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SYNTHESIS OF NEW ORTHOMETALLATED IRIDIUM(III) COMPOUNDS BY CHEMICAL AND ELECTROCHEMICAL METHODS

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Summary

Replacement of one phosphine ligand in $IrCl_3(\eta^2\text{-PCBr})(\eta^1\text{-PCBr})$ (**1**) (PCBr = $P(o\text{-BrC}_6F_4)Ph_2$), by various P-donor ligands has given compounds of stoichiometry $IrCl_3(\eta^2\text{-PCBr})L$ (**3**: L = $PMePh_2$; **4**: L = $P(p\text{-MeC}_6H_4)_3$; **5**: L = $P(OMe)_3$, **6**: L = $P(OPh)_3$). All of these show two irreversible reduction peaks in the range −1.1, −1.3 and ca. −2.0 V. The electrochemical reduction of compound **1** at −1.5 V (at 0 °C) leads to a very reactive iridium(I) species, probably $IrCl(PCBr)_2$, which undergoes intramolecular orthometallation at room temperature. Three compounds are obtained as the results of this chemical conversion: $IrBr_2(PC)(PCBr)$ (**7**), $IrCl_2(PC)(PCBr)$ (**8**) and (as a mixture of isomers) $IrClBr(PC)(PCBr)$ (**9**) (PC = $P(C_6F_4)Ph_2$). The different behaviour of rhodium and iridium complexes in these reactions are discussed.

Introduction

We have recently observed that rhodium(I) compounds containing the ortho-haloarylphosphine $P(o\text{-BrC}_6F_4)Ph_2$, denoted by PCBr, can undergo an orthometallation by breaking of the C–Br bond of the phosphine to give a variety of rhodium(III) compounds containing four-atom metallocycles [1]. The molecular structures of some of these compounds show distorted octahedral coordination around the rhodium atom, especially in the bonds involved in the metallocycle [1].

We decided to extend our studies to iridium in order to compare the behaviour of rhodium and iridium centers in this type of reaction. A simple way of activating the metallation of PCBr involves the reaction of $RhCl_3$ with the phosphine in refluxing ethanol [2]. However, this procedure with $IrCl_3$ does not produce any metallated species $IrCl_3(\eta^2\text{-PCBr})(\eta^1\text{-PCBr})$ (**1**) being isolated instead in high yield [3]. This remarkable difference in behaviour between the rhodium and iridium systems prompted us to examine other ways of promoting this type of metallation in iridium complexes. We describe here the isolation and spectroscopic identification of new

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metallated iridium(III) species prepared by chemical or electrochemical reduction of compound **1**.

Results

We have found that treatment of **1** with equimolar amounts of various P-donor ligands causes displacement of one PCBr ligand to give compounds of the type $IrCl_3(PCBr)L$ (**2**: L = PPh_3 [3], **3**: L = $PMePh_2$; **4**: L = $P(p\text{-}MeC_6H_4)_3$; **5**: L = $P(OMe)_3$; **6**: L = $P(OPh)_3$) (eq. 1).

$$IrCl_3(\eta^2\text{-}PCBr)(\eta^1\text{-}PCBr) + L \rightarrow IrCl_3(\eta^2\text{-}PCBr)L + PCBr \qquad (1)$$

All these compounds have been identified by elemental analysis and ^{31}P NMR spectroscopy (Table 1). All of them give large values for the $^2J(PP')$ coupling constants, indicating that, as observed for compound **2** [3], the phosphorus ligands are in mutually *trans* positions. As is usual [4], the compounds containing phosphite ligands give larger $^2J(PP')$ coupling constants. The chemical shifts observed for the PCBr ligand, +20.8 to +8.5 ppm, also suggest a bidentate coordination of the phosphine [7]. Spectroscopic data for these compounds are given in Table 1.

