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REACTION OF $[Ir(CO)_3PPh_3]_2$ WITH SUBSTITUTED ACETYLENES. SYNTHESIS, CRYSTAL AND MOLECULAR STRUCTURE OF DIPHENYLACETYLENE/BIS(TRIPHENYLPHOSPHINEDICARBONYLIRIDIUM)BENZENE (1/1)

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Summary

The reaction of $[Ir(CO)_3PPh_3]_2$ with diphenylacetylene in boiling benzene gives the complex $\{[Ir(CO)_2PPh_3]_2(CPh)_2\} \cdot C_6H_6$, whose structure has been determined by X-ray diffraction. The compound is monoclinic, space group $C2/c$, with a 19.714(3), b 14.257(2), c 18.953(5) Å, β 109.85(2)°. The $\{[Ir(CO)_2PPh_3]_2(CPh)_2\}$ structure is similar to that of binuclear carbonylcobalt-acetylene complexes such as $Co_2(CO)_6(\mu\text{-}C_6H_5C_2C_6H_5)$, and consists of two $Ir(CO)_2PPh_3$ moieties bridged by diphenylacetylene with the C≡C bond approximately normal to the Ir–Ir bond, which has a length of 2.689(1) Å.

Introduction

The reactions of $[Ir(CO)_3PPh_3]_2$ (I) with substituted alkyne derivatives yield a variety of products. We have reported [1] the preparation and the structure of a type of 'ferrole' [2] analogue of iridium, obtained from the reaction of I with bis(ethoxycarbonyl)acetylene and, have also described the structure of phenylacetylenebis(triphenylphosphinedicarbonyliridium) (II) [3]. Crystals of compound II contain clathrated molecules of dichloromethane which are disordered in a way that we could not satisfactorily interpret, and the bonding parameters of compound II thus showed relatively high e.s.d.'s. We wish to report here an accurate structural information of the title compound which can be crystallized as an ordered species.

Experimental

Sample preparation

Diphenylacetylene (0.065 g) was added to a suspension of $[Ir(CO)_3PPh_3]_2$ (0.20 g)

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in 50 ml of boiling benzene. After 5 h the orange solution was concentrated to 10 ml and the product was precipitated out by addition of n-hexane (crude yield, 60%). The microcrystalline solid, recrystallized from a benzene/ethanol mixture, had m.p. 205°C (Found: C, 54.09; H, 3.39; O, 5.11, P, 5.88. $C_{54}H_{40}Ir_2O_4P_2$ calcd.: C, 54.08; H, 3.36; O, 5.34; P, 5.17%.)

Crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of n-hexane into a benzene solution of the complex; these have been shown, by solution of the structure, to have benzene molecules trapped in the crystal lattice (molar ratio 1/1, see below).

$\nu(C{\equiv}O)$ at 2000s, 1980ms, 1950s, 1930sh.

Crystal data

$C_{54}H_{40}Ir_2O_4P_2 \cdot C_6H_6$, $M = 1277.4$, air-stable orange prisms with monoclinic habit, a 19.714(3), b 14.257(2), c 18.953(5) Å, β 109.85(2)°, U 5011 Å^3, D_c 1.69 g cm^{-3}, $Z = 4$, D_m 1.70 g cm^{-3}, $F(000)$ 2488 electrons, space group $C2/c$ (nr. 15) after refinement; graphite-monochromated Mo-K_α radiation, λ 0.71069 Å, μ(Mo-K_α) 53.95 cm^{-1}.

Crystallographic measurements

A crystal with maximum dimensions 0.24, 0.22 and 0.46 mm along a, b, and c axes, respectively, was mounted on the BASIC diffractometer [4], with the direction of maximum elongation approximately coincident with the φ axis of the instrument. The unit cell parameters were obtained from least-squares fitting of the accurate setting angles of 37 reflections in the θ range 5–18°. Intensity data were measured by a ω–2θ scan with a ω scan range of 0.84° and an angular speed of 3.3° min^{-1}. Background measurements with stationary counter were made on both sides of each reflection for a total time equal to that spent on the scan. No decrease in the scattering power of the crystal was observed from intensity measurement of three standard reflections. The net intensities were corrected for Lorentz and polarization effects, the latter taking into account the polarization of the incident beam. The transmission factors for the absorption correction were computed by numerical integration over a Gaussian grid of 512 point (8 × 8 × 8) with the methods described in ref. 5.

