Journal of Organometallic Chemistry, 204 (1981) C10—C12
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

NEW TETRAHEDRAL CLUSTERS OF IRIDIUM. CRYSTAL AND MOLECULAR STRUCTURE OF μ_3-PHENYLPHOSPHIDOTRI-μ-CARBONYLTRICARBONYLTETRAKIS(TRIPHENYLPHOSPHINE)-TETRAHEDRO-TETRAIRIDIUM

FRANCESCO DEMARTIN, MARIO MANASSERO, MIRELLA SANSONI*,
Istituto di Chimica Generale, Reparto Strutture, via G. Venezian 21, 20133 Milano (Italy)
LUIGI GARLASCHELLI*, and UGO SARTORELLI
Istituto di Chimica Generale, Reparto Sintesi, via G. Venezian 21, 20133 Milano (Italy)

(Received October 8th, 1980)

Summary

The reaction of $Ir_4(CO)_{12}$ with PPh_3 in toluene, under forcing conditions, yields a mixture of products, one of which has been identified by X-ray diffraction as $Ir_4(\mu_3\text{-}PPh)(\mu_2\text{-}CO)_3(CO)_3(PPh_3)_4$. It is the first iridium cluster to contain four triphenylphosphine groups and a phenylphosphido ligand. The metal tetrahedron displays a trigonal pyramidal distortion with average apical and basal edges of 2.747 and 2.894 Å, respectively. The latter value is ca. 0.18 Å longer than the usual metal—metal bond length in iridium tetrahedra.

Tetrasubstituted derivatives of $Ir_4(CO)_{12}$, of general formula $Ir_4(CO)_8L_4$, are known for a large variety of phosphorus donor ligands (L = PEt_3, PBu_3, $PMePh_2$, PMe_2Ph, $P(OPh)_3$, etc.) [1], but in the case of triphenylphosphine only mono-, di-, and tri-substituted derivatives have previously been reported [1]. In an attempt to obtain tetrasubstitution with triphenylphosphine we refluxed for 12 h a suspension of $Ir_4(CO)_{12}$ and PPh_3 in 1/6 molar ratio in toluene. The crude product (a mixture of variously substituted derivatives, as shown by IR)* was dissolved in CH_2Cl_2, and vapours of n-hexane were allowed to diffuse into the solution. After two months' standing, well-shaped brown crystals were obtained in low yields (≈ 5%), which show IR bands at 1960vs, 1785s, 1740vs cm^{-1}. The stoichiometry and the molecular structure of this compound were established by a single crystal X-ray diffraction study.

---

*The mother liquor was shown by GLC to contain benzene, in agreement with the presence of a phenylphosphido ligand in the product (see below).

Crystal data: $Ir_4(CO)_6(PPh_3)_4(PPh)$, $M = 2094.15$, monoclinic, space group $P2_1/c$, *a* 23.615(5), *b* 13.778(3), *c* 26.359(8) Å, β 116.51(5)°, *V* 7674 Å^3. The structure was solved by Patterson and Fourier methods using 8605 independent absorption-corrected counter data, collected with graphite-monochromatized Mo-K_α radiation in the 2θ range 6—50°. In the block matrix least-squares refinement, anisotropic thermal factors were assigned to the atoms of the $Ir_4(CO)_6P_5$ fragment. The phenyl groups were refined rigidly. The current conventional *R* value is 0.036.

The structure of $Ir_4(\mu_3\text{-PPh})(\mu_2\text{-CO})_3(CO)_3(PPh_3)_4$ is shown in Fig. 1. It is based on a tetrahedral metal framework slightly distorted towards a squeezed trigonal pyramid, with Ir(1) in the apical position. Mean values of