Compound **1** in dichloromethane exhibits two irreversible reduction peaks of similar intensities, at −1.28 V (A_1) and −2.00 V (A_2). If the sweep is reversed after peak A_1 or A_2 a low intensity oxidation peak A'_3 is detected at about +0.30 V (Fig. 1a). No significant difference is observed when the voltammogram is performed in THF. Similar electrochemical behaviour is observed for compounds **2**–**6**. The potential values corresponding to the first reduction peak are not very sensitive to the nature of the L (Table 3).

The potential controlled electrolysis of compound **1** at −1.5 V in THF or CH_2Cl_2 at room temperature involved a consumption of 2.1–2.3 Faradays per mol of compound. When the reduction was performed at 0°C the transferred charge was 2.0 Faradays per mol within the experimental error. The solution, initially pale yellow, turns red during the electrolysis at 0°C. The intensity of the reduction peak A_1 decreases with the amount of charge transferred and becomes zero when two Faradays are consumed (Fig. 1b). If the reduced solution is left at room temperature it becomes yellow-orange after 1–2 h with some changes in the voltammogram; a new reduction peak appears at −1.2 V (A_4), and at the same time peak A'_3 slowly disappears. These results clearly indicate that the species electrogenerated undergoes

TABLE 1

^{31}P AND ^1H NMR SPECTROSCOPIC DATA FOR COMPOUNDS 1–6

Compound $IrCl_3(PCBr)L$	$\delta(P)$ [a] (ppm)	$\delta(P)$ [b] (ppm)	$^2J(PP')$ (Hz)	$\delta(Me)$ (ppm)
1, L = PCBr [3]	18.6	−14.4	509	
2, L = PPh_3 [3]	11.7	−23.5	492	
3, L = $PMePh_2$	13.5	−28.5	488	2.2
4, L = $P(p\text{-}MeC_6H_4)_3$	8.5	−24.7	492	2.3
5, L = $P(OMe)_3$	17.5	50.5	722	4.02
6, L = $P(OPh)_3$	20.8	39.8	777	

[a] $\delta(\eta^2\text{-}PCBr)$. [b] $\delta(L)$; positive shifts are downfield from aqueous H_3PO_4 85%.

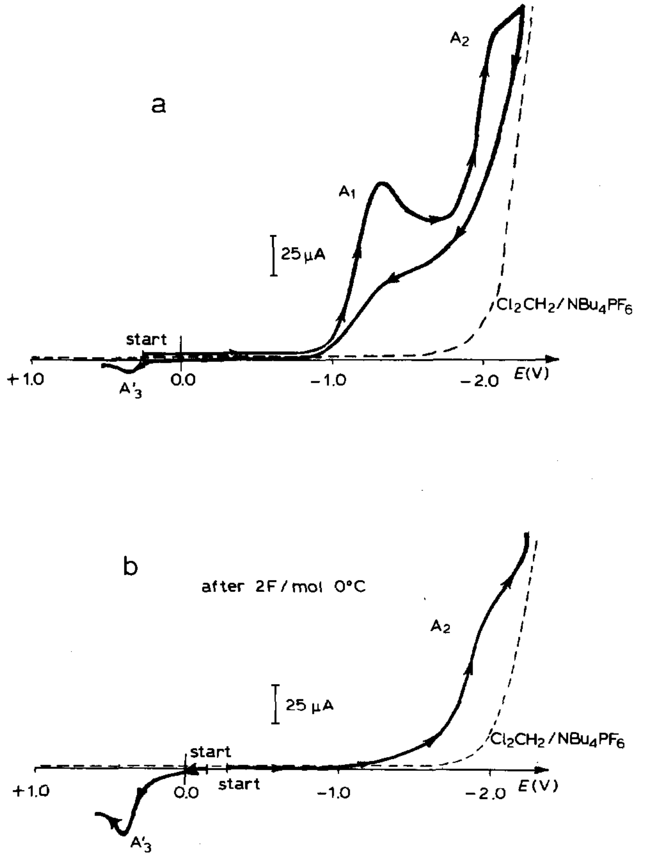


Fig. 1. (a) Cyclic voltammogram of compound **1** in CH_2Cl_2 at platinum electrode (sweep rate 0.1 V s^{-1}); (b) linear sweep voltammogram of compound **1** in CH_2Cl_2 after potential controlled electrolysis at ca. 0°C (sweep rate 0.1 V s^{-1}).

chemical change at room temperature to yield a new species reducible at A_4. After 2 h at room temperature no further changes were observed in the voltammogram, and the product was extracted and purified as described in the Experimental section.

