Reaction of [{Ir(CO)$_3$(PPh$_3$)}$_2$] with Substituted Acetylenes. Part 1. Synthesis and Crystal and Molecular Structure of [η-1,1-Dicarbonyl-2,3,4,5-tetrakis(ethoxycarbonyl)-1-triphenylphosphineiridacyclopentadienyl]dicarbonyliridium

By **Maria Angoletta, Pier L. Bellon, Francesco Demartin,** and **Mario Manassero,** Istituto di Chimica Generale ed Inorganica, Università Studi, via G. Venezian 21, 20133 Milano, Italy

The title compound [Ir(CO)$_2${C$_4$(CO$_2$Et)$_4$Ir(CO)$_2$(PPh$_3$)}] has been obtained by reaction of [{Ir(CO)$_3$(PPh$_3$)}$_2$] with EtO$_2$CC≡CCO$_2$Et in boiling benzene. The compound crystallizes as orthorhombic prisms in space group $P2_12_12_1$ with a = 20.655(9), b = 18.496(8), c = 10.027(5) Å, and Z = 4. The structure has been refined to R = 0.027 from 5 299 independent reflections. One metal atom is bonded to two carbonyl groups and to a metallacyclopentadienyl moiety *via* a η^5 interaction; the other is bonded to two CO, one PPh$_3$, and to a buta-1,3-diene-1,4-diyl radical. The molecular parameters are compared with those of known cyclopentadienyl and metallacyclopentadienyl complexes of transition metals.

THE compound [{Ir(CO)$_3$(PPh$_3$)}$_2$] [1] reacts with substituted acetylenes to give a variety of products.[2] The title compound, the first η-iridacyclopentadienyliridium complex so far reported, is obtained by reaction of the former compound with bis(ethoxycarbonyl)acetylene. Several transition-metal complexes containing η-metallacyclopentadienyl ligand moieties are known. Representative members of this family of compounds are the binuclear iron complexes, first prepared by Reppe,[3] whose structures have been elucidated in some cases (see ref. 4 and references therein). Rhodium [5] and osmium [6] complexes of the same type have also been described.

EXPERIMENTAL

Sample Preparation.—Bis(ethoxycarbonyl)acetylene (0.6 g) was added to a suspension of [{Ir(CO)$_3$(PPh$_3$)}$_2$] (0.2 g) in boiling benzene. After 1 h the orange solution was concentrated to 10 cm^3 and the product was precipitated with n-hexane, yield 60%. To obtain good crystals the product was slowly precipitated by slow diffusion of the precipitating n-hexane in the benzene solution. Melting point 170 °C (Found: C, 41.05; H, 3.15; P, 2.75. Calc. for $C_{38}H_{35}Ir_2O_{12}P$: C, 41.5; H, 3.70; P, 2.85%); ν(C≡O) at 2 060s, 2 040s, 2 020s, 1 970s; ν(C=O) at 1 720s and 1 680ms cm^{-1}.

Crystal Data.—$C_{38}H_{35}Ir_2O_{12}P$, M = 1 098.4, air-stable bright orange orthorhombic prisms, a = 20.655(9), b = 18.496(8), c = 10.027(5) Å, U = 3 830.7 Å^3, D_m = 1.89(2), Z = 4, D_c = 1.90 g cm^{-3}, $F(000)$ = 3 024, space group $P2_12_12_1$ (no. 19) from systematic absences, graphite-monochromatized Mo-K_α radiation, λ = 0.710 69 Å, μ(Mo-K_α) = 74.6 cm^{-1}.

Crystallographic Measurements.—A crystal bounded by faces {100}, {010}, {001}, {110}, and {111}, with maximum dimensions 0.20, 0.15, and 0.35 mm along a, b, and c, respectively, was mounted on a BASIC diffractometer † with c approximately parallel to the ϕ axis of the instrument. The unit-cell parameters were determined by least-squares treatment of the accurate setting angles of 30 reflections. Data were collected by the ω-scan technique with a scan range of ±0.5° and a scan speed of 3° min^{-1}. Backgrounds were counted at either side of each peak for a total time equal to the time of scan. Periodical remeasurement of three standard reflections did not reveal any crystal decay. 7 225 Intensity data were obtained by exploring the $\pm h$, $+k$, $+l$ region of reciprocal space in the range 2θ 6—50°. Lorentz, polarization, and absorption corrections were applied to the 6 155 reflections with $I \geqslant 2\sigma(I)$. The absorption correction was made by numerical integration, sampling the crystal on a 8 × 8 × 8 gaussian grid.[7] Transmission factors were in the range 0.33—0.50. Symmetry-equivalent reflections were averaged to give 5 893 independent reflections (Friedel pairs were not merged) of which 5 299 with $I \geqslant 3\sigma(I)$ were used in the structure analysis.

