C---Br INSERTION REACTIONS IN RHODIUM AND IRIDIUM COMPOUNDS CONTAINING AN ORTHO-HALO-ARYLPHOSPHINE. X-RAY STRUCTURES OF TWO ORTHO-METALLATED COMPOUNDS OF FORMULA $IrX_2[P(C_6F_4)Ph_2][P(o-BrC_6F_4)Ph_2], (X = Cl, Br)$

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Abstract—A comparative study of the reaction of Rh and Ir complexes with the orthobromo-arylphosphine PCBr [PCBr = P(o-BrC₆F₄)(C₆H₅)₂], is presented. Various PCBr complexes of Ir(I) and Rh(I) undergo rapid insertion of the metal atom into a C—Br bond provided the phosphine is coordinated in a η^2 -mode (P—Br). If the Br coordination is substituted by a superior ligand such as CO or an olefin, no reaction occurs under normal conditions. PCBr complexes of the tervalent metals require a two-electron reduction step prior to the ortho-metallation reaction. Most intermediates were characterized by chemical and spectroscopic analysis. Two intermediates of general formula IrX₂(η^2 -PC)(η^2 -PCBr), [PC = P(C₆F₄)(C₆H₅)₂] (X = Cl, 5, X = Br, 6), were characterized by a single crystal analysis. 5 crystallizes in the monoclinic space group P2₁/n with cell dimensions a =14.741(5) Å, b = 13.558(5) Å, c = 18.303(7) Å, $\beta = 112.35(2)^\circ$, Z = 4. 6 crystallizes in the same space group P2₁/n and has cell dimensions a = 19.05(1) Å, b = 19.554(6) Å, c =20.337(5) Å, $\beta = 93.63(5)^\circ$, Z = 8. Both compounds have distorted octahedral coordination around the metal centre.

Reactions of coordinated phosphine ligands to give cyclometallated products have received considerable attention.¹ In particular, cyclometallated rhodium or iridium compounds obtained by C—H bond activation in triarylphosphites² or triarylphosphines³ have been reported. Activation of C—H bonds in alkyl phosphines⁴ is less common.

We have observed that rhodium(I) compounds containing PCBr can undergo thermal *ortho*-metal-

lation by metal insertion into the C—Br bond. Mononuclear rhodium(III) compounds⁵ containing a four atom metallocycle and binuclear compounds with an *ortho*-metallated PCBr phosphine bridging a dirhodium(+4) unit have been isolated.⁶ Examples of *ortho*-metallation of this phosphine with activation of a C—H aryl bond are also known.⁷

We report here the results of a comparative study of the *ortho*-metallation reaction in rhodium and iridium compounds with PCBr. Included are the

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X-ray structures of two metallated iridium(III) compounds 5 and 6.

EXPERIMENTAL

RhCl₃·3H₂O was purchased from Johnson Matthey Ltd and IrCl₃·3H₂O was purchased from Englehard Industries. Chemical reactions were carried out in a dry argon or nitrogen atmosphere using standard Schlenck-type procedures. All the solvents were of reagent grade and were dried and distilled prior to use. The starting materials were prepared by literature methods.⁸⁻¹⁵ ¹H NMR spectra were recorded on a BRUKER AC200 (200.132 MHz) spectrometer, using TMS as internal reference. The ³¹P NMR spectra were recorded on a

BRUKER AC200 (81.015 MHz) spectrometer, with H_3PO_4 85% as external reference. IR spectra were recorded on a PYE-UNICAM SP8-100 spectrophotometer.

X-ray crystallography

The crystallographic work followed the general procedures which were described previously.¹⁶ The crystal parameters and basic information corresponding to data collection and structure refinement for compounds **5** and **6** are given in Table 1. The structure of compound **6** contains two independent molecules per asymmetric unit. Important bond distances and angles are given in Table 2. In both structures the positions of the iridium atoms