Structure determination. The structure was solved by inspection of a Patterson map, which revealed the conformation of the Ir_2P_2 moiety: subsequent Fourier syntheses revealed all the remaining non-hydrogen atoms. The final full-matrix least-squares refinement was based on a set of 3411 independent reflections having $I \geqslant 3\sigma(I)$. Scattering factors for non-hydrogen atoms were taken from ref. 6 and those for hydrogen atoms from ref. 7; anomalous dispersion coefficients of Ir and P atoms were taken into account [8]. The phenyl rings of the phosphine ligands were constrained to D_{6h} symmetry (C–C 1.392 Å). The contributions of the hydrogen atoms were included in calculation of the structure factors (most of these atoms were detected in a difference Fourier computed before the final stage of refinement, at distances from the corresponding carbon atom in the range 0.94–1.09 Å). Individual weights were assigned according to the equation $w^{-1} = \{K^2\sigma^2(F_o) + (0.15KF_o)^2\}$, which yields fairly constant distributions of $w(F_c - KF_o)^2$ as a function of $\sin\theta/\lambda$ and of F_o. Final values of R and R_w were 0.028 and 0.010 respectively; a difference Fourier map computed at the end of the refinement was everywhere less than 0.4 e

TABLE 1

POSITIONAL PARAMETERS WITH e.s.d.'s IN PARENTHESES FOR NON-HYDROGEN ATOMS

Atom	x	y	z
Ir	0.07243(1)	0.05537(1)	0.27200(1)
P	0.1794(1)	−0.0304(1)	0.2957(1)
C(1)	0.0914(3)	0.1422(4)	0.2045(3)
O(1)	0.1014(3)	0.1962(3)	0.1651(2)
C(2)	0.0971(3)	0.1312(4)	0.3602(3)
O(2)	0.1075(3)	0.1787(3)	0.4109(2)
C(3)	−0.0035(3)	−0.0474(3)	0.2120(3)
C(11)	−0.0047(3)	−0.1099(3)	0.1506(3)
C(12)	0.0176(3)	−0.2031(4)	0.1619(3)
C(13)	0.0167(3)	−0.2590(4)	0.1017(3)
C(14)	−0.0077(4)	−0.2237(4)	0.0296(3)
C(15)	−0.0292(3)	−0.1321(4)	0.0177(3)
C(16)	−0.0271(3)	−0.0752(4)	0.0777(3)
C(21)	0.2100(2)	−0.0458(3)	0.2151(2)
C(22)	0.2806(2)	−0.0728(2)	0.2253(2)
C(23)	0.3010(1)	−0.0921(3)	0.1634(2)
C(24)	0.2510(2)	−0.0843(3)	0.0913(2)
C(25)	0.1804(2)	−0.0573(2)	0.0811(2)
C(26)	0.1599(1)	−0.0381(3)	0.1430(2)
C(31)	0.1786(3)	−0.1504(2)	0.3287(2)
C(32)	0.1719(2)	−0.1632(2)	0.3989(2)
C(33)	0.1717(2)	−0.2534(3)	0.4269(2)
C(34)	0.1781(3)	−0.3308(2)	0.3848(2)
C(35)	0.1847(2)	−0.3179(2)	0.3146(2)
C(36)	0.1849(2)	−0.2277(3)	0.2866(2)
C(41)	0.2598(2)	0.0192(3)	0.3676(2)
C(42)	0.2671(2)	0.1162(3)	0.3740(2)
C(43)	0.3262(2)	0.1553(2)	0.4293(2)
C(44)	0.3781(2)	0.0975(3)	0.4781(2)
C(45)	0.3708(2)	0.0005(3)	0.4715(2)
C(46)	0.3117(2)	−0.0387(2)	0.4163(2)
CB(1)	0.0000	0.3496(7)	0.2500
CB(2)	0.0147(4)	0.3961(6)	0.1952(5)
CB(3)	0.0153(5)	0.4911(7)	0.1937(6)
CB(4)	0.0000	0.5379(8)	0.2500

Å^{-3}. All computations were carried out on a UNIVAC 1100/80 computer, with programs from our own library. Johnson's ORTEP was used to prepare the drawings. Final atomic coordinates for all non-hydrogen atoms are given in Table 1.

