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Registry No. **1**, 103712-54-5; **2**, 103712-55-6; $KC_5H_7\cdot THF$, 51197-67-2; *fac*-$ReCl_3(PMe_2Ph)_3$, 24627-46-1; $KC_7H_{11}\cdot THF$, 103712-56-7.

Supplementary Material Available: Detailed description of X-ray diffraction data collection, data reduction, and structure refinement and listings of final atomic coordinates, thermal parameters, bond lengths, bond angles, and significant least-squares planes including subtended dihedral angles (10 pages); a listing of observed and calculated structure factor amplitudes (10 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry
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Preparation of Iridium(III) Complexes Containing the Phosphine $P(o\text{-}BrC_6F_4)(Ph)_2$. A New Example of η^2-Coordination and Halocarbon Binding in an (*o*-Haloaryl)phosphine

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It has recently been observed that (*o*-haloaryl)phosphines can act as bidentate ligands coordinating via the phosphorus and a halogen atom. Examples of such behavior have been encountered in rhodium[1,2] and iridium[3] complexes.

Rhodium(I) compounds containing the title ligand (abbreviated PCBr) can undergo thermal orthometalation by metal insertion into the C–Br bond. In general, mononuclear products are isolated that contain a four-membered metallocycle.[4] There is, however, one example of an orthometalated phosphine bridging a dirhodium(4+) unit, produced in a 2c–2e oxidative addition reaction.[2]

In probing the reactivity of PCBr in complexes of Ir, we now find that the reaction of $IrCl_3\cdot xH_2O$ in refluxing ethanol does not yield metalated species. Instead, a mononuclear complex, $IrCl_3(PCBr)_2$ (**1**), is isolated in high yield. The ^{31}P NMR spectrum shows two different P environments. Subsequent reaction with PPh_3 leads to the replacement of one of the PCBr ligands to yield $IrCl_3(PCBr)(PPh_3)$ (**2**). It is an octahedral complex with an unusual bonding mode of the PCBr ligand.

Experimental Section

PCBr was prepared by published procedures.[5] All solvents were dried and purified by standard procedures. All reactions were carried out in an atmosphere of dry dinitrogen.

Preparation of $IrCl_3(PCBr)_2$. Weighed amounts of 75 mg (0.21 mmol) of $IrCl_3\cdot xH_2O$ and 352 mg (0.84 mmol) of PCBr were refluxed in 10 mL of EtOH (96%) for 2 h. The resulting yellow solution was cooled to room temperature, and a cream colored product was obtained upon vacuum concentration. It was filtered off, washed with hexane, and recrystallized from a CH_2Cl_2/hexane mixture. Yield: 70%. Anal. Calcd for $C_{36}H_{20}F_8Cl_3Br_2P_2Ir$: C, 38.4; H, 1.6; Cl, 9.6. Found: C, 38.4; H, 1.6; Cl, 9.5. IR: C–F stretches at 1000–1100 cm^{-1}. $^{31}P\{^1H\}$ NMR: δ = 18.6, −14.4 (relative H_3PO_4); $^2J_{PP}$ = 509 Hz.

Table I. Crystal Data for $IrCl_3(PCBr)(PPh_3)$ (**2**)

formula	$IrCl_3P_2F_4BrC_{36}H_{25}$
fw	974.01
space group	$P2_1/n$
syst absences	$h0l$, $h + l = 2n$; $0k0$, $k = 2n$
a, Å	12.723 (7)
b, Å	15.066 (8)
c, Å	18.939 (9)
α, deg	90.0
β, deg	108.14 (2)
γ, deg	90.0
V, Å^3	3450 (6)
Z	4
d_{calcd}, g/cm^3	1.875
cryst size, mm	0.2 × 0.1 × 0.08
μ(Mo Kα), cm^{-1}	53.758
data collcn instrum	Syntex P$\bar{1}$
radiation (monochromated in incident beam)	Mo Kα ($\lambda_{\bar{a}}$ = 0.71073 Å)
orientation reflcns: no., range (2θ)	15, 16–28
temp, °C	25
scan method	ω–2θ
data collcn range 2θ, deg	4.5–50
no. of unique data, total with $F_o^2 > 3\sigma(F_o^2)$	2550, 2391
no. of params refined	244
transmissn factors: max, min	1.0, 0.69
R^a	0.0544
$R_w{}^b$	0.0675
quality-of-fit indicator^c	1.347
largest shift/esd, final cycle	1.75
largest peak, e/Å^3	0.7

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o\times - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. [c] Quality-of-fit $= [\sum w(|F_o| - |F_c|)^2/(N_{observns} - N_{params})]^{1/2}$.