	X = Cl	X = Br		
Formula	IrBrCl ₂ P ₂ F ₈ C ₃₆ H ₂₀	IrBr ₃ Cl ₂ P ₂ F ₈ C ₄₂ H ₃₄		
Formula weight	1008.5	1144.35		
Space group	$P2_{1}/n$			
Systematic absences	$0k0, k \neq 2n;$			
	$h0l, h+l \neq 2n$			
<i>a</i> , Å	14.741(5)	19.05(1)		
<i>b</i> , Å	13.558(5)	19.554(6)		
<i>c</i> , Å	18.303(7)	20.337(5)		
α, deg	90.0	90.0		
β , deg	112.35(2)	93.63(6)		
y, deg	90.0	90.0		
$V, Å^3$	3383(4)	7562(7)		
Z	4	8		
$d_{\rm calc}$, g/cm ³	1.98	2.01		
Crystal size, mm	$0.30 \times 0.30 \times 0.20$	$0.30 \times 0.30 \times 0.30$		
μ (Mo-K _*), cm ⁻¹	54.24	69.41		
Data collection instrument	Syntex P1			
Radiation (monochromated in	-			
incident beam)	Mo- K_a ($\lambda_a = 0.71073$ Å)			
Orientation reflections,				
number, range (2θ)	15, 20–31	15, 20-32		
Temperature, °C	10	10		
Scan method	ω -2 θ	ω -2 θ		
Data col. range, 2θ , deg	$4 < 2\theta < 45$	$4 < 2\theta < 45$		
No. unique data, total	3831	7351		
with $F_a^2 > 3\sigma(F_a^2)$	2659	5483		
Number of parameters refined	451	925		
R^a	0.0397	0.0430		
$R_w^{\ b}$	0.0518	0.0530		
Quality-of-fit indicator ^e	0.996	1.040		
Largest shift/esd, final cycle	0.00	0.22		
Largest peak, e/Å ³	1.30	1.13		

Table 1. Crystallographic data for $IrX_2[P(C_6F_4)Ph_2][P(o-BrC_6F_4)Ph_2]$

 ${}^{a}R = \Sigma ||F_{o}| - |F_{c}|| / \Sigma |F_{o}|.$

 ${}^{b}R_{w} = [\Sigma w(|F_{o}| - |F_{c}|)^{2} / \Sigma w|F_{o}|^{2}]^{1/2}; w = 1/\sigma^{2}(|F_{o}|).$

^c Quality-of-fit = $[\Sigma w(|F_o| - |F_c|)^2/(N_{obs} - N_{parameters})]^{1/2}$.

		Compound 5		
Ir(1)—Br(1)	2.550(2)	Br(1)	⊢Ir(1)−P(1)	168.71(8)
Ir(1) - P(1)	2.253(4)	Br(1)	-Ir(1) - P(2)	86.2(1)
Ir(1) - P(2)	2.274(3)	Br(1)	-Ir(1)-Cl(1)	85.1(1)
Ir(1)Cl(1)	2.418(3)	Br(1)	-Ir(1)-Cl(2)	83.10(9)
Ir(1)—Cl(2)	2.403(3)) Br(1)	-Ir(1)-C(16)	101.8(4)
Ir(1)C(16)	2.03(1)	P(1)-	-Ir(1)-P(2)	100.8(1)
P(1)-C(11)	1.80(1)	P(1)-	-Ir(1)Cl(1)	103.3(1)
P(1)C(21)	1.83(1)	P(1)-	-Ir(1)-Cl(2)	89.4(1)
P(1)C(31)	1.81(2)	P(1)-	-Ir(1)-C(16)	69.2(4)
C(11)C(16)	1.43(2)	P(2)-	Ir(1)Cl(1)	92.0(1)
P(2)-C(41)	1.82(1)	P(2)-	-Ir(1)-Cl(2)	169.1(1)
P(2)C(51)	1.83(1)	P(2)-	-Ir(1)-C(16)	93.4(3)
P(2)C(61)	1.83(1)	Cl(1)	-Ir(1)-Cl(2)	89.3(1)
Br(1) - C(46)	1.90(1)	Cl(1)	-Ir(1)-C(16)	171.5(4)
C(41)C(46)	1.37(2)	Cl(2)	-Ir(1)-C(16)	86.6(3)
		Ir(1)	-P(1)-C(11)	86.3(5)
		Ir(1)	-P(1)-C(21)	119.9(5)
		Ir(1)	-P(1)-C(31)	123.6(5)
		Ir(2)	-P(1)-C(41)	106.0(4)
		Ir(2)	-P(1)-C(51)	112.3(4)
		Ir(2)	-P(1)-C(61)	122.0(4)
		Ir—(C(16)—C(11)	106.6(5)
	Molecule A	Compound 6	Molecu	le B
Ir(1)—Br(11)	2.549(2)) Ir(2)-	—Br(2)	2.561(2)
Ir(1)—P(11)	2.262(4)) Ir(2)	-P(22)	2.251(4)
Ir(1)P(12)	2.283(4)) Ir(2)	-P(21)	2.274(4)
Ir(1)—Br(12)	2.568(2)) Ir(2)	—Br(22)	2.550(2)
Ir(1)—Br(1)	2.542(2)) Ir(2)	-Br(21)	2.517(2)

