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Synthesis and Crystal Structure of Two Isomorphous Rhodium and Iridium Complexes with *cyclo*-triphosphorus and 1,1,1-tris(diphenylphosphinomethyl)ethane

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It has been recently shown that by reaction of white phosphorus with hydrated cobalt(II) salts and the tripod-like polytertiary phosphines (L) 1,1,1-tris-(diphenylphosphinomethyl)ethane, triphos, and tris-(2-diphenylphosphinoethyl)amine, np$_3$, mononuclear compounds with formula [LCo(η^3-P$_3$)] are obtained [1, 2]. The complexes, which are diamagnetic, contain a *cyclo*-triphosphorus unit linked to the metal as a *trihapto* η^3-P$_3$ ligand. We have now succeeded in synthesizing the analogous rhodium and iridium derivatives having the formulae [(triphos)Rh-(η^3-P$_3$)] and [(triphos)Ir(η^3-P$_3$)] respectively. They were characterized by standard physical methods and complete X-ray analyses.

Experimental

All operations were carried out under a nitrogen atmosphere. All solvents and materials were reagent grade. Benzene and THF were purified by standard methods. The ligand triphos and the complexes [Rh(C$_2$H$_4$)$_2$Cl]$_2$, [Rh(CO)$_2$Cl]$_2$ and [Ir(PPh$_3$)$_2$(CO)-Cl] were prepared by published procedures [3–6].

[(triphos)Rh(η^3-P$_3$)] (I)

An excess (50%) of white phosphorus in 15 ml of THF was added to a mixture of [Rh(C$_2$H$_4$)$_2$Cl]$_2$ (0.19 g, 0.5 mmol) and triphos (0.62 g, 1 mmol) in 30 ml of THF. Ethanol was added. On warming the resulting red brown solution, sand coloured crystals precipitated. They were recrystallized from methylene chloride–ethanol. The complex (*I*) was also obtained from [Rh(CO)$_2$Cl]$_2$ under similar conditions. *Anal.* Calcd. for C$_{41}$H$_{39}$RhP$_6$: C, 60.02; H, 4.79; Rh, 12.54; P, 22.65. Found: C, 60.40; H, 4.93; Rh, 13.11; P, 22.71.

[(triphos)Ir(η^3-P$_3$)] (II)

The orange mixture of [Ir(PPh$_3$)$_2$(CO)Cl] (0.78 g, 1 mmol) and triphos (0.62 g, 1 mmol) in 50 ml of benzene was heated to 60 °C for 2 h. On adding an excess (50%) of white phosphorus in 15 ml of THF, a yellow solution was formed which was reduced to half its volume by heating. Upon addition of 40 ml of ethanol white crystals were obtained. They were recrystallized from chloroform–ethanol. *Anal.* Calcd. for C$_{41}$H$_{39}$IrP$_6$: C, 54.12; H, 4.32; Ir, 21.12; P, 20.42. Found: C, 54.43; H, 4.27; Ir, 21.40; P, 20.30.

The crystals and complexes (*I*) and (*II*) are both isomorphous with those of the compound [(triphos)-Co(η^3-P$_3$)] [1]. The space group is rhombohedric *R*3 and the unit cell parameters measured by using Mo-K$_\alpha$ radiation are a = 10.625(4), α = 109.24(7) and a = 10.610(5), α = 109.23(7) for Rh and Ir respectively. The two crystals chosen for X-ray work on a Philips PW 1100 diffractometer had both an irregular rhombododecahedron shape. The volume of the crystal of compound (*II*) was at least ten times smaller than that of the compound (*I*) (*ca.* 0.001–0.002 mm^3). Collection and treatment of intensity data were those routinely used in this laboratory. 3271 independent reflections with $I \geqslant 2.5\sigma$ (*I*) were measured at $\theta \leqslant 30°$ for compound (*I*). Due to the smallness of the crystal no reflections were measured beyond θ = 25 for compound (*II*) thus limiting the number of independent observed reflections to 2095. The final atomic parameters of the structure of the [(triphos)Co(η^3-P$_3$)] complex were used to start the refinement of both structures. Final reliability factors are: R = 0.043, R$_W$ = 0.050 and R = 0.037, R$_W$ = 0.040 for (*I*) and (*II*) respectively. A list of the observed and calculated structure factors can be obtained from the authors. The final atomic parameters are given in Table I.

Results and Discussion

The complexes [(triphos)Rh(η^3-P$_3$)] and [(triphos)-Ir(η^3-P$_3$)] are air stable both in the solid state and in solution in THF, methylene chloride, or nitroethane. They are diamagnetic and behave as non-electrolytes in methylene chloride.