Preparation of $IrCl_3(PCBr)(PPh_3)$ (2). $IrCl_3(PCBr)_2$ (112 mg, 0.1 mmol) and 26 mg (0.1 mmol) of PPh_3 were dissolved in 5 mL of $CHCl_3$. The solution was stirred until all of the starting material had reacted as monitored by TLC. After addition of hexane and vacuum evaporation of part of the solvent a light colored product precipitated. It was collected by filtration, washed with hexane, and recrystallized from CH_2Cl_2/hexane. Crystals suitable for X-ray analysis were grown by slow diffusion of hexane into a CH_2Cl_2 solution. Yield: 85%. Anal. Calcd for $C_{36}H_{25}F_4Cl_3BrP_2Ir$: C, 43.4; H, 2.5. Found: C, 42.8; H, 2.4. $^{31}P\{^1H\}$ NMR: δ = 11.7, −20.6 $^2J_{PP}$ = 492 Hz.

X-ray Procedures. A yellow crystal of approximate dimensions 0.2 × 0.1 × 0.08 mm^3 was mounted on the tip of a glass fiber. All geometrical and intensity data were gathered from this crystal. Preliminary cell parameters were derived from 15 centered reflections and confirmed, together with the monoclinic symmetry, by axial photographs.

The systematic absences uniquely determined the space group $P2_1/n$. The data were corrected for Lorentz and polarization effects before structure factors were derived.[6] A semiempirical absorption correction was based on nine azimuthal scans at Eulerian angle χ close to 90°.

The position of the Ir center was derived from a three-dimensional Patterson map. The remaining non-hydrogen atoms were located and refined by alternating difference Fourier maps and least-squares cycles.

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(6) The Enraf-Nonius Structure Determination Package (SDP Plus) was used for all crystallographic computation.

Table II. Positional Parameters and Their Estimated Standard Deviations for $IrCl_3(PCBr)(PPh_2)$

atom	*x*	*y*	*z*	*B*, Å^2
Ir	0.48755 (6)	0.55542 (5)	1.28767 (4)	2.25 (1)
Br	0.5508 (2)	0.4154 (1)	1.3566 (1)	3.34 (5)
Cl(1)	0.4119 (4)	0.6841 (3)	1.2211 (3)	3.1 (1)
Cl(2)	0.4699 (4)	0.4741 (3)	1.1775 (3)	3.5 (1)
Cl(3)	0.5185 (4)	0.6239 (3)	1.4052 (2)	3.2 (1)
P(1)	0.3097 (4)	0.5164 (3)	1.2865 (3)	2.3 (1)
P(2)	0.6694 (4)	0.6005 (3)	1.2920 (3)	2.7 (1)
F(13)	0.5262 (9)	0.2601 (7)	1.4462 (7)	4.5 (3)
F(14)	0.349 (1)	0.2021 (7)	1.4838 (6)	5.1 (3)
F(15)	0.1575 (9)	0.2936 (8)	1.4392 (6)	4.7 (3)
F(16)	0.1363 (8)	0.4342 (7)	1.3508 (6)	4.0 (3)
C(11)	0.320 (2)	0.426 (1)	1.352 (1)	3.0 (5)*
C(12)	0.419 (2)	0.381 (1)	1.378 (1)	2.9 (4)*
C(13)	0.430 (1)	0.307 (1)	1.421 (1)	3.4 (5)*
C(14)	0.342 (2)	0.274 (1)	1.4417 (9)	3.1 (5)*
C(15)	0.244 (1)	0.320 (1)	1.4187 (9)	3.3 (4)*
C(16)	0.233 (1)	0.394 (1)	1.372 (1)	3.2 (4)*
C(21)	0.219 (1)	0.473 (1)	1.197 (1)	2.5 (4)*
C(22)	0.168 (1)	0.392 (1)	1.194 (1)	3.7 (5)*
C(23)	0.107 (2)	0.359 (1)	1.123 (1)	4.1 (5)*
C(24)	0.094 (2)	0.411 (1)	1.061 (1)	4.4 (6)*
C(25)	0.145 (2)	0.494 (1)	1.067 (1)	3.8 (5)*
C(26)	0.213 (2)	0.526 (1)	1.137 (1)	4.3 (5)*
C(31)	0.235 (1)	0.601 (1)	1.317 (1)	2.9 (4)*
C(32)	0.159 (1)	0.653 (1)	1.267 (1)	3.5 (5)*
C(33)	0.109 (2)	0.725 (2)	1.291 (1)	6.3 (7)*
C(34)	0.137 (2)	0.748 (2)	1.367 (1)	6.1 (6)*
C(35)	0.211 (2)	0.692 (1)	1.418 (1)	5.6 (6)*
C(36)	0.264 (2)	0.619 (1)	1.394 (1)	4.2 (5)*
C(41)	0.716 (1)	0.708 (1)	1.3350 (9)	2.9 (4)*
C(42)	0.643 (1)	0.773 (1)	1.335 (1)	3.4 (5)*
C(43)	0.684 (2)	0.860 (1)	1.366 (1)	4.2 (5)*
C(44)	0.796 (2)	0.876 (1)	1.394 (1)	5.5 (6)*
C(45)	0.872 (2)	0.807 (1)	1.393 (1)	5.3 (6)*
C(46)	0.831 (2)	0.722 (1)	1.363 (1)	4.6 (6)*
C(51)	0.700 (2)	0.609 (1)	1.204 (1)	3.7 (5)*
C(52)	0.618 (2)	0.626 (1)	1.139 (1)	4.1 (5)*
C(53)	0.643 (2)	0.637 (1)	1.071 (1)	4.9 (5)*
C(54)	0.754 (2)	0.630 (2)	1.072 (1)	5.5 (6)*
C(55)	0.833 (2)	0.611 (1)	1.134 (1)	5.9 (5)*
C(56)	0.813 (2)	0.600 (2)	1.205 (1)	4.7 (6)*
C(61)	0.764 (1)	0.518 (1)	1.3455 (9)	3.1 (4)*
C(62)	0.802 (2)	0.528 (1)	1.423 (1)	4.4 (5)*
C(63)	0.869 (2)	0.459 (1)	1.465 (1)	5.0 (6)*
C(64)	0.894 (2)	0.384 (2)	1.432 (1)	5.3 (6)*
C(65)	0.852 (2)	0.371 (2)	1.355 (1)	5.2 (6)*
C(66)	0.787 (2)	0.444 (1)	1.311 (1)	4.0 (5)*