2.283(4)	Ir(2) - P(21)	2.2/4(4)
2.568(2)	Ir(2)—Br(22)	2.550(2)
2.542(2)	Ir(2)—Br(21)	2.517(2)
2.06(1)	Ir(2)C(106)	2.05(2)
1.79(2)	P(22)C(111)	1.79(2)
1.81(1)	P(22)-C(121)	1.82(2)
1.79(1)	P(22)-C(101)	1.79(2)
1.40(2)	C(101)-C(106)	1.41(2)
1.86(1)	P(21)C(91)	1.86(1)
1.84(1)	P(21)C(71)	1.85(1)
1.80(2)	P(21)-C(81)	1.81(2)
1.88(1)	Br(2)C(96)	1.89(2)
1.41(2)	C(91)C(96)	1.41(2)
168.9(1)	Br(2)—Ir(2)—P(22)	169.7(1)
86.4(1)	Br(2)—Ir(2)—P(21)	85.9(1)
86.63(6)	Br(2)—Ir(2)—Br(22)	86.16(6)
82.21(6)	Br(2)—Ir(2)—Br(21)	82.93(6)
102.9(4)	Br(2)-Ir(2)-C(106)	103.0(5)
99.5(1)	P(22)— $Ir(2)$ — $P(21)$	100.5(2)
102.3(1)	P(22)—Ir(2)—Br(22)	101.5(1)
91.1(1)	P(22)— $Ir(2)$ — $Br(21)$	90.1(1)
67.6(4)	P(22)Ir(2)C(106)	68.7(5)
93.5(1)	P(21)—Ir(2)—Br(22)	92.6(1)
167.7(1)	P(21)—Ir(2)—Br(21)	168.3(1)
92.3(4)	P(21)-Ir(2)-C(106)	94.2(4)
90.40(6)	Br(22)— $Ir(2)$ — $Br(21)$	90.22(6)
169.2(4)	Br(22)—Ir(2)—C(106)	169.0(4)
85.9(4)	Br(21)— $Ir(2)$ — $C(106)$	84.9(4)
87.5(6)	Ir(2)-P(22)-C(101)	86.7(5)
118.5(5)	Ir(2)P(22)C(121)	119.4(6)
123.0(5)	Ir(2)—P(22)—C(111)	121.1(5)
107.4(5)	Ir(2)P(21)C(91)	107.7(5)
123.7(5)	Ir(2)P(21)C(81)	123.5(5)
112.6(5)	Ir(2)—P(21)—C(71)	112.5(5)
107(1)	Ir(2)C(106)C(101)	106(1)
	2.283(4) 2.568(2) 2.542(2) 2.06(1) 1.79(2) 1.81(1) 1.79(1) 1.40(2) 1.86(1) 1.84(1) 1.84(1) 1.84(1) 1.89(2) 1.88(1) 1.41(2) 168.9(1) 86.4(1) 86.63(6) 82.21(6) 102.9(4) 99.5(1) 102.3(1) 91.1(1) 67.6(4) 93.5(1) 167.7(1) 92.3(4) 90.40(6) 169.2(4) 85.9(4) 87.5(6) 118.5(5) 123.0(5) 107.4(5) 123.7(5) 112.6(5) 107(1)	2.283(4) $Ir(2) - P(21)$ 2.568(2) $Ir(2) - Br(22)$ 2.542(2) $Ir(2) - Br(21)$ 2.06(1) $Ir(2) - C(106)$ 1.79(2) $P(22) - C(111)$ 1.81(1) $P(22) - C(101)$ 1.40(2) $C(101) - C(106)$ 1.86(1) $P(21) - C(91)$ 1.86(1) $P(21) - C(91)$ 1.84(1) $P(21) - C(96)$ 1.84(1) $P(21) - C(96)$ 1.88(1) $Br(2) - Ir(2) - P(22)$ 86.4(1) $Br(2) - Ir(2) - P(21)$ 86.63(6) $Br(2) - Ir(2) - Br(22)$ 86.4(1) $Br(2) - Ir(2) - Br(21)$ 102.9(4) $Br(2) - Ir(2) - Br(21)$ 102.9(4) $Br(2) - Ir(2) - Br(21)$ 102.3(1) $P(22) - Ir(2) - Br(22)$ 91.1(1) $P(22) - Ir(2) - Br(21)$ 67.6(4) $P(22) - Ir(2) - Br(21)$ 67.6(4) $P(21) - Ir(2) - Br(21)$ 92.3(4) $P(21) - Ir(2) - Br(21)$ 90.40(6) $Br(22) - Ir(2) - C(106)$ 85.9(4) $Br(21) - Ir(2) - C(106)$ 85.9(4) $Br(21) - Ir(2) - C(106)$ 85.9(4) $Br(21) - Ir(2) - C(106)$ 87.5(6) $Ir(2) - P(22) - C(111)$ 118.5(5) $Ir(2) - P(22) - C(121)$ 123.0(5) $Ir(2) - P(21) - C(81)$ 112.6(5) $Ir(2) - P(21) - C(71)$ 107(1) $Ir(2) - C(106) - C(101)$

