Journal of Organometallic Chemistry, 54 (1973) C51–C52

Preliminary communication

The crystal and molecular structure of ethylene and carbonyl complexes of internal metallated triphenyl- and triisopropyl-phosphineiridium(I)

G. PEREGO, G. DEL PIERO, M. CESARI, M.G. CLERICI and E. PERROTTI

S.N.A.M. Progetti, Direzione Ricerca e Sviluppo, 20097 San Donato Milanese (Italy)

(Received March 14th, 1973)

We report the crystal and molecular structure of three new iridium(I) complexes, (I) $Ir(C_2H_4)_2PPh_2C_6H_4PPh_3 \cdot 1.5\ C_6H_5CH_3$, (II) $Ir(CO)_2PPh_2C_6H_4PPh_3 \cdot THF$, and (III) $Ir(C_2H_4)_2P\text{-}i\text{-}Pr_2C_3H_6P\text{-}i\text{-}Pr_3$. Their common features are the metallation of one phosphine ligand and the coordination of two molecules of ethylene (I and III) or carbon monoxide (II). To our knowledge, only a few such ethylene iridium(I) complexes have been studied[1,2], moreover this is the first example of well-characterised internal metallated iridium(I).

Crystal data: (I) triclinic, $a = 21.357 \pm 0.02$, $b = 11.847 \pm 0.015$, $c = 10.03 \pm 0.01$ Å, α 112.3 ± 0.3°, β 114.3 ± 0.3°, γ 86.5 ± 0.3°, space group $P1$, $Z = 2$; (II) monoclinic, $a = 15.072 \pm 0.015$, $b = 13.717 \pm 0.015$, $c = 18.517 \pm 0.02$ Å, β 101.4 ± 0.3°, space group $P2_1/c$, $Z = 4$; (III) tetragonal, $a = 14.077 \pm 0.015$, $c = 25.598 \pm 0.025$ Å, space group $P4_12_12$, $Z = 8$.

Single crystals of the three compounds, prepared in our laboratories, were examined on automated Siemens diffractometer with Mo-K_α radiation. Resolution of the structure was performed by standard procedures; no absorption correction was made. The refinement was carried out by the anisotropic block-matrix least-squares method using 5413 (I), 5249 (II) and 1562 (III) independent reflections. Final R index was 0.056, 0.058 and 0.032 for (I), (II) and (III) respectively. The standard deviations of the bond distances are about 0.003 Å for Ir–P, 0.015 Å for Ir–C, 0.010 Å for P–C and 0.025 Å for C–C. The essential features of the structures can be best discussed by referring to Fig.1. The coordination around iridium is similar in all three compounds, the metal atom lying at the centre of a distorted trigonal bipyramid. The ethylene molecules in (I) and (III) lie on the equatorial plane (A and B positions of Fig.1); the mean value of Ir–C bond distance, 2.168 Å, in (I) is quite similar to the corresponding distance in (III), 2.150 Å. The ethylene C–C distances average 1.45 Å (I) and 1.43 Å (III). The carbonyl groups in (II) are also in the equatorial plane, the mean value of Ir–C distance being 1.846 Å, The non-metallated phosphine group occupies the apical position P(1) of the bipyramid, while the phosphorous atom of the metallated phosphine

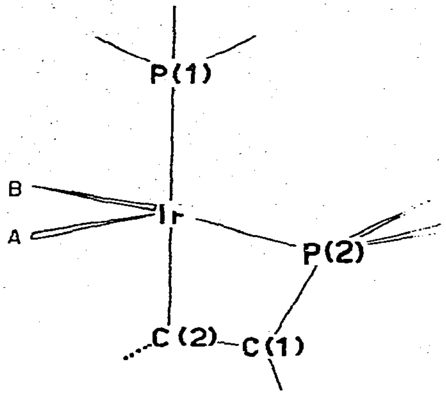

Fig.1. Schematic view of the coordination around Iridium in complexes (I), (II) and (III). The hybridization of the C(1) and C(2) atoms is sp^2 in (I) and (II) and sp^3 in (III).

lies at the corner of the equatorial plane P(2) with its *ortho*-carbon, (I) and (II), or β-carbon, (III), at the apical position C(2). The mean Ir–P bond distance is 2.370 Å (I), 2.374 Å (II) and 2.400 Å (III) these values being similar to those found in other phosphine–iridium complexes[3,4].

The metallation gives rise to a four-membered ring Ir–P(2)–C(1)–C(2) which is planar for triphenylphosphine, (I) and (II), but deviates considerably from planarity for triisopropylphosphine (III).

The Ir–C(2) bond distances, 2.070, 2.113 and 2.141 Å for (I), (II) and (III) respectively, are very close to the value of 2.10 Å, recently found in an *ortho*-metallated triphosphiteiridium derivative[5].

A significant distortion of the valence angles, with respect to the typical tetrahedral and trigonal values, arises in the chelating ring, particularly on the P(2) and C(1) atoms. The Ir–P(2)–C(1) valence angle ranges from 83.7 to 85.7° while the P(2)–C(1)–C(2) angle is 101.2° (I), 101.9° (II) and 95.5° (III). When the different hybridisation of C(1), sp^2 in (I) and (II) and sp^3 in (III), is taken into account, the type and amount of distortion may be considered similar in the three complexes.

ACKNOWLEDGMENT

We thank E.N.I. Direction for allowing publication of this work.

REFERENCES

1 A. Van der Ent and T.C. Van Soest, *Chem. Commun.*, (1970) 225.
2 H. Van Gool, H.G.A.M. Cuppers and A. Van der Ent, *Chem. Commun.*, (1970) 1694.
3 J.S. Ricci, J.A. Ibers, M.S. Fraser and W.H. Baddley, *J. Amer. Chem. Soc.*, 92 (1970) 3489.
4 J.A. McGinnety, R.J. Doedens and J.A. Ibers, *Inorg. Chem.*, 6 (1967) 2243.
5 J.M. Guss and R. Mason, *Chem. Commun.*, (1971) 58.