[a] Values marked with an asterisk indicate that the atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

The last cycle of refinement gave residuals of $R = 5.4\%$ and $R_w = 6.7\%$ with a quality-of-fit indicator of 1.35 for the fit of 244 variables to 2391 unique data with $F_o^2 \geq \sigma(F_o^2)$.

Data pertaining to data collection and refinement are summarized in Table I. Table II lists the atomic coordinates, and important bond distances and angles are listed in Table III.

Results and Discussion

Upon reaction of $IrCl_3{\cdot}xH_2O$ and PCBr in a molar ratio of 1:4 in refluxing ethanol a cream colored precipitate is obtained in near-quantitative yield. It is soluble in $CHCl_3$, CH_2Cl_2, acetone, and THF and can be recrystallized from $CHCl_3$/hexane mixtures. The chemical analysis is consistent with composition $IrCl_3(PCBr)_2$. Two doublets are detected in the $^{31}P\{^1H\}$ NMR spectrum at δ = 18.6 and −14.4. The large PP coupling constant is indicative of a trans arrangement.[7]

Table III. Important Bond Distances and Angles in $IrCl_3(PCBr)(PPh_3)$ (**2**)

(a) Bond Distances (Å)

Ir–Br	2.479 (2)	P(1)–C(11)	1.83 (2)
–Cl(1)	2.348 (4)	–C(21)	1.84 (2)
–Cl(2)	2.369 (5)	–C(31)	1.78 (2)
–Cl(3)	2.372 (5)	P(2)–C(41)	1.82 (2)
–P(1)	2.331 (5)	–C(51)	1.82 (2)
–P(2)	2.388 (5)	–C(61)	1.81 (2)
Br–C(12)	1.92 (2)	C(11)–C(12)	1.37 (3)

(b) Bond Angles (deg)