were obtained from the three-dimensional Patterson map. The remaining atoms were located by using successive least-squares refinement and difference Fourier maps. The refinement converged at residuals of R = 0.040, $R_w = 0.052$ for 5 and R = 0.043, $R_w = 0.053$ for 6.*

Preparation of RhClBr(PC)(PCBr) (1)

(a) From RhCl₃· $3H_2O$. RhCl₃· $3H_2O$ (52.7 mg, 0.2 mmol) and PCBr (330 mg, 0.8 mmol) were refluxed in 10 cm³ of ethanol. After 1 h the solution became lighter yellow and a yellow precipitate was obtained. It was then filtered off, washed with ethanol and air dried. Yield : 70–80%.

(b) From $[RhCl(C_8H_{14})_2]_2$. A weighted amount (100 mg, 0.14 mmol) of $[RhCl(C_8H_{14})_2]_2$ was added to a solution of 230.4 mg (0.56 mmol) of PCBr in 15 cm³ of ethanol. The solution became red and then orange and a yellow product precipitated. This product was filtered off, washed with ethanol/ether and air dried. Yield : 70%.

(c) From RhCl(COD)PCBr. A solution of 100 mg (0.15 mmol) of RhCl(COD)(PCBr) and 62.5 mg (0.15 mmol) of PCBr were refluxed in 10 cm³ of xylene. The reaction was followed by TLC and after 30 min no free phosphine was observed. The solvent was then evaporated to dryness and the product recrystallized from dichloromethane/ethanol. Yield: 80%. Molecular weight measurement by osmometry in benzene: Found: 980 (average of three determinations). Calc. for RhClBr(PC) (PCBr): 964. Found: C, 45.1; H, 2.2%. Calc. for $C_{36}H_{20}F_8P_2ClBr_2Rh: C, 44.8; H, 2.1\%$.

Preparation of RhBr₂(PC)(PCBr)

RhCl₃·3H₂O (52.7 mg, 0.2 mmol) and NaBr (206 mg, 2.0 mmol) were refluxed in 20 cm³ of ethanol for 1 h. Then PCBr (330 mg, 0.8 mmol) was added and the mixture was refluxed again for 1 h. The resulting yellow precipitate was separated and washed with a 1:1 mixture of water: ethanol and later with ethanol. The compound was crystallized from dichloromethane/hexane. Found: C, 43.0; H, 2.0%. Calc. for $C_{36}H_{20}F_8P_2Br_3Rh$: C, 42.9; H, 2.0%.