The ^{31}P NMR spectrum of the isolated product shows two sets of signals in the ranges +15 to +10 ppm and −60 to −70 ppm, indicating that a mixture of compounds is involved. The observation of resonances at very high field is clear evidence of the presence of four-atom metallated phosphines [5,6]. Signals in low field range are common for a bidentate PCBr phosphine coordinating via P and Br atoms [3,7]. On the basis of the spectroscopic data (Table 2) and the elemental analysis we tentatively assume that the final product of the reaction was IrClBr(PC)(PCBr), containing one metallated phosphine (PC) and one PCBr acting as bidentate ligand. The absence of $^2J(PP')$ coupling in the spectrum indicates that the two phosphorus atoms must be mutually *cis*.

Fortunately this mixture of products could be partially separated by chromatography into three fractions, A, B, and C. The ^{31}P NMR spectra indicated that A and C correspond to single compounds, **7** and **8**, respectively, while B is a mixture of two

TABLE 2

^{31}P NMR SPECTROSCOPIC DATA FOR COMPOUNDS 7–9

IrXY(PC)(PCBr)	δ(P) [a] (ppm)	δ(P) [b] (ppm)
7, XY = Br_2	14.6	−68.6
8, XY = Cl_2	10.2	−66.8
9, XY = BrCl	9.7	−67.8
	15.2	

[a] δ(η^2-PCBr). [b] δ(PC); positive shifts are downfield from aqueous H_3PO_4 85%.

TABLE 3

ELECTROCHEMICAL DATA FOR COMPOUNDS 1–9

Compound	E_p [a] (V)	
	A_1	A_2
1	−1.3	−2.0
2	−1.1	−2.2
3	−1.2	−1.9
4	−1.1	−2.1
5	−1.15	−2.1
6	−1.1	−2.1
7	−1.2	
8	−1.2	
9	−1.2	

[a] All potential values are refered to SCE and have been recorded at a sweep rate of 0.1 V s^{-1} in THF and using Bu_4NPF_6 as supporting electrolyte.

isomers of **9**, which cannot be separated by the available chromatographic methods. Preliminary X-ray studies on compounds **7** and **8**, show that they are $IrBr_2$(PC)(PCBr) and $IrCl_2$(PC)(PCBr), respectively. The phosphorus atoms are *cis* and the bromine atom of the bidentate phosphine is *trans* to the P atom of the metallated phosphine. The elemental analyses of the three fractions are consistent with the prelimminary X-ray data for **7** and **8**, and with the composition IrClBr(PC)(PCBr) for the isomeric mixture **9**.

Chemical reduction of **1** with a Na-Hg amalgam at 0°C in THF also leads to the orthometallated complexes **7**–**9**. However, the yields are always lower than those obtained by electrochemical reduction.

Discussion

Reaction of $IrCl_3$ and PCBr in refluxing ethanol did not yield any metallated species, but only $IrCl_3$ (η^2-PCBr)(η^1-PCBr) [3]. Chemical or electrochemical reduction of this compound gives a new iridium(I) species (eq. 2), which spontaneously undergoes orthometallation at room temperature. We assume that this intermediate reduced species is IrCl(η^2-PCBr)(η^1-PCBr); in this compound one phosphine must be acting as bidentate ligand in order to satisfy the electronic requirement of the iridium atom.

$$IrCl_3(\eta^2\text{-PCBr})(\eta^1\text{-PCBr}) \xrightarrow[T<0^\circ C]{+2e^-} IrCl(\eta^2\text{-PCBr})(\eta^1\text{-PCBr}) + 2Cl^- \tag{2}$$