Structure Determination.—The positions of all non-hydrogen atoms were obtained by the usual Patterson and Fourier methods. Scattering factors for non-hydrogen atoms were taken from ref. 8, those for hydrogen atoms from ref. 9. The anomalous-dispersion factors for iridium and phosphorus were taken from ref. 10. In space group $P2_12_12_1$ two enantiomeric models, related to each other by an inversion of all the positional co-ordinates, can be refined; the choice of the correct enantiomorph was made by comparing the results of two parallel blocked-matrix least-squares refinements, performed on a set of 2 461 strong reflections, with anisotropic thermal factors for iridium and phosphorus and isotropic ones for the remaining non-hydrogen atoms. Here, and in the subsequent refinements, phenyl rings were constrained to D_{6h} symmetry (C–C 1.392 Å), with individual isotropic thermal parameters. At this stage the values of R and $R'\{[\Sigma w(F_o - k|F_c|)^2/\Sigma w F_o^2]^{\frac{1}{2}}\}$ were 0.045 8 and 0.059 0 for one enantiomorph, which was taken to be the correct one, and 0.054 6 and 0.072 0 for the other.

After further refinement of the correct enantiomorph, a difference-Fourier map was computed which revealed the positions of all hydrogen atoms with C–H distances varying from 0.80 to 1.13 Å. No refinement of these atoms was attempted, and in the final cycles of refinement they were fixed in calculated positions (C–H 1.00 Å). The final full-matrix refinement, in which anisotropic thermal parameters were assigned to all atoms except carbon atoms of the phenyl rings, was terminated when no parameter shifted more than one third of its estimated standard deviation.

Individual weights were computed from the expression $w^{-1} = 20.7 - 0.26kF_o + 0.001\,2\,(kF_o)^2$, which yielded a fairly constant distribution of $w(F_c - F_o)^2$ as a function of sin θ and F_o. The final values of R and R' were 0.027 and

---

† Assembled by one of us (P.L.B.) from a Hoppe four-circle goniometer and HP-2100 computer. The programming for crystal centring and data collection was done in the Dartmouth College BASIC language.

0.031. The final difference-Fourier map was everywhere less than 0.50 e Å^{-3}. All computations were carried out on a UNIVAC 1 100/80 computer using well checked programs from our library, partly derived from entries 7 528, 7 531, and 7 535 of the 1966 World List of Crystallographic Programs. Johnson's ORTEP was used in preparing the drawings.

Final atomic co-ordinates are given in Table 1, bond distances and angles in Table 2, and least-squares planes in Table 3. Anisotropic thermal parameters and structure-factor tables are available as Supplementary Publication No. SUP 22881 (22 pp.).*

TABLE 1

Final parameters (× 10^4)

(*a*) Of individually refined atoms [a]

Atom	*x*	*y*	*z*
Ir(1)	776(0)	−123(0)	−1 495(0)
Ir(2)	−485(0)	−485(0)	−1 003(0)
P	−1 204(0)	−628(1)	790(2)
C(1)	1 114(5)	675(5)	−2 358(10)
C(2)	1 231(4)	−724(5)	−2 620(10)
C(3)	−670(4)	−1 331(4)	−2 001(8)
C(4)	−992(4)	97(5)	−2 227(9)
C(11)	4(3)	402(4)	−249(8)
C(12)	−153(4)	1 172(4)	−430(9)
C(13)	−1 013(5)	2 033(5)	−724(13)
C(14)	−1 101(6)	2 366(6)	588(15)
C(21)	554(3)	250(4)	580(7)
C(22)	879(4)	840(4)	1 336(9)
C(23)	1 771(6)	1 643(6)	1 471(14)
C(24)	2 046(8)	2 105(7)	452(17)
C(31)	715(3)	−499(4)	683(6)
C(32)	1 244(4)	−793(4)	1 538(0)
C(33)	1 978(5)	−545(7)	3 284(11)
C(34)	2 145(5)	66(8)	4 143(12)
C(41)	333(3)	−946(4)	−172(8)
C(42)	480(4)	−1 732(4)	−317(8)
C(43)	340(7)	−2 885(7)	680(14)
C(44)	8(9)	−3 273(9)	−286(22)
O(1)	1 341(5)	1 169(5)	−2 865(11)
O(2)	1 516(4)	−1 078(4)	−3 354(8)
O(3)	−741(4)	−1 846(3)	−2 635(6)
O(4)	−1 248(3)	421(4)	−3 018(7)
O(12)	228(3)	1 664(4)	−496(10)
O(13)	−782(3)	1 282(3)	−546(7)
O(22)	641(3)	1 111(4)	2 312(7)
O(23)	1 439(2)	1 041(3)	836(6)
O(32)	1 426(3)	−1 409(3)	1 485(8)
O(33)	1 471(3)	−307(3)	2 377(6)
O(42)	836(3)	−1 984(3)	−1 151(6)
O(43)	155(3)	−2 107(3)	579(7)