Results and discussion

The crystals of $\{[Ir(CO)_2PPh_3]_2(CPh)_2\} \cdot C_6H_6$ consist of discrete monomeric molecules packed in space group $C2/c$. The unit cell contains four molecules of the complex and four molecules of clathrated solvent; therefore only half a molecule of complex is crystallographically independent and is related to the equivalent moiety by a C_2 axis which passes through the midpoints of the metal–metal bond Ir–Ir′ and bisects also the C(3)–C(3′) bond of the alkyne ligand. A binary axis of the benzene molecule, the one passing through two opposite C–H bonds, coincides with the

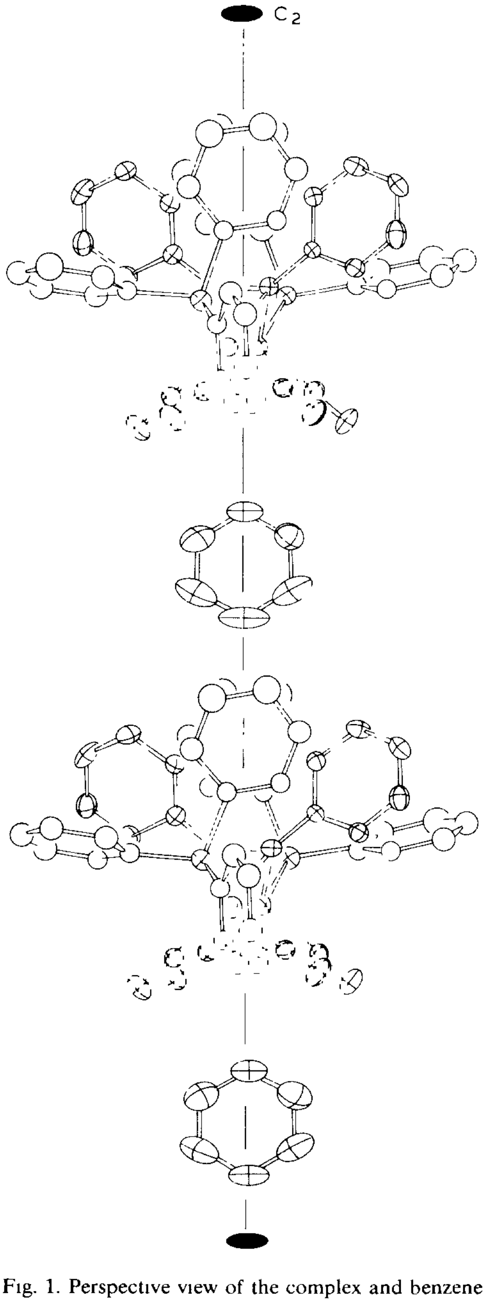

Fig. 1. Perspective view of the complex and benzene molecules along the binary axis

crystallographic axis so that half a molecule of the solvent is crystallographically independent. In the present species, complex and solvent molecules alternate along the crystal diad as shown in Fig. 1. Two phenyl rings, one for each of the symmetry related phosphine ligands, lie on roughly parallel planes, 7.0 Å apart; these form a kind of Van der Waals cavity which hosts the solvent molecule. Interestingly, in the present compound the overall conformation of the triphenylphosphine is almost the same that in II, in which the two ligands are related by a rough mirror. In the present case, because of the presence of a symmetric alkyne and of the interstitial benzene molecule, these two ligands are related by a two-fold axis.