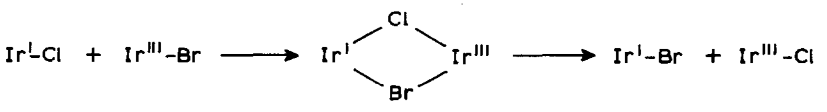
$$IrCl(\eta^2\text{-PCBr})(\eta^1\text{-PCBr}) \rightarrow IrXY(PC)(\eta^2\text{-PCBr}) \tag{3}$$

We have prepared some other iridium(I) complexes from PCBr, namely IrCl(COD)(PCBr) and $IrCl(CO)(PCBr)_2$, and they do not undergo phosphine metallation even in refluxing toluene [11]. Apparently the presence of π-acid ligands such as CO or COD make these two compounds less susceptible to the metallation.

The reaction of $RhCl_3$ and PCBr in refluxing ethanol yields directly rhodium(III) metallated compounds of the type RhClBr(PC)(PCBr), but only the product from oxygen, insertion, RhClBr(OPC)(η^2-PCBr), has been crystallographically characterized [2]. Comparison of the results obtained for the rhodium and iridium reactions suggests that the reaction in the case of rhodium may also proceed via $RhCl(PCBr)_2$, analogous to the iridium species that we have described and tentatively formulated above.

Apparently the octahedral iridium(III) complex **1** is more stable than the analogous rhodium one involving, and no reduction of **1** to $IrCl(PCBr)_2$ takes place under the same conditions.

The observed exchange of halogen in the metallated iridium products requires some comment. The expected product is IrClBr(PC)(PCBr) in one or more isomeric structures. We have observed that compounds **7** and **8** do not exchange halogens during 24 h stirring in THF, and so we suggest that the exchange must be between $IrCl(PCBr)_2$ and IrClBr(PC)(PCBr) via an intermediate containing a double halogen bridge (eq. 4). This type of exchange has been observed for other rhodium(I) and iridium(I) compounds [10].



(4)

Experimental

Chemical reactions were carried out under dry argon by use of standard Schlenk-line procedures. All solvents were reagent grade and were dried and distilled before use. $IrCl_3 \cdot 3H_2O$ was purchased from Engelhard Industries. Phosphine and phosphite ligands were purchased from Strem and were used without purification, except that PPh_3 was previously recrystallized from hot ethanol. $[IrCl(COD)]_2$ was prepared by a modification of a published method [8] as was PCBr [9]. The complexes $IrCl_3(PCBr)_2$ (**1**) and $IrCl_3(PCBr)(PPh_3)$ (**2**) were prepared by published methods [3]. The ^1H and ^{31}P NMR spectra were recorded on a Bruker AC 200 spectrometer, operating at 200.032 MHz (^1H) and 81.015 MHz (^{31}P); TMS was used as the internal reference for the ^1H NMR and aqueous 85% H_3PO_4 as the external standard for the ^{31}P NMR spectra.

The electrochemical experiments were carried out in a three electrode cell. The working and auxiliary electrode were platinum, the reference electrode was a saturated calomel electrode electrically connected to the solution by a "salt bridge" containing a saturated solution of the supporting electrolyte in the solvent. Cyclic voltammograms were obtained with a programming function generator 305 HQ

Instruments connected to a 552 Amel potentiostat and were recorded with a Riken-Denshi F-35 X-Y recorder. The solvent was THF which had been freshly distilled over sodium benzophenone. The supporting electrolyte, Bu_4NPF_6, was recrystallized from ethanol and dried at 80°C under vacuum for 48 h. Potential controlled electrolysis were carried out in a three compartment cell separated by fritted glass. Working and auxiliary electrode were a platinum mesh. The charge transferred was calculated by recording intensity versus the time and carrying out a further integration. The system was calibrated against cobaltocene.