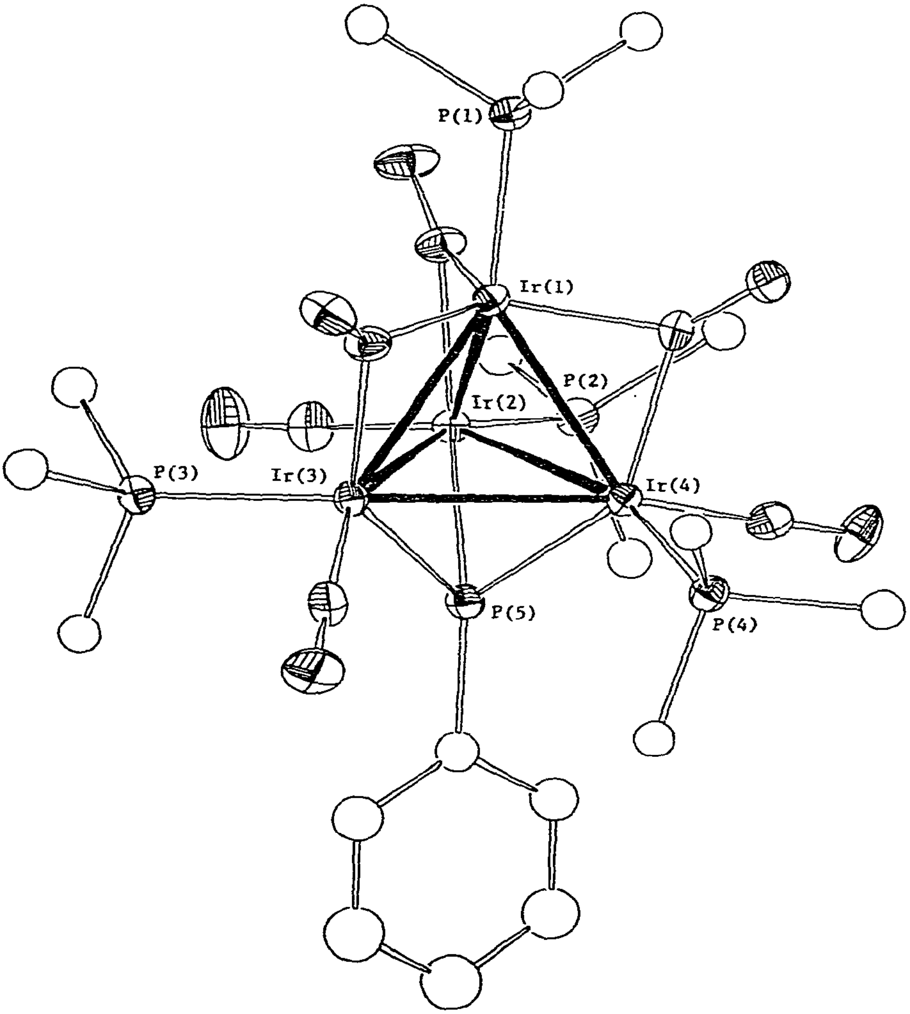

Fig. 1. ORTEP view of $Ir_4(\mu_3\text{-PPh})(\mu_2\text{-CO})_3(CO)_3(PPh_3)_4$ (only the first carbon atoms of the triphenylphosphine phenyl groups are shown for clarity). Ir—Ir bond lengths are: Ir(1)—Ir(2), 2.735(1), Ir(1)—Ir(3) 2.758(1), Ir(1)—Ir(4) 2.748(1), Ir(2)—Ir(3) 2.880(1), Ir(2)—Ir(4) 2.914(1), Ir(3)—Ir(4) 2.888(1) Å.