A perspective view of the complex molecule is shown in Fig. 2, together with the numbering scheme of the atoms. For the sake of clarity hydrogen atoms have been omitted: their numbering is the same as that of the corresponding carbon atoms. Most relevant bond distances and angles are reported in Table 2. Each of the two equivalent iridium atoms displays a distorted octahedral coordination in which four

TABLE 2

RELEVANT DISTANCES (Å) AND ANGLES (°)

Coordination around the iridium atoms			
Ir–Ir′	2.689(1)	Ir′–Ir–P	148.2(1)
Ir–P	2.346(1)	Ir′–Ir–C(1)	102.8(2)
Ir–C(1)	1.906(6)	Ir′–Ir–C(2)	101.5(2)
Ir–C(2)	1.910(5)	Ir′–Ir–C(3)	49.8(1)
C(1)–O(1)	1.136(8)	Ir′–Ir–C(3)′	51.0(1)
C(2)–O(2)	1.135(7)	P–Ir–C(1)	95.6(2)
Ir–C(3)	2.127(4)	P–Ir–C(2)	100.5(2)
Ir–C(3)′	2.090(5)	P–Ir–C(3)	99.6(1)
		P–Ir–C(3)′	101.2(1)
		C(1)–Ir–C(2)	99.8(2)
		C(1)–Ir–C(3)	110.6(2)
		C(1)–Ir–C(3)′	147.2(2)
		C(2)–Ir–C(3)	141.4(2)
		C(2)–Ir–C(3)′	104.8(2)
		C(3)–Ir–C(3)′	38.7(2)
		Ir–C(1)–O(1)	177.7(5)
		Ir–C(2)–O(2)	175.6(5)
Geometry of the diphenylacetylene ligand			
C(3)–C(3)′	1.398(7)	Ir–C(3)–C(3)′	69.2(3)
C(3)–C(11)	1.460(7)	Ir–C(3)′–C(3)	72.1(3)
C(11)–C(12)	1.393(7)	C(3)′–C(3)–C(11)	142.2(4)
C(11)–C(16)	1.392(7)	C(3)–C(11)–C(12)	122.7(4)
C(12)–C(13)	1.387(9)	C(3)–C(11)–C(16)	119.2(4)
C(13)–C(14)	1.380(9)	C(12)–C(11)–C(16)	118.0(5)
C(14)–C(15)	1.368(9)	C(13)–C(14)–C(15)	119.8(6)
C(15)–C(16)	1.386(9)	C(11)–C(12)–C(13)	120.4(5)
C(1i)–C(1j)$_{\mathrm{av}}$	1.384(9)	C(11)–C(16)–C(15)	121.1(5)
		C(12)–C(13)–C(14)	120.5(5)
		C(14)–C(15)–C(16)	120.1(5)
Within the triphenylphosphine ligand			
P–C(21)	1.835(4)	Ir–P–C(21)	115.5(1)
P–C(31)	1.823(4)	Ir–P–C(31)	116.2(2)
P–C(41)	1.844(3)	Ir–P–C(41)	115.6(1)
		C(21)–P–C(31)	102.6(2)
		C(21)–P–C(41)	102.6(2)
		C(31)–P–C(41)	102.2(2)