(*b*) Of group-refined atoms [b]

Atom	*x*	*y*	*z*
C(51)	−1 746(3)	135(3)	1 068(4)
C(52)	−2 141(3)	324(2)	0(4)
C(53)	−2 604(3)	865(3)	151(4)
C(54)	−2 671(3)	1 216(3)	1 371(4)
C(55)	−2 276(3)	1 027(2)	2 439(4)
C(56)	−1 812(3)	487(3)	2 287(4)
C(61)	−1 767(2)	−1 389(2)	694(6)
C(62)	−1 556(2)	−2 043(3)	164(6)
C(63)	−1 978(2)	−2 628(2)	88(6)
C(64)	−2 612(2)	−2 559(2)	542(6)
C(65)	−2 824(2)	−1 905(3)	1 071(6)
C(66)	−2 401(2)	−1 320(2)	1 147(6)
C(71)	−779(3)	−769(3)	2 365(5)
C(72)	−805(2)	−1 437(2)	3 004(6)
C(73)	−451(3)	−1 552(2)	4 165(5)
C(74)	−70(3)	−999(3)	4 687(5)
C(75)	−44(2)	−332(2)	4 048(6)
C(76)	−399(3)	−217(3)	2 887(6)

[a] Carbon-atom numbering as follows: C(*i*, 1) for the butadiene fragment; C(*i*, *j*) (*j* = 2–4) for the ethoxycarbonyl groups. [b] Ring-atom numbering as follows: C(*i*, *j*) (*j* = 1–6) for the ring, C(*i*, 1) being bonded to the P atom and C(*i*, 4) *para* to them.

TABLE 2

Relevant distances (Å) and angles (°)

(*a*) Co-ordination around Ir(1)

Ir(1)–C(1)	1.849(11)	C(1)–Ir(1)–Ir(2)	129.7(3)
Ir(1)–C(2)	1.841(10)	C(1)–Ir(1)–C(11)	100.5(4)
Ir(1) · · · O(1)	2.994(10)	C(1)–Ir(1)–C(21)	105.4(4)
Ir(1) · · · O(2)	2.988(9)	C(1)–Ir(1)–C(31)	135.1(4)
C(1) · · · C(2)	2.615(15)	C(1)–Ir(1)–C(41)	169.9(4)
C(1)–O(1)	1.146(15)	C(2)–Ir(1)–Ir(2)	116.6(3)
C(2)–O(2)	1.147(14)	C(2)–Ir(1)–C(11)	164.5(4)
Ir(1)–Ir(2)	2.737(1)	C(2)–Ir(1)–C(21)	149.3(4)
Ir(1)–C(11)	2.248(8)	C(2)–Ir(1)–C(31)	115.4(4)
Ir(1)–C(21)	2.241(8)	C(2)–Ir(1)–C(41)	99.3(4)
Ir(1)–C(31)	2.297(7)	Ir(1)–Ir(2)–P	140.2(1)
Ir(1)–C(41)	2.217(8)	Ir(1)–Ir(2)–C(3)	107.4(3)
Ir(1)–C(*i*1)	2.25 (mean)	Ir(1)–Ir(2)–C(4)	105.3(3)
C(1)–Ir(1)–C(2)	90.2(5)	Ir(1)–Ir(2)–C(11)	53.6(2)
Ir(1)–C(1)–O(1)	177.7(11)	Ir(1)–Ir(2)–C(41)	52.7(2)
Ir(1)–C(2)–O(2)	177.4(10)	Ir(1)–C(11)–C(12)	120.5(6)
		Ir(1)–C(21)–C(22)	127.3(6)
		Ir(1)–C(31)–C(32)	128.1(5)
		Ir(1)–C(41)–C(42)	121.8(6)