Br–Ir–Cl(1)	175.1 (1)	Cl(2)–Ir–P(1)	92.0 (2)
Br–Ir–Cl(2)	87.1 (1)	Cl(2)–Ir–P(2)	90.2 (2)
Br–Ir–Cl(3)	86.8 (1)	Cl(3)–Ir–P(1)	89.8 (2)
Br–Ir–P(1)	86.9 (1)	Cl(3)–Ir–P(2)	88.1 (2)
Br–Ir–P(2)	94.1 (1)	P(1)–Ir–P(2)	177.7 (2)
Cl(1)–Ir–Cl(2)	92.5 (2)	Ir–Br–C(12)	100.4 (5)
Cl(1)–Ir–P(1)	88.2 (2)	P(1)–C(11)–C(12)	118. (2)
Cl(1)–Ir–P(2)	90.8 (2)	Br–C(12)–C(11)	124. (1)
Cl(2)–Ir–Cl(3)	173.6 (2)		

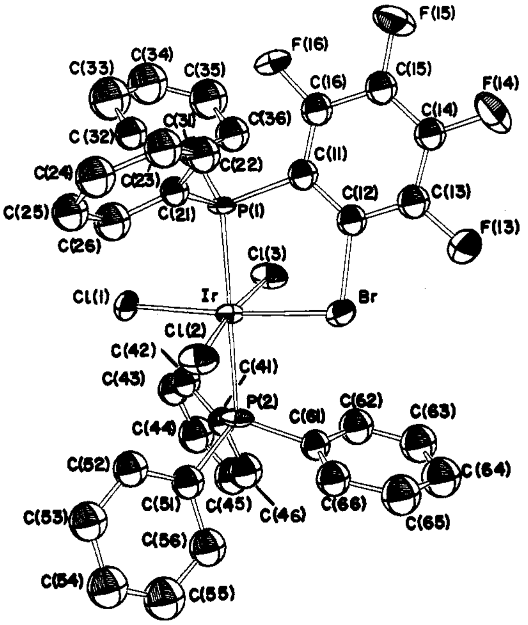

Figure 1. ORTEP drawing of $IrCl_3(PCBr)(PPh_3)$ (**2**).

This compound reacts slowly at room temperature with PPh_3 to yield $IrCl_3(PCBr)(PPh_3)$ (**2**), whose structure was elucidated by a single-crystal X-ray analysis. A perspective view of a molecule of **2** is shown in Figure 1. It is a mononuclear complex of octahedral coordination geometry. The two P atoms occupy the apical positions in a trans configuration. The equatorial coordination sites are occupied by three chlorine atoms and by the Br atom of the PCBr ligand. The Ir, P, C, C, and Br atoms thus form a five-membered metallocycle. The coordination metric of the Ir atom approximates the ideal geometry very closely with bond angles ranging from 87 to 94° and from 173 to 178° for the angles between cis and trans ligands, respectively.

The five-membered metallocycle that results from the η^2-coordination mode deserves special attention. The Ir–Br distance is 2.479 (2) Å and the average Ir–Cl distance 2.363 [13] Å. Since chlorine and bromine differ in both their ionic radii and their single-bond covalent radii by about 0.15 Å,[8] the Ir–Br interaction in **2** appears to be a real bond. A similar coordination mode of the PCBr ligand has previously been observed in rhodium compounds[1,2,9] albeit with much weaker M–Br interactions (ca. 2.65 Å). Perhaps the closest example to **2** is Crabtree's [Ir(cod)(η^2-$PPh_2C_6H_4$-*o*-Br)]SbF_6,[3] in which an Ir–Br distance of 2.473 (4) Å was observed in a similar chelate system.

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Despite the strong Ir–Br interaction in **2** there are no dramatic changes in the bond distances and angles of the PCBr ligand. A comparison of the dimensions of PCBr in **2** with those observed[9] in $Rh_2(O_2CCH_3)_3[(C_6H_4)P(C_6H_5)(C_6F_4Br)]\cdot PCB$ (**3**) suggests that there may be a slight lengthening of the C–Br bond (1.85 (2) and 1.92 (2) Å in **3** and **2**, respectively), but this is barely significant in a statistical sense.

The interaction between the iridium and bromine atoms is best described as a dative bond. This model results in what may be described as either a $t_{2g}{}^6$ or a rare-gas configuration at the Ir center assuming oxidation state +III. The assignment of the trivalent oxidation state (d^6 configuration) not only agrees with the observed diamagnetism but also entails a favorable comparison of the dimensions with those of an authentic Ir(III) halophosphine complex. For example, in *mer*-$IrCl_3P_3$[10] the Ir–Cl and Ir–P distances were reported to be 2.364 [3] and 2.373 [9] Å, respectively.

In light of the similarity of the ^{31}P NMR