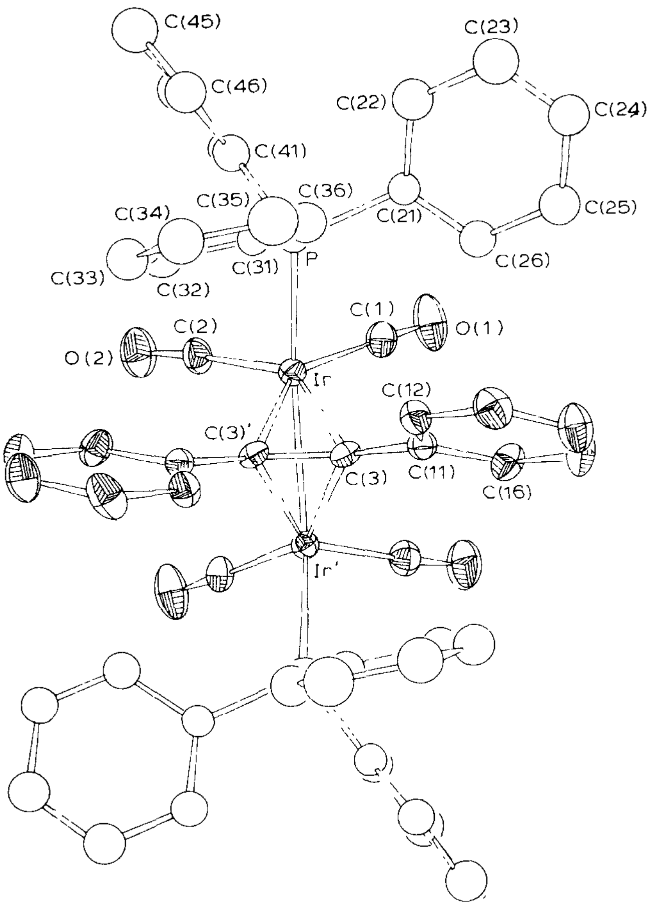

Fig. 2. ORTEP view of the $\{[Ir(CO)_2PPh_3]_2(CPh)_2\}$ molecule, with the hydrogen atoms omitted for clarity. Thermal ellipsoids are drawn at 30% probability

apices of an equatorial plane are occupied by two carbonyl groups and by the alkyne ligand, and two more apices are defined by the second metal atom and by the phosphine ligand.

The pseudo-tetrahedral moiety M_2C_2 is similar to that in a number of alkyne derivatives of dinuclear carbonyl [9,10], cyclopentadienyl [11,12] and phosphine [13] clusters, and is closely similar to that found in compound II. Slight differences can be found when one compares the present structure and that of II, but in the latter, owing to the disordered solvent, the atomic coordinates have e.s.d.'s values which make it impossible to assign significance to slight differences in bonding parameters.

In the present compound the distorted tetrahedron departs from strict *mm* symmetry, and only mantains the two-fold axis because of a slight tilting of the vector C(3)–C(3)′ with respect to that of Ir–Ir′, the angle between the two being 87.6°. This deformation arises from a series of steric repulsions, as follows: the bent alkyne ligand cannot have its phenyl rings parallel because of the repulsion between atoms H(12) and H(12)′, which lie 2.38 Å apart; H(16)′ then makes contact with

C(2) [C(2) · · · H(16)′ 2.65 Å], and C(11) and C(16) are both at 2.7 Å from H(26). As a result, there are two slightly different iridium–carbon distances, 2.090(5) and 2.127(4) Å. The Ir–Ir′ distance is 2.689(1) Å long as in compound II. This length is strictly comparable with the mean distances found in the tetrahedral cluster $Ir_4(CO)_{12}$ [14] 2.693 Å, and shorter than those in two iridacyclopentadienyliridium complexes 2.737(1) Å [1,11].

The electron count in the present compound requires a single bond connecting the two metal atoms, and the distance observed corresponds to a bond order of one. A sounder description of the electronic situation would, however, involve a more or less complete delocalisation of six electrons (four from the alkyne ligand and two more from the metal atoms) over the M_2C_2 tetrahedron.

For this particular complex, as for II, we report the longest C–C bond length (1.398(7) Å) so far reported for bridging alkyne ligands in binuclear clusters; for example, using data only for structures of comparable accuracy, the corresponding distances in di-t-butylacetylenehexacarbonyl-diiron and -dicobalt which are 1.311(10) and 1.335(6) Å long [10], and in $\{Rh_2(PF_3)_4[P(C_6H_5)_3]_2(C_6H_5C_2C_6H_5)\} \cdot (C_2H_5)_2O$ [13], which is 1.369(7) Å. Clearly, π-donation of acetylene toward the binuclear cluster is greatest in the case of iridium. The angle at the carbon atoms bonded to the cluster, 142.2(4)° are in the range observed for all complexes of the same type. All the other parameters in the molecule are normal: thus the Ir–C(carbonylic) bonds, with mean length of 1.908 Å, compare well with those in II (1.84(1)–1.94(1) Å) and in III (1.89(2) Å), and the Ir–P distance of 2.346(1) Å represents another example of the comparatively long metal–P bonds commonly found in Ir and Pt complexes in which a stronger acceptor ligand, such as carbon monoxide, is also present in the metal coordination sphere [3,15].

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