Preparation of IrXY(PC)(PCBr). $(XY = Cl_2, 5; Br_2, 6; ClBr, 7a, 7b)$

(a) From $[IrCl(C_8H_{14})_2]_2$. A weighted amount (90 mg, 0.1 mmol) of $[IrCl(C_8H_{14})_2]_2$ was dissolved in 10 cm³ of dichloromethane on an ice-bath and 166 mg (0.4 mmol) of PCBr were added with stirring. The initially orange solution turned red rapidly. After 15 min the solution was slowly warmed to room temperature, and the stirring continued for 6 h, the colour becoming yellow. The solution was concentrated to ca. 2 ml and transferred to a chromatography column $(30 \times 2 \text{ cm})$ packed with silicagel in hexane. Elution with dichloromethane/ hexane 1:1 separated two vellow bands, which contained compounds 6 (fraction 1) and 7a and b (fraction 2). Further elution with dichloromethane yielded a new yellow band, which contained compound 5. All the fractions were evaporated to dryness and recrystallized from dichloromethane/ hexane. Yields: 6, 18; 7a and b, 40; 5, 25%. Found: C, 40.1; H, 2.1%. Calc. for $C_{36}H_{20}F_8P_2Br_3IrH(6)$: C, 39.4; H, 1.8%. Found: C, 41.5; H, 1.9. Calc. for $C_{36}H_{20}F_8P_2ClBr_2Ir$ (7): C, 41.0; H, 1.9%. Found: C, 43.2; H, 2.0%. Calc. for $C_{36}H_{20}F_8P_2Cl_2BrIr$ (5): C, 42.8; H, 2.0%. When the reaction was carried out in the presence of a large excess of NEt₄X (X = Cl, Br) the compounds 5 and 6 were isolated in high yield (70-75%), respectively.

(b) From IrCl(COD)PCBr. A weighted amount of IrCl(COD)(PCBr) (150 mg, 0.2 mmol) and 83 mg (0.2 mmol) of PCBr were refluxed in 12 cm³ of xylene for 10 h. During this time, the solution, initially orange, changed to yellow. The completeness of reaction was followed by TLC and ³¹P NMR. The solvent was then evaporated to dryness, the resulting oil dissolved in dichloromethane and chromatographed on a column (30×2 cm) packed with silica-gel in hexane. The chromatographic separation was as described for method (a). Yields : 5, 20; 6, 15; 7, 35%.

(c) From $IrCl(CO)(PCBr)_2$. A solution of $IrCl(CO)(PCBr)_2$ (112 mg, 0.1 mmol) in 8 cm³ of xylene was boiled under reflux until IR and TLC showed no traces of starting material in solution. After 13 h the solution was cooled and evaporated to dryness. The isomers were separated as above. Yield: 5, 18; 6, 16; 7, 30%.

Preparation of IrBr₂(PC)(PCBr), (6)

A solution of IrBr(COD)(PCBr) (80 mg, 0.1 mmol) and PCBr (41 mg, 0.1 mmol) in 8 cm³ of xylene was refluxed for 6 h, until the TLC and ³¹P NMR showed no starting material in solution. The solvent was evaporated under vacuum, and the

^{*} Supplementary material available: Fractional coordinates have been deposited with the Director, Cambridge Crystallographic Centre. Complete listings of bond distances and angles are available from the Editor.

crude product was recrystallized from dichloromethane/hexane. Yield 85%. Found: C, 39.8; H, 1.9%. Calc. for $C_{36}H_{20}F_8P_2Br_3Ir: C, 39.4; H, 1.8\%$.

Preparation of RhCl(CO)(PCBr)₂, (8)

[RhCl(C₈H₁₄)₂]₂ (143 mg, 0.2 mmol) and PCBr (165 mg, 0.4 mmol) were dissolved in 12 cm³ of dichloromethane at -10° C. CO was bubbled through the solution until TLC showed no free phosphine in the reaction medium. The pale yellow solution was concentrated to *ca.* 2 ml and transferred to a column (25 × 1.5 cm) packed with silica-gel in hexane. Elution with dichloromethane/hexane 1:1 yielded a pale yellow band, which was collected and evaporated to dryness. Recrystallization from dichloromethane/hexane gave the pure product. Yield: 65%. Found: C, 44.7; H, 2.0%. Calc. for C₃₇H₂₀OF₈P₂ClBr₂: C, 45.0; H, 2.1%. IR ν (CO) = 1970 cm⁻¹ (in CHCl₃).