Preparation of compounds 3–6

$IrCl_3(PCBr)(PMePh_2)$ (3). A mixture of $IrCl_3(PCBr)_2$ (170 mg; 0.15 mmol) with an excess of $PMePh_2$ in 10 ml $CHCl_3$ was stirred at room temperature until TLC showed that no starting material remained. Concentration and addition of hexane led to precipitation of a light-coloured solid which was recrystallized from dichloromethane/hexane. Yield 82%. Analysis: Found: C, 38.9; H, 2.5. $C_{37}H_{23}F_4Cl_3P_2BrIr \cdot 0.5CH_2Cl_2$ calcd.: 38.5; H, 2.4%.

$IrCl_3(PCBr)(P(p\text{-}MeC_6H_4)_3)$ (4). The stoichiometric amount of $P(p\text{-}MeC_6H_4)_3$ was added with stirring to a solution of 150 mg (0.13 mmol) of **1** in 8 ml CH_2Cl_2 and the stirring was continued until disappearance of **1** was repeated by TLC. The solvent was partly evaporated and hexane was added to precipitate the light coloured product, which was recrystallized from dichloromethane/hexane. (Yield: 70%. Analysis: Found: C, 46.1; H, 3.6. $C_{39}H_{31}F_4Cl_3P_2BrIr \cdot 0.5CH_2Cl_2$ calcd.: C, 46.7; H, 3.2%.

$IrCl_3(PCBr)(P(OMe)_3)$ (5). The procedure used for **3** was followed. Yield: 75%. Analysis: Found: C, 29.6; H, 2.3. $C_{21}H_{19}F_4Cl_3P_2BrIr$ calcd.: C, 30.1; H, 2.2%.

$IrCl_3(PCBr)(P(OPh)_3)$ (6). The method used for **5** was followed. Yield: 85%. Analysis: Found: C, 40.9; H, 2.2. $C_{36}H_{25}O_3F_4Cl_3P_2BrIrCH_2Cl_2$ calcd.: C, 41.1; H, 2.4%.

Preparation of compounds 7–9

By electrochemical reduction of 1. A solution of 200 mg (0.18 mmol) of **1** in 30 ml CH_2Cl_2 were placed in the cathodic compartment of the electrolytic cell immersed in an ice-bath (ca. 0°C). The electrolysis was performed at -1.5 V. The solution initially yellow turns red during this process. The electrolysis was considered completed when the intensity fell below 1% of the initial intensity (about 60 min). The chemical evolution of the resulting red-orange solution was monitored by CV at room temperature. After 5 h the evolution was complete. The yellow solution was evaporated to dryness and the products were separated from the supporting electrolyte by successive extractions with toluene. These extracts were evaporated to dryness and the residue was dissolved in dichloromethane and chromatographed on a column (25×1.5 cm) packed with silica gel in hexane. Elution with dichloromethane/hexane 1/1 gave first a pale yellow band that contained the unreacted compound **1**. Further elution with the same eluent gave a second yellow band which contained compound **7**. Elution with 3/2 dichloromethane/hexane then yielded another yellow band which contained the isomeric mixture **9**. Final elution with neat dichloromethane gave a yellow fraction which contained compound **8**. All the fractions were evaporated to dryness and recrystallizated from CH_2Cl_2/hexane. Compound **7**: Yield: 12%. Analysis: Found: C, 40.0; H, 2.1. $C_{36}H_{20}F_4Br_2Ir$ calcd.:

C, 39.3; H, 1.8%. Compound **8**: Yield: 8%. Analysis: Found: C, 43.1; H, 1.9. $C_{36}H_{20}F_4Cl_2P_2Ir$ calcd.: C, 42.8; H, 1.9%. Isomeric mixture **9**: Yield: 18%. Analysis: Found: C, 41.5; H, 1.8. $C_{36}H_{20}F_4ClBrP_2Ir$ calcd.: C, 40.9; H, 1.8%.

By chemical reduction of 1. A solution of 202 mg (0.18 mmol) of **1** in 5 ml THF at 0°C was treated with Na-Hg amalgam (8 mg Na, 0.1 ml Hg) during 30 min with vigorous stirring. The resulting orange-red solution was filtered through kieselgur and left at room temperature for 6 h. The yellow solution was then evaporated to dryness and the residue worked up as described above.

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