the basal and apical Ir—Ir edges are 2.894 and 2.747 Å, respectively. The four triphenylphosphine ligands are terminally bonded, one per each metal atom, while of the six carbonyl groups three are terminally bonded to the basal metal atoms and three asymmetrically bridge the apical Ir—Ir edges, with shorter contacts to Ir(1). The basal metal plane is triply bridged by the μ_3-phenylphosphido ligand, in such a way that the overall idealized symmetry of the $Ir_4(CO)_6P_5$ core is C_3, with the three-fold axis passing through P(1), Ir(1) and P(5). Important bond parameters are: Ir(1)—P(1) 2.280(3), Ir—P(2,3,4)$_{(average)}$ 2.310,. Ir—P(5)$_{(av.)}$ 2.297, Ir(1)—CO$_{(av.)}$ 2.016, Ir(2,3,4)$_{(bridging,av.)}$ 2.156, Ir(2,3,4)—CO$_{(terminal,av.)}$ 1.847, C—O$_{(bridg.,av.)}$ 1.170, C—O$_{(term.,av.)}$ 1.141 Å, Ir—P(5)—Ir$_{(av.)}$ 78.3°. Typical e.s.d.'s are Ir—Ir 0.001, Ir—P 0.003, Ir—C 0.011 and C—O 0.015 Å.

Regarding the μ_3-PPh ligand as a four-electron donor, the complex is a 60 valence electron species, which can be compared to a number of similar tetrahedral Ir clusters previously reported, such as $Ir_4(CO)_{12}$ [2], $[Ir_4(CO)_{10}H_2]^{2-}$ [4], $Ir_4(CO)_{9-10}(PPh_3)_{3-2}$ [3], $[Ir_4(CO)_{11}Br]^-$ [5], $Ir_4(CO)_{11}$(CNBu-t) [6], and $Ir_4(CO)_{10}$(diars) [7]. In comparison with these complexes, however, it displays two novel structural features, namely, the simultaneous presence of four triphenylphosphine groups and coordination of a μ_3-phenylphosphido ligand. Both of these features probably act together to cause the unusual lengthening of the Ir—Ir basal edges*, the triply-bridging ligand because of its electronic and stereochemical requirements (cf. for instance the constancy of the mean metal—phosphorus—metal angle here, 78.3°, and in $Fe_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}PPh)$ [8], 77.7°), and the bulky triphenylphosphine groups by causing interligand overcrowding which is apparent in a number of H···C and H···O short contacts (some of the latter attractive) between PPh_3 groups and bridging carbonyls. The Ir—CO bond lengths are in the usual range. The Ir—PPh_3 distances are slightly shorter than in $Ir_4(CO)_{9-10}(PPh_3)_{3-2}$ [3] (mean 2.301 vs. 2.36 Å), where the higher number of carbonyl groups gives rise to less Ir→P π-back-donation.

We thank the Italian C.N.R. for financial support.

References

1 P. Chini and B.T. Heaton, Topics Curr. Chem., 71 (1977) 1, and ref. therein.
2 (a) G.R. Wilkes, Ph.D. thesis, University of Wisconsin, Madison, 1965;
(b) M.R. Churchill, and J.P. Hutchinson, Inorg. Chem., 17 (1978) 3528.
3 V.G. Albano, P.L. Bellon, and V. Scatturin, J. Chem. Soc. Chem. Commun., (1967) 730.
4 G. Ciani, M. Manassero, V.G. Albano, F. Canziani, G. Giordano, S. Martinengo, and P. Chini, J. Organometal. Chem., 150 (1978) C17.
5 P. Chini, G. Ciani, L. Garlaschelli, M. Manassero, S. Martinengo, A. Sironi, and F. Canziani, J. Organometal. Chem., 152 (1978) C35.
6 J.R. Shapley, G.F. Stuntz, M.R. Churchill, and J.P. Hutchinson, J. Chem. Soc. Chem. Commun., (1979) 219; M.R. Churchill, and J.P. Hutchinson, Inorg. Chem., 9 (1979) 2451.
7 J.R. Shapley, G.F. Stuntz, M.R. Churchill, and J.P. Hutchinson, J. Amer. Chem. Soc., 101 (1979) 7425.
8 G. Huttner, J. Schneider, G. Mohr, and J. von Seyerl, J. Organometal. Chem., 191 (1980) 161.

---

*The "normal" Ir—Ir distance observed in the tetranuclear clusters described in ref. 2—7 is in the range 2.685—2.740 Å, i.e. 0.18 Å shorter on the average than the Ir—Ir basal bond lengths in the present compound.