Preparation of IrCl(CO)(PCBr)₂, (9)

This compound was made using an equivalent procedure to that for the rhodium analogue. Yield: 60%. Found: C, 40.9; H, 2.0. Calc. for $C_{37}H_{20}OF_8P_2ClBr_2$. C, 41.1; H, 1.8%. IR $\nu(CO) = 1965 \text{ cm}^{-1}$ (in CHCl₃).

RESULTS AND DISCUSSION

An overview of the various chemical interconversions for the Rh and Ir phosphine compounds is given in Scheme 1. Most structures were derived by a combination of chemical methods and NMR spectroscopy. Additionally, compounds 5 and 6 were subjected to an X-ray structure analysis and thus served as structural anchors.

We have shown before that the ³¹P spectroscopic parameters are of direct diagnostic value with respect to the various modes of ligation of the PCBr

(V)(VII) (11) RhCl(C9H12)PCBr RhCl (m) (IV) (Cl)Br Br C (Br)Cl la, ib 2 (VI)<u>(VII)</u> 1/2[IrCl(C8H14)2 IrCl(C,H,)PCBr (11) (IX) (viii) (X) (CL)Br (Br)CI 7a.7b

Scheme 1. Reactivity pattern for Rh and Ir compounds; (I) +4 PCBr, refluxing in EtOH; (II) CH₂Cl₂, R.T.; (III) refluxing in toluene; (IV) +PCBr, refluxing in toluene; (V) +PCBr, CH₂Cl₂, R.T.; (VI) +CO, CH₂Cl₂, R.T.; (VII) +PCBr, +CO, CH₂Cl₂, R.T.; (VIII) refluxing in xylene; (IX) +PCBr, refluxing in xylene; (X) electrochemical reduction (2e⁻).



Scheme 2. ³¹P chemical shifts vs coordination mode of the phosphine PCBr.

ligand in dirhodium systems.⁶ This is equally true for mononuclear complexes.⁵ The expected chemical shift ranges for various rhodium compounds are given in Scheme 2.¹⁷ Although there are fewer examples of Ir(PCBr) complexes, the respective chemical shifts are systematically observed at lower frequencies (20–40 ppm).

Starting with the rhodium system we find that upon reaction of $RhCl_3 \cdot 3H_2O$ and PCBr in a 1:4 molar ratio in refluxing ethanol a yellow precipitate is obtained in high yield. It is soluble in most solvents but insoluble in hexane or ethyl ether. The elemental analysis is consistent with a composition "RhCl(PCBr)₂", 1. Molecular weight measurements, by osmometry in benzene, confirm the mononuclear formulation.

The ³¹P NMR spectrum shows two blocks of signals centred at 45–50 ppm and at about -27 ppm. The low field region shows two well resolved doublets: δ_{Pa} 51.9 ppm (¹J_{Rh-Pa} 122 Hz) and δ_{Pb} 47.0 ppm (¹J_{Rh-Pb} 123 Hz). THe high field region can be interpreted as the result of two partially overlapping doublets P'_a and P'_b centred at about -24 ppm.

The relative intensities of these signals assigned to P_a and P_b and consequently to P'_a and P'_b were observed to vary with the experimental conditions so as to indicate that compound 1 is in fact a mixture of two isomers **a** and **b**. The observed chemical shifts together with the analysis and molecular weight are consistent with the formulation RhClBr(η^2 -PC)(η^2 -PCBr). The signals at

higher field are thereby assigned to P atoms of the four-membered metallocycle.^{5,18} The signals at lower field are in the chemical shift range which is typical for the chelating (P—Br) bonding mode.^{6,7} All signals exhibit additional splitting due to intramolecular $J_{\rm F-P}$ long range coupling and possibly also due to ${}^{2}J_{\rm PP}$. The magnitudes of these couplings are small (<20 Hz) in all cases, indicating that the phosphorus atoms in all the isomers are mutually in *cis*-configurations.

The above formulation of 1 is further corroborated by a comparison with the structurally characterized Ir analogues 5 and 6 (see below). Furthermore, two crystalline derivatives of 1 were isolated after prolonged exposure to air. They were structurally characterized by X-ray crystallography¹⁹ and turned out to be isomers of RhClBr[η^2 -OP(C₆F₄)(C₆H₅)₂](η^2 -PCBr) formed by air oxidation of the metallocycle. Concomitantly the ³¹P spectrum lacks the high field signal characteristic for the metallocycle and shows a singlet at 70.2 ppm instead, without a resolved Rh—O—P splitting.