(*b*) Geometry of the iridapentadiene ring

Ir(2)–P	2.348(2)	P–Ir(2)–C(3)	100.7(3)
Ir(2)–C(3)	1.895(9)	P–Ir(2)–C(4)	101.9(3)
Ir(2)–C(4)	1.940(9)	P–Ir(2)–C(11)	96.8(2)
Ir(2) · · · O(3)	3.047(7)	P–Ir(2)–C(41)	99.4(2)
Ir(2) · · · O(4)	3.063(8)	Ir(2)–C(3)–O(3)	175.6(8)
Ir(2)–C(11)	2.073(8)	Ir(2)–C(4)–O(4)	174.1(8)
Ir(2)–C(41)	2.070(8)	C(3)–Ir(2)–C(4)	90.9(4)
C(3)–O(3)	1.155(11)	C(3)–Ir(2)–C(11)	160.9(3)
C(4)–O(4)	1.127(12)	C(3)–Ir(2)–C(41)	92.1(3)
C(11)–C(21)	1.435(11)	C(4)–Ir(2)–C(11)	93.1(4)
C(21)–C(31)	1.430(11)	C(4)–Ir(2)–C(41)	157.6(3)
C(31)–C(41)	1.430(11)	C(11)–Ir(2)–C(41)	77.3(3)
P · · · C(3)	3.279(9)	Ir(2)–C(11)–C(21)	116.3(6)
P · · · C(4)	3.339(9)	Ir(2)–C(41)–C(31)	117.0(6)
P · · · C(11)	3.110(8)	C(11)–C(21)–C(31)	114.6(7)
P · · · C(41)	3.373(8)	C(21)–C(31)–C(41)	112.9(7)
C(3) · · · C(4)	2.735(13)		
C(3) · · · C(41)	2.858(12)		
C(4) · · · C(11)	2.914(12)		
C(11) · · · C(41)	2.587(12)		

(*c*) Geometry of the ethoxycarbonyl groups

C(11)–C(12)	1.472(12)	C(21)–C(31)–C(32)	124.5(7)
C(21)–C(22)	1.489(12)	C(41)–C(31)–C(32)	122.5(7)
C(31)–C(32)	1.491(12)	C(31)–C(41)–C(42)	120.7(7)
C(41)–C(42)	1.493(12)	Ir(2)–C(41)–C(42)	121.9(6)
C(*i*1)–C(*i*2)	1.48 (mean)	C(11)–C(12)–O(12)	126.2(9)
C(12)–O(12)	1.207(12)	C(21)–C(22)–O(22)	122.3(8)
C(22)–O(22)	1.205(12)	C(31)–C(32)–O(32)	123.4(9)
C(32)–O(32)	1.201(11)	C(41)–C(42)–O(42)	124.6(8)
C(42)–O(42)	1.207(11)	C(*i*1)–C(*i*2)–O(*i*2)	124.1 (mean)
C(*i*2)–O(*i*2)	1.20 (mean)	C(11)–C(12)–O(13)	112.4(7)
C(12)–O(13)	1.320(12)	C(21)–C(22)–O(23)	114.3(7)
C(22)–O(23)	1.314(10)	C(31)–C(32)–O(33)	112.3(7)
C(32)–O(33)	1.318(11)	C(41)–C(42)–O(43)	110.0(7)
C(42)–O(43)	1.319(11)	C(*i*1)–C(*i*2)–O(*i*3)	112.2 (mean)
C(*i*2)–O(*i*3)	1.32 (mean)	O(12)–C(12)–O(13)	121.5(9)
O(13)–C(13)	1.479(13)	O(22)–C(22)–O(23)	123.5(8)
O(23)–C(23)	1.454(14)	O(32)–C(32)–O(33)	124.3(9)
O(33)–C(33)	1.454(13)	O(42)–C(42)–O(43)	125.5(8)
O(43)–C(43)	1.493(15)	O(*i*2)–C(*i*2)–O(*i*3)	123.7 (mean)
O(*i*3)–C(*i*3)	1.47 (mean)	C(12)–O(13)–C(13)	118.2(8)
C(13)–C(14)	1.465(20)	C(22)–O(23)–C(23)	117.7(8)
C(23)–C(24)	1.448(21)	C(32)–O(33)–C(33)	116.7(8)
C(33)–C(34)	1.465(19)	C(42)–O(43)–C(43)	114.9(8)
C(43)–C(44)	1.387(26)	C(*i*2)–O(*i*3)–C(*i*3)	116.9 (mean)
C(*i*3)–C(*i*4)	1.44 (mean)	O(13)–C(13)–C(14)	109.1(10)
Ir(2)–C(11)–C(12)	127.8(6)	O(23)–C(23)–C(24)	109.1(12)
C(21)–C(11)–C(12)	115.9(7)	O(33)–C(33)–C(34)	107.6(10)
C(11)–C(21)–C(22)	120.6(7)	O(43)–C(43)–C(44)	108.9(13)
C(31)–C(21)–C(22)	124.6(7)	O(*i*3)–C(*i*3)–C(*i*4)	108.7 (mean)

---

* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

TABLE 2 (*continued*)

(*d*) The triphenylphosphine ligand

P–C(51)	1.823(7)	C(51)–P–C(61)	102.4(3)
P–C(61)	1.829(6)	C(51)–P–C(71)	105.9(3)
P–C(71)	1.825(6)	C(61)–P–C(71)	103.9(3)
Ir(2)–P–C(51)	114.7(2)	P–C(51)–C(54)	174.2(4)
Ir(2)–P–C(61)	116.6(2)	P–C(61)–C(64)	179.3(3)
Ir(2)–P–C(71)	112.0(2)	P–C(71)–C(74)	176.9(3)

