(5)	1·43(2)	As(2)–C(231)	1·98(2)

[a] The corresponding distance in the Br complex is 1·506(15) Å.[4] [b] The range in the Br complex is 1·447(17)—1·455(18) Å. [c] The range is 1·108(14)—1·157(16) Å in the Br complex.

As in the bromo(phosphine) complex, the tcne ligand is among the most distorted yet studied in comparison with the neutral molecule, although the distortion is slightly less for the arsine complex. The angle between least-squares planes of the two $C(CN)_2$ groups, defined by Ibers as α, and with a value of 0° in free tcne and 70·4° in the bromo(phospine) complex,[4] is 68·5° in the chloroarsine complex. Correspondingly, the angle between the C=C bond and the $C(CN)_2$ plane, which Ibers defines as β, has values of 90, 54·8, and 56·0° in the three compounds. The Ir–C and C=C distances in the two complexes (given in Table 3) are also slightly different, but these differences are of marginal statistical significance. In fact if, as appears to be the general rule,

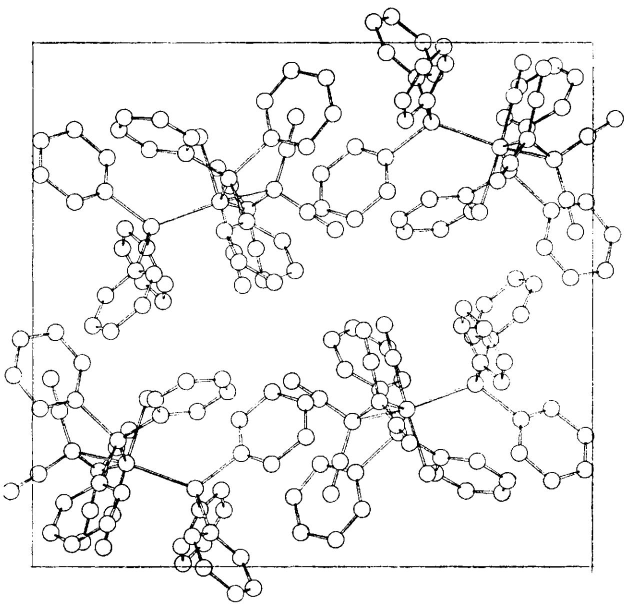

FIGURE 3 Molecular packing, as shown in the [100] projection: *b* extends from left to right, and *c* vertically downward

TABLE 4

Selected interatomic angles (°) with estimated standard deviations in parentheses

As(1)–Ir–As(2)	107·43(6)	Ir–C(1)–C(3)	115·8(12)
As(1)–Ir–Cl	90·0(1)	Ir–C(1)–C(4)	119·7(12)
As(1)–Ir–C(CO)	86·0(4)	Ir–C(2)–C(5)	115·3(14)
As(2)–Ir–Cl	89·3(1)	Ir–C(2)–C(6)	121·5(11)
As(2)–Ir–C(CO)	93·6(5)	C(2)–C(1)–C(3)	118·1(14)
Cl–Ir–C(CO)	176·3(5)		
As(1)–Ir–C(1)	106·4(4)	C(2)–C(1)–C(4)	120·7(15)
As(2)–Ir–C(2)	106·0(4)	C(1)–C(2)–C(5)	116·4(15)
Cl–Ir–C(1)	91·0(5)	C(1)–C(2)–C(6)	119·7(14)
Cl–Ir–C(2)	87·8(4)	C(1)–C(3)–N(1)	179·2(19)
C(1)–Ir–C(2)	40·1(6)	C(1)–C(4)–N(2)	177·9(18)
Ir–C(1)–C(2)	69·7(8)	C(2)–C(5)–N(3)	177·8(21)
Ir–C(2)–C(1)	70·1(8)	C(2)–C(6)–N(1)	178·1(19)

The Ir–As–C angles range from 106·7(8) to 121·9(6)°, mean 115·1° with a root-mean-square deviation of 5·9°. C–C–C Angles range from 113·4(2·4) to 126·4(2·4)°, with a mean root-mean-square deviation of 119·9(2·7)°.

increased adduct stability implies greater metal–ligand electron transfer [1] one would expect arsine [6] to be either a better σ donor or poorer π acceptor than phosphine and hence the C=C distance to be longer in the arsine compound. One would also expect the angular distortions reflected by α to be greater, and that somewhat greater electron density on the metal would lead to a slightly larger radius and hence greater Ir–C distance in the arsine. In all cases the observed, marginal, differences are opposite to these expectations.

The triphenylarsine ligands are essentially as expected. Their geometric parameters are summarized in Tables 3 and 4. Finally, the observed geometry is consistent with McGinnety and Ibers' view of the metal–ligand bonding as being of the classical σ-bond, π*-back-bond type rather than a sigmoid type.

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[2/250 *Received, 7th February,* 1972]