If the reaction of RhCl₃·3H₂O and PCBr is performed in the presence of a 10 molar excess of NaBr, only one major product which analyses as RhBr₂(η^2 -PC)(η^2 -PCBr), **2**, is obtained. It shows signals at δP 51.6 ppm, ¹J_{Rh-P} 121 Hz, and $\delta P'$ 24.7 ppm (¹J_{Rh-P} 107 Hz).¹⁷ Small amounts of **1a** and **1b** are also observed in solution.

A comparison of products **1a**, **b** and **2*** with the starting material RhCl₃ suggests a complex reaction mechanism involving a redox process. Whether or not this redox reaction precedes the *ortho*-metallation step was proved by the following experiment: [RhCl(C_8H_{14})₂]₂ was reacted with PCBr in a 1:4 molar ratio at room temperature to give a yellow product with analytical and spectroscopic results

^{*} There is indication that 2 is a minor component (< 5%) of the reaction mixture containing 1a, b, as peaks approximately corresponding to those of 2 are detected in high quality ³¹P spectra.

Compound	Σ(PCBr)	J(Rh—P)	Σ(PC)	J(Rh-P)
RhCl(COD)(PCBr)	31.6	148		
IrCl(COD)(PCBr)	23.8			
RhCl(CO)(PCBr)	36.4	135		
IrCl(CO)(PCBr) ₂	28.4			
RhCl(PCBr) ₂	52.3	213		
	81.7	182		
IrCl(PCBr) ₂	15.5			
	44.6			
RhBr ₂ (PC)(PCBr)	51.6	121	-24	107
IrBr ₂ (PC)(PCBr)	14.6		-68.6	
IrCl ₂ (PC)(PCBr)	10.2		-66.8	
RhClBr(PC)(PCBr)	51.9	122	-25ª	90ª
	47.4	123	-24	90 ^a
IrClBr(PC)[PCBr)	9.7		-67.8	
,	15.2		-67.8	

Table 3. ³¹P NMR data

 Σ in ppm. J in Hz.

^a estimated values.

similar to 1, albeit with a different ratio of the two isomers a and b. If the reaction is carried out at 0°C an intermediate red compound is obtained. In agreement with the elemental analysis and the ³¹P NMR spectrum (CDCl₃, -40° C) we formulate this new compound as RhCl(η^2 -PCBr)(η^1 -PCBr) 3. The bidentate phosphine shows a resonance at δP 81.76 ppm (¹J_{Rh-P}182 Hz), and the monodentate one at δP 53.02 ppm (¹J_{Rh-P} 213 Hz). The ²J_{P-P'} coupling constant is 41 Hz indicative of a cir disposition of the two P nuclei in a square planar environment.

Compound 3 in dichloromethane undergoes intramolecular ortho-metallation yielding 1. If this reaction is monitored by ³¹P NMR, new signals $(\partial P - 41.1 \text{ ppm}; {}^{1}J_{Rh-P} 525 \text{ Hz})$ corresponding to a new intermediate ortho-metallated compound with the two P atoms in a mutually trans disposition can be observed. If 3 is exposed to 1 atm of CO



Fig. 1. ORTEP representation (thermal ellipsoid 50% probability) and labelling scheme of compound 5.

at -10° C a carbonyl containing product **8** is obtained which analyses as RhCl(CO)(PCBr)₂. It shows only one signal in the ³¹P spectrum (36.4 ppm; ¹J_{Rh-P} 135 Hz) and is therefore proposed to be a square planar RhCl(CO)(η^{1} -PCBr)₂ complex with a *trans* arrangement of the phosphines. This compound does not undergo *ortho*-metallation at room temperature and reacts only sluggishly in refluxing toluene to yield 1.