RESULTS AND DISCUSSION

Packing and Overall Geometry.—Crystals of this compound consist of discrete monomeric molecules with no specific intermolecular interactions. A perspective view of the monomeric unit is shown in Figure 1. It can be described as an $Ir(CO)_2$ fragment bonded, *via* an η^5 interaction, to an iridacyclopentadienyl ring. Alternatively, the η^5 interaction takes place between a $[Ir(CO)_2]^+$ cation and the metallacyclopentadienide ring. The central part of the molecule, excepting the CO_2Et and Ph substitutents, shows almost exact mirror symmetry, as can be seen in Figure 1; the mirror contains the two Ir and P atoms and bisects the central bond C(21)–C(31) of the butadiene fragment. The ethoxycarbonyl groups and phenyl rings induce an overall asymmetric configuration in the molecule which packs in a chiral space group. The presence of strong anomalous scattering allows, therefore, the absolute configuration of the particular crystal mounted on the diffractometer to be established unambiguously (see Experimental section).

Co-ordination at Ir(1).—Atom Ir(1) obtains four electrons from two CO ligands and five more from the metallacycle and so achieves an inert-gas configuration.

TABLE 3

Weighted * least-squares planes in the form $Ax + By + Cz + D = 0$

(*a*) Equations of planes through selected groups of atoms

Plane	Atoms	*A*	*B*	*C*	*D*
1	Ir(1), C(1), O(1), C(2), O(2)	15.915	−0.074	6.391	−0.281
2	C(3), C(4), C(11), C(41)	13.451	2.341	−7.503	−0.323
3	Ir(2), C(3), O(3), C(4), O(4)	−17.214	−2.968	5.303	−0.448
4	Ir(2), C(11), C(41)	9.937	1.928	−8.728	−0.230
5	C(11), C(21), C(31), C(41)	13.103	2.477	−7.634	−0.316
6	C(11), C(12), O(12), O(13)	1.330	−2.170	−9.937	−0.160
7	C(21), C(22), O(22), O(23)	9.530	−12,530	5.744	−0.548
8	C(31), C(32), O(32), O(33)	14.049	4.972	−6.838	−0.291
9	C(41), C(42), O(42), O(43)	15.854	1.682	6.362	−0.261

(*b*) Angles (°) between selected pairs of planes

Plane	2	3	4	5	6	7	8	9
1	88.6	72.3	79.4	89.8				
2		16.5	12.1	1.3				
3			28.6	17.7				
4				10.9				
5					38.8	76.5	9.4	89.1

(*c*) Distances (Å × 10^3) of selected atoms from planes

Plane	
1	Ir(1) 0(0), C(1) −20(11), C(2) 8(10), O(1) 13(11), O(2) −4(9)
2	Ir(2) −336(0), C(3) −34(9), C(4) 37(9), C(11) −35(9), C(21) 46(8), C(31) 10(7), C(41) 34(8)
3	Ir(2) 0(0), C(3) 39(8), C(4) 50(9), O(3) −21(8), O(4) −24(8), C(11) −707(8), C(41) −833(8)
4	C(3) 525(9), C(4) 677(9)
5	Ir(1) 1 813(0), Ir(2) −306(0), C(11) −20(9), C(21) 29(8), C(31) −24(7), C(41) 19(8), C(12) 102(9), C(22) 25(9), C(32) −57(9), C(42) 127(9)
6	C(11) 2(9), C(12) −6(10), O(12) 3(10), O(13) 1(8)
7	C(21) −1(8), C(22) 5(9), O(22) −1(7), O(23) −1(6)
8	C(31) −2(7), C(32) 10(9), O(32) −3(8), O(33) −2(7)
9	C(41) −2(8), C(42) 7(9), O(42) −2(7), O(43) −2(7)

* Weights assigned on the basis of individual e.s.d.s.

TABLE 4

A comparison of bonding parameters in M–CO_2R fragments

		M			
		C[a]	Pt[b]	Ir[c]	C[d]
(*a*) Distances (Å)					
	M–C(*i*2)	1.48	2.059(7)	2.05(2)	1.485(3)
	C(*i*2)=O(*i*2)	1.20	1.228(7)	1.18(2)	1.199(2)
	C(*i*2)–O(*i*3)	1.32	1.351(7)	1.28(2)	1.329(2)
	O(*i*3)–C(*i*3)	1.47	1.459(11)	1.48(3)	1.444(2)
	C(*i*3)–C(*i*4)	1.44	1.476(16)		
(*b*) Angles (°)					
	M–C(*i*2)=O(*i*2)	124.1	125.9(5)	126.6(16)	126.3(1)
	M–C(*i*2)–O(*i*3)	112.2	114.6(4)	112.8(11)	111.2(1)
	O(*i*2)=C(*i*2)–O(*i*3)	123.7	119.5(6)	120.6(19)	122.6(19)
	C(*i*2)–O(*i*3)–C(*i*3)	116.9	118.8(5)	118.3(14)	117.0(1)
	O(*i*3)–C(*i*3)–C(*i*4)	108.7	110.1(7)		

[a] Mean values found in the present compound. [b] Ref. 16. [c] Ref. 17. [d] Ref. 18.

