Synthesis and Crystal Structures of the Metallacyclopentane Complexes (η^5-Cyclopentadienyl)(triphenylphosphine)(butane-1,4-diyl)cobalt(III) and (η^5-Pentamethylcyclopentadienyl)(triphenylphosphine)-(butane-1,4-diyl)iridium(III)

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Summary Reactions of (**3**) and (**4**) with the organomagnesium reagents (**1**) or (**2**) lead to the metallacyclopentane derivatives (**5**) and (**6**), respectively; the *X*-ray structures of these compounds are reported.

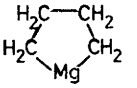
The reaction of $[RhI_2(PPh_3)(\eta^5\text{–}C_5Me_5)]$ with the organomagnesium reagents (**1**) or (**2**) quite surprisingly leads[1] to the ethylene complex $[Rh(PPh_3)(C_2H_4)(\eta^5\text{–}C_5Me_5)]$[2] as the major product along with minor amounts of a compound postulated as the expected rhodacyclopentane derivative.

We have now observed that the reactions of the isostructural derivatives of cobalt (**3**) and of iridium (**4**) with (**1**) or (**2**) give the metallacycles (**5**) and (**6**) in a pure form; free ethylene or ethylene–metal complexes have not been detected as by-products.

Thus, (**5**) was prepared (yield, *ca.* 15%) by the reaction of (**3**) with (**1**) or (**2**) (molar ratio, 1 : 3) in diethyl ether, at room temperature. From the reaction mixture, after filtration and removal of solvent, an oily residue was obtained which was extracted with pentane, and chromatographed on neutral alumina. From the orange pentane eluate, compound (**5**) crystallized as orange-red needles, at -20 °C.

$BrMg[CH_2]_4MgBr$

(1)



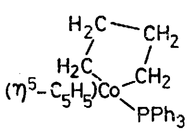
(2)

$[CoI_2(PPh_3)(\eta^5\text{-}C_5H_5)]$

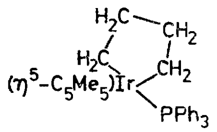
(3)

$[IrCl_2(PPh_3)(\eta^5\text{-}C_5Me_5)]$

(4)



(5)



(6)

Similarly pure (**6**) was obtained (yield, *ca.* 25%) as pale yellow needles by the reaction of (**4**) with (**1**) or (**2**), using tetrahydrofuran (THF) as solvent.

A single-crystal *X*-ray diffraction study was undertaken on (**5**) and (**6**). For both crystals lattice parameters and integrated intensities were measured by means of a PW1100 computer-controlled diffractometer. In both cases corrections for Lorentz and polarization factors were applied and for (**6**) absorption was corrected for by using the experimental procedure described by North *et al.*[3]

Crystal data: (**5**) $C_{27}H_{28}CoP$, $M = 442{\cdot}43$, $a = 16{\cdot}018(2)$, $b = 15{\cdot}673(2)$, $c = 8{\cdot}977(1)$ Å, $\beta = 103{\cdot}33(1)^\circ$; $Z = 4$; $D_c = 1{\cdot}34$ g cm^{-3}; $U = 2193{\cdot}0$ Å^3; space group $P2_1/n$ (No. 14); $\lambda = 0{\cdot}71069$ Å; μ (Mo-K_α) $= 8{\cdot}97$ cm^{-1}; $F(000) = 928$; 2181 reflections ($I > 3\sigma$) were considered observed and the final R value was 0·054.† (**6**) $C_{32}H_{38}$ IrP, $M = 645{\cdot}83$; $a = 12{\cdot}423(1)$, $b = 23{\cdot}949(1)$, $c = 9{\cdot}344(1)$ Å, $\beta = 98{\cdot}25(1)^\circ$; $Z = 4$; $D_c = 1{\cdot}56$, g cm^{-3}; $U = 2751{\cdot}3$ Å^3; space group $P2_1/n$ (No. 14); $\lambda = 1{\cdot}54178$ Å; μ (Cu-K_α) $= 99{\cdot}39$ cm^{-1}; copper radiation was used in place of Mo-K_α in view of the very small crystal volume ($5{\cdot}0 \times 10^{-5}$ mm^3); $F(000) = 1288$; 1285 reflections ($I > 3\sigma$) were considered observed and the final R value was 0·067.†

TABLE. Selected interatomic distances (Å) of (**5**) and (**6**), with e.s.d.'s in parentheses.

Co–P	2·145(2)	Ir–P	2·216(9)
Co–C(1)	2·025(6)	Ir–C(1)	2·10(4)
Co–C(4)	2·024(7)	Ir–C(4)	2·14(5)
Co–C(5)	2·084(9)	Ir–C(5)	2·23(4)
Co–C(6)	2·086(12)	Ir–C(6)	2·25(5)
Co–C(7)	2·104(10)	Ir–C(7)	2·26(3)
Co–C(8)	2·095(11)	Ir–C(8)	2·36(4)
Co–C(9)	2·090(9)	Ir–C(9)	2·24(4)

Since the structural features of the two complexes are essentially identical, only the co-ordination geometry of (**5**) is given in the Figure. Principal bond lengths are given in the Table.

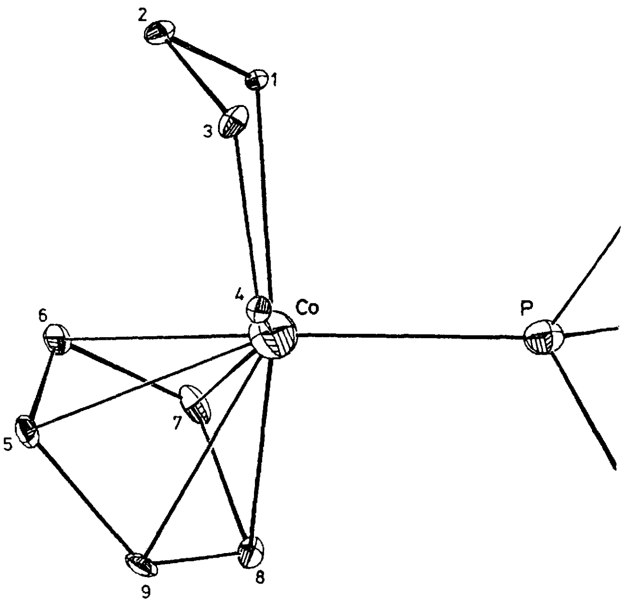


FIGURE. Molecule of (**5**) viewed normally to the plane formed by Co, P, and C(1). Phenyl groups have been omitted; unlettered atoms are C.

When (**5**) and (**6**) are thermally decomposed in mesitylene, at 110 °C, C_4-hydrocarbons are obtained as the only volatile products. Similar decomposition modes have been observed in the case of some platinum(II) metallacyclopentane derivatives.[4]

Work is in progress to explain the different behaviour exhibited by the cobalt and iridium complexes (**3**) and (**4**) from that shown by the isostructural rhodium compound[1] towards the alkylating agents (**1**) and (**2**).

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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