Focusing our attention now on the Ir system

we find an analogous reaction pattern for the Ir(1) starting material IrCl(η^2 -PCBr)(η^1 -PCBr), 4. Compound 4 shows ³¹P resonances at 44.6 ppm (chelating phosphine, P—Br) and 15.5 ppm (monodentate, PCBr). The coupling constant J_{PP} 25 Hz is indicative of a *cis*-configuration. Compound 4 undergoes rapid *ortho*-metallation at room temperature in CH₂Cl₂ solution. The reaction is completed within 30–40 min analogously to the Rh system. CO substitution yields a carbonyl con-



Fig. 2. (A and B). ORTEP representations (thermal ellipsoid 50% probability) and labelling scheme for the two independent molecules of compound 6.

taining product $IrCl(CO)(PCBr)_2$, 9, which is deactivated with respect to the *ortho*-metallation reaction. The single ³¹P resonance at 28.4 ppm is consistent with the proposed *trans* arrangement.

The intramolecular ortho-metallation reaction of compound 4 yields three products 5, 6 and 7 of general stoichiometry IrXX(PC)(PCBr) which differ in their halogen content. The following analyses were found: compound 5: $XY = Cl_2$; compound 6: $XY = Br_2$; compound 7: XY = ClBr(isomeric mixture). For compound 7 which is the mixed Cl, Br species two isomers are detected by ³¹P NMR. All the ³¹P NMR data are given in Table 3.

The crystal structures of 5 and 6 have been determined. The compounds are isostructural though not crystallographically isomorphous because 6crystallizes with two independent molecules per asymmetric unit and a molecule of solvent. Perspective views of the molecular complexes are shown in Figs 1 and 2 for 5 and 6, respectively. Important bond lengths and angles are given in Table 3.

The coordination geometries of the iridium centres are based on the octahedron with distortions imposed by the geometrical constraints of the bidentate ligands. One of the phosphines is bonded through the phosphorus atom and the ortho-carbon atom of the perfluorinated phenyl ring such as to form a four-membered metallocycle. Consequently the Ir-P-C bond angles are compressed with respect to the octahedral geometry, viz. 69.2(4) and 68.1(8) for 5 and 6, respectively. The second phosphine exhibits an η^2 -mode of coordination through the phosphorus and the o-Br atoms, resulting in a five-membered metallocyle with P-Ir-Br bond angles of 86.2(1) and 86.1(3) for 5 and 6, respectively. The average Ir—X distances are 2.41[1] and 2.54[2] Å for Cl and Br. In light of the octahedral coordination and diamagnetic NMR behaviour a t_{2q}^{6} electron configuration is postulated.

That the η^2 -PCBr coordination mode is a precondition for the *ortho*-metallation step can be shown in an experiment other than the CO substitution reaction. Reaction of [IrCl(COD)]₂ (COD = *cis*-1,5-cyclooctadiene) with 1 equivalent of PCBr leads to the known mononuclear complex IrCl(COD)PCBr.¹⁵ Because of the bidentate nature of the COD ligand the phosphine acts as a monodendate ligand. *Ortho*-metallation occurs in this compound only under vigorous conditions such as 10 h reflux in xylene to afford a mixture of **5**, **6** and **7**. The homologous Rh compound RhCl(COD)(PCBr) also gives **1a**, **b** after 3 h reflux in toluene.

Finally when $IrCl_3 \cdot 3H_2O$ is reacted with PCBr

(1:4) in refluxing ethanol a complex of Ir(III) of composition $IrCl_3(\eta^2-PCBr)(\eta^1-PCBr)$ is obtained in near-quantitative yield.⁸ This compound can be chemically or electrochemically reduced to yield a very reactive Ir(I) species assumed to be 4.⁹

In conclusion we propose that the ortho-metallation reactions of mononuclear Rh and Ir compounds with PCBr occur from the univalent oxidation state of the metals. While this can be achieved, starting from the M(III) halides, by in situ reduction of the Rh(III) by the excess of phosphine, the Ir(III) has to be reduced chemically or electrochemically. The resulting square planar complexes MCl(η^2 -PCBr)(η^1 -PCBr) undergo orthometallation at room temperature provided that one of the phosphines assumes the η^2 -PCBr mode of ligation. If the *o*-halogen ligation is competitively substituted by a superior ligand such as CO or olefin, no ortho-metallated products are formed under normal reaction conditions. Finally, the Ir compounds are subject to halogen exchange while such reactions are only of marginal importance in the case of the Rh system.

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