The co-ordination round Ir(1) is similar to that reported for the compound [Ir(η-C_5H_5)(CO)(PPh_3)] (1).[11] The mean length of the Ir(1)–CO bonds [1.845(6) Å] is within the range [1.800(8)—1.873(11) Å] reported for mononuclear iridium complexes (see ref. 11 and references therein); the angle C(1)–Ir–C(2) is 90.2(5)°, close to the corresponding P–Ir–C angle in compound (1), 89.2(3)°.

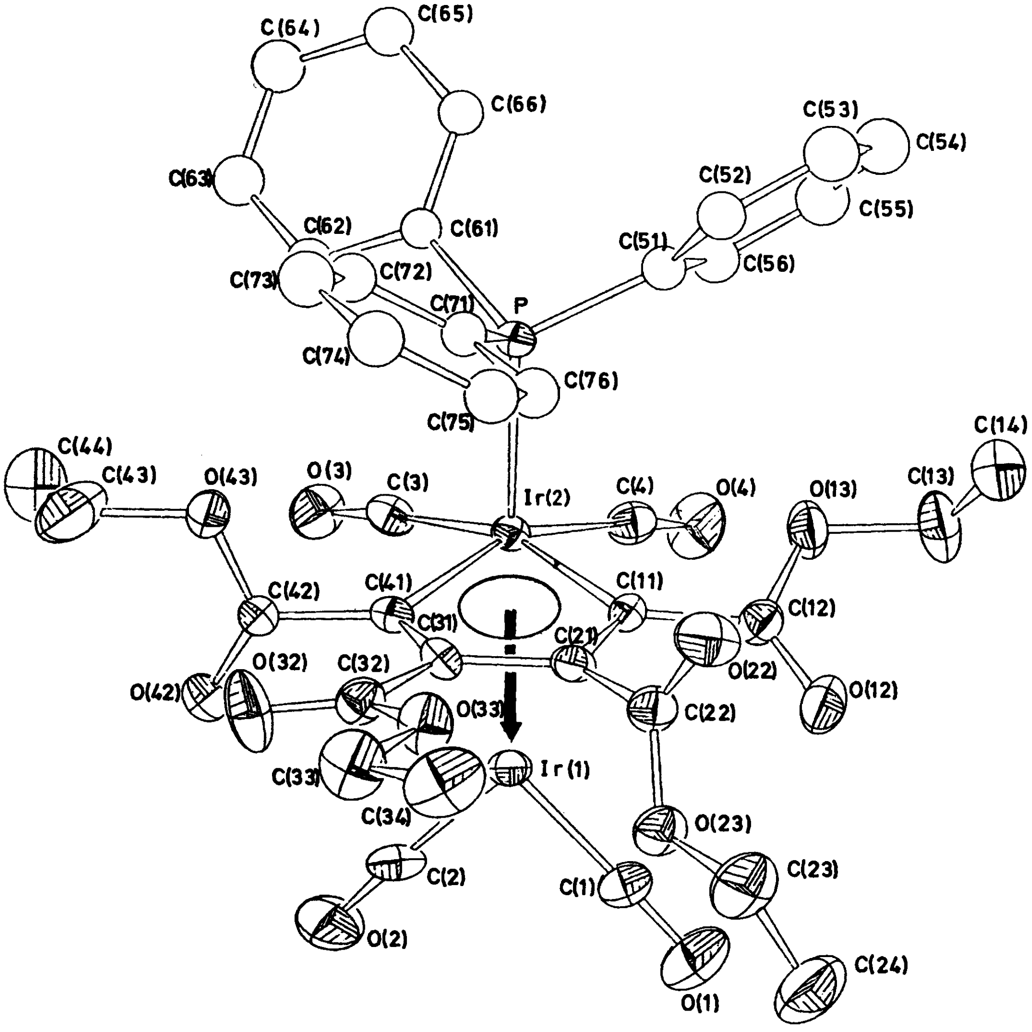

FIGURE 1 Perspective view of the molecule

The P–Ir–C plane in (1) is strictly orthogonal to the cyclopentadienyl ring (interplanar angle 89.8°). The corresponding angle in the present molecule is exactly the same [since the metallacycle is not planar, the interplanar angle is defined by the Ir(1)–$(CO)_2$ plane and the *cis*-butadiene fragment]. Figure 2, a projection of the $Ir_2(C–C)_4(CO)_4$ moiety on the plane of the four butadiene carbon atoms, shows a slight twisting of the Ir(1)$(CO)_2$ group with respect to the mirror described above, which is probably due to packing forces.