A sketch of the skeleton of the molecules is reported in Fig. 1. The coordination geometry is the same as that of the isomorphous cobalt derivative with the metal linked to the three phosphorus atoms of a triangular P$_3$ unit and to the three phosphorus atoms of the tripod ligand. For comparative purposes the geometrical parameters of the rhodium and iridium complexes are reported together with those of the cobalt analog in Table II. As expected all the metal to phosphorus bond distances in both the complexes of rhodium and iridium are longer than in the cobalt derivative due to the larger atomic sizes of the two metals. No relevant differences however are observed between the corresponding Rh–P and Ir–P bond distances for the tripod ligand as well as for the

TABLE I. Positional Parameters of Non-Hydrogen Atoms (X 10^4) in the Structures of [(triphos)Rh(η^3-P_3)] and [(triphos)Ir(η^3-P_3)].

	[(triphos)Rh(η^3-P_3)]			[(triphos)Ir(η^3-P_3)]		
	X	Y	Z	X	Y	Z
Metal	0	0	0	0	0	0
P(1)	63(1)	1314(1)	2240(1)	62(3)	1307(3)	2226(3)
P(2)	−1145(2)	−2094(1)	−2551(1)	−1162(3)	−2111(3)	−2575(3)
C(1)	4654(8)	4654	4654	4691(15)	4691	4691
C(2)	3238(7)	3238	3238	3213(16)	3213	3213
C(3)	2081(6)	2590(6)	3765(5)	2110(13)	2615(13)	3814(11)
C(4)	−778(6)	2582(6)	2457(6)	−792(11)	2563(10)	2423(11)
C(5)	−1780(7)	2525(7)	1177(7)	−1772(15)	2494(13)	1127(15)
C(6)	−2467(8)	3446(8)	1368(9)	−2524(18)	3417(18)	1305(19)
C(7)	−2213(7)	4350(7)	2796(9)	−2225(14)	4333(13)	2752(18)
C(8)	−1241(8)	4411(8)	4057(8)	−1250(15)	4421(17)	4010(17)
C(9)	−520(7)	3523(7)	3901(7)	−557(14)	3482(15)	3839(14)
C(10)	−888(5)	157(5)	2928(5)	−882(12)	143(11)	2933(11)
C(11)	−2476(8)	−702(8)	2053(8)	−2512(19)	−727(18)	2035(18)
C(12)	−3320(10)	−1666(10)	2442(10)	−3356(20)	−1695(17)	2388(19)
C(13)	−2576(9)	−1808(8)	3688(7)	−2605(16)	−1800(15)	3636(15)
C(14)	−1025(8)	−984(7)	4535(8)	−1088(17)	−1011(15)	4525(16)
C(15)	−157(7)	23(7)	4187(7)	−215(14)	15(13)	4176(12)

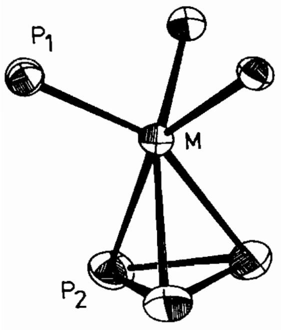

Fig. 1. Sketch of the skeleton of the isomorphous compounds [(triphos)M(η^3-P_3)], M = Co, Rh, Ir.

TABLE II. Selected Bond Distances (Å) and Angles (deg) in [(triphos)M(η^3-P_3)] Complexes (M = Co, Rh, Ir).

	Co	Rh	Ir
M–P(1)	2.186(1)	2.294(1)	2.277(2)
M–P(2)	2.301(2)	2.418(2)	2.436(2)
P(2)–P(2)′	2.141(2)	2.152(2)	2.159(4)
P(1)–M–P(1)	93.55(4)	91.25(4)	91.22(7)
P(2)–M–P(2)′	55.43(5)	52.86(5)	52.60(8)
M–P(2)–P(2)′	62.3(4)	63.57(4)	63.70(7)
P(1)–M–P(2)	154.97(5)	154.90(5)	154.80(8)
P(1)–M–P(2)′	105.31(5)	108.38(5)	108.38(8)
P(1)–M–P(2)″	101.40(4)	103.43(5)	103.64(8)

cyclo-triphosphorus unit, a fact which can be referred to the *lanthanide contraction*. Curiously the Ir–P(triphos) distance is even shorter than the Rh–P (triphos) distance (2.277(2) *vs.* 2.293(1) Å). The P–P distances in the *cyclo*-triphosphorus units, which are in all cases shorter than in the tetrahedral P_4 molecule (2.21 Å) [7] increase from cobalt through rhodium to iridium being equal to 2.141(2), 2.152(2) and 2.159(4) Å respectively. On the basis of a previously employed electron pair repulsion approach [8], one can infer that the charge delocalization from the P_3 unit to the metal becomes progressively less effective on going from cobalt to iridium on account of the lessening overlaps between d orbitals from the metal and phosphorus p_π orbitals. The energies of 4d and 5d orbitals which are higher than those of 3d orbitals, as well as the longer distances between interacting centers probably account for the observed trend within the series of isomorphous compounds.

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