Co-ordination at Ir(2).—Atom Ir(2) receives six electrons from two CO and one PPh_3 ligand and two more from the buta-1,3-diene-1,4-diyl chelating diradical; the unpaired electron, together with the two π-electron pairs from the ring, contributes to the five-electron pool of the iridacyclopentadienyl group. Apart from its interactions with the Ir(1)$(CO)_2$ fragment, Ir(2) has a square-pyramidal co-ordination with atoms C(3), C(4), C(11), and C(41) defining the basal plane; the butadiene fragment lies essentially on this plane. Atom Ir(2) is 0.34 Å above this plane and the bond Ir(2)–P is perpendicular to it. In other words, the orientation of the co-ordination axes at Ir(2) is dictated by the plane of the butadiene fragment and not by the metal–metal interaction [angle P–Ir(2)–Ir(1), 140.2(1)°, is rather far from the 180° needed for pseudo-octahedral co-ordination]. This feature is common to most of the other metallacyclopentadienylmetal complexes.

The two metal–carbonyl interactions at Ir(2) are quite long, 1.895(9) and 1.940(9) Å, and fall outside the range reported above; this is probably an effect of the *trans* influence of atoms C(11) and C(41) of the chelating butadiene fragment. The Ir(2)–P bond [2.348(2) Å] is also long; long metal–phosphorus bonds are a common feature in phosphine complexes of Ir and Pt in which the stronger π-acceptor CO ligand is also present.[12] The two Ir(2)–C bonds involving the chelating ligand are 2.071(2) Å.* We might compare these distances with those observed in three orthometallated aryldiazene complexes of iridium, which are consistently 2.01 Å.[13]

The Metallacycle and its Interactions with $Ir(CO)_2$.—The *cis*-butadiene fragment is essentially planar with statistically equal C(*i*1)–C(*j*1) distances [1.432(2) Å]; * it seems important that the corresponding distances in the cyclopentadienyl ring of compound (1) are significantly shorter [1.388(7) Å].* Atom Ir(2) is lifted 0.31 Å above the plane of the four butadiene carbon atoms to make possible a not-too-short Ir–Ir distance; in the rhodacyclopentadiene complex described by Dahl and co-workers [5] the metal atom is lifted by 0.38 Å, whereas in ferracyclopentadieneiron complexes smaller offsets have, as expected, been observed (0.11—0.26 Å). The Ir(1)–Ir(2) bond length [2.737(1) Å] is comparable with those observed in $[Ir_4(CO)_{12}]$, 2.685(1) Å,[14] and in $[Ir_2(NO)_4(PPh_3)_2]$, 2.715(1) Å.[15]

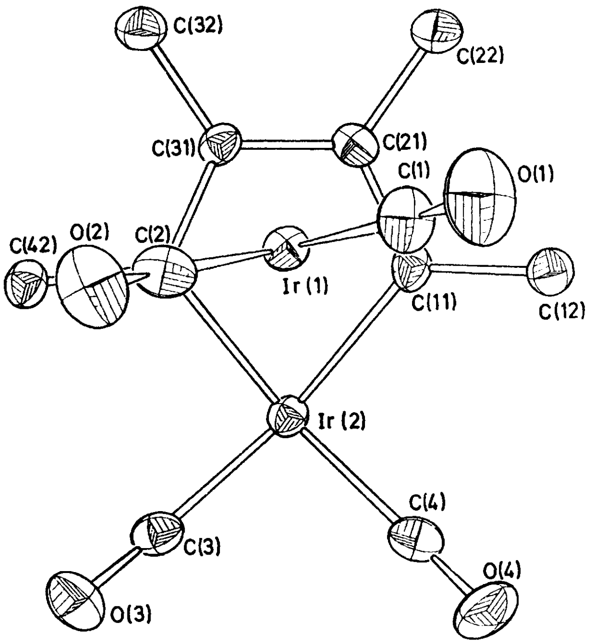

FIGURE 2 Projection of the $Ir_2(C-C)_4(CO)_4$ on the plane of the butadiene fragment

Atom Ir(1) lies 1.813 Å from the plane of the cyclobutadiene fragment whereas in compound (1) the distance is much longer (1.940 Å). This suggests that the iridacycle is a stronger π donor than cyclopentadienyl itself, and is probably why, within the metallacycle, C–C and Ir–C distances are longer than usual. The Ir(1)–C(*i*1) bonds are subjected to two effects: shortening of the distance between the metal atom and the butadiene fragment which tends to yield shorter Ir–C distances; and stronger donation of π electrons to the second metal atom tending to enlarge the ring and therefore to yield longer Ir–C distances. Furthermore, the presence of a metal atom in the ring gives a distortion which also tends to yield longer metal–carbon interactions. As a net result the Ir(1)–C(*i*1) distances observed are essentially the same as those reported for compound (1).

The Ethoxycarbonyl Groups.—Four ethoxycarbonyl groups are attached to the carbon atoms of the iridacyclopentadienyl ring. The carboxylic carbon atoms are essentially coplanar with the butadiene fragment, showing that there is no distortion from sp^2 hybridization of the four carbon atoms of the ring; strict planarity is also observed for the –C–C(=O)O– moieties. The four C(*i*1)–C(*i*2) bonds have a mean value of 1.49 Å, in good agreement with the expected value for a single bond connecting two sp^2-hybridized carbon atoms. The entire pattern of bonds and angles (mean values) for the ethoxycarbonyl groups in this compound may be compared (Table 4) to the corresponding values found in $[Pt(CO_2Et)_2(PPh_3)_2]$,[16] $[Ir(CO_2Me)I_2(CO)(bipy)]$,[17] and a very accurate structural determination on a methoxycarbonyl derivative of dimethanoannulene.[18] Table 4 shows a nice agreement between all values; it is interesting that short bonds within the ethyl groups are found here (mean 1.44 Å) and in the Pt complex [1.476(16) Å].

We thank the Italian National Research Council for support.

[0/482 *Received, 31st March, 1980*]

---

* The distances *d* quoted here are the so-called ' external mean ' calculated on chemically equivalent interactions; their estimated standard deviation (e.s.d.) is defined by the expression $\sigma = [(n-1)^{-1}\sum_{i=1}^{n}(d_i - d)^2]^{\frac{1}{2}}$.

REFERENCES

[1] L. Malatesta, M. Angoletta, and G. Caglio, *J. Organometallic Chem.*, 1974, **73**, 265.

[2] M. Angoletta, P. L. Bellon, F. Demartin, and M. Manassero, unpublished work.

[3] W. Reppe, ' Neue Entwicklungen auf dem Gebiet der Chemie des Acetylens und Kohlenoxyds,' Springer, Berlin, 1949, pp. 122—125; W. Reppe and H. Vetter, *Annalen* 1953, **582**, 133.

[4] L. J. Todd, J. P. Hickey, J. R. Wilkinson, J. C. Hoffmann, and K. Folting, *J. Organometallic Chem.*, 1976, **167**, 112.

[5] L. R. Bateman, P. M. Maitlis, and L. F. Dahl, *J. Amer. Chem. Soc.*, 1969, **91**, 7292.

[6] R. P. Dodge, O. S. Mills, and V. Shomaker, *Proc. Chem. Soc.*, 1963, 380.

[7] G. Ciani, M. Manassero, and M. Sansoni, *J. Appl. Cryst.*, 1971, **4**, 173.

[8] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[9] J. B. Forsyth and M. Wells, *Acta Cryst.*, 1959, **12**, 412.

[10] D. T. Cromer and J. T. Weber, ' International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4, pp. 149—150.

[11] M. J. Bennett, J. L. Pratt, and R. M. Tuggle, *Inorg. Chem.*, 1974, **13**, 2408.

[12] V. G. Albano, P. L. Bellon, and M. Manassero, *J. Organometallic Chem.*, 1972, **35**, 423; V. G. Albano, P. L. Bellon, and M. Sansoni, *J. Chem. Soc.* (*A*), 1971, 2421.

[13] P. L. Bellon, G. Caglio, M. Manassero, and M. Sansoni, *J.C.S. Dalton*, 1974, 897; P. L. Bellon, F. Demartin, M. Manassero, M. Sansoni, and G. Caglio, *J. Organometallic Chem.*, 1978, **157**, 209; M. Angoletta, P. L. Bellon, M. Manassero, and M. Sansoni, *Gazzetta*, 1977, 441.

[14] M. R. Churchill and J. P. Hutchinson, *Inorg. Chem.*, 1978, **17**, 3528.

[15] M. Angoletta, G. Ciani, M. Manassero, and M. Sansoni, *J.C.S. Chem. Comm.*, 1973, 789.

[16] P. L. Bellon, M. Manassero, F. Porta, and M. Sansoni, *J. Organometallic Chem.*, 1974, **80**, 139.

[17] V. G. Albano, P. L. Bellon, and M. Sansoni, *Inorg. Chem.*, 1969, **8**, 298.

[18] C. M. Gramaccioli, A. S. Mimun, A. Mugnoli, and M. Simonetta, *J. Amer. Chem. Soc.*, 1973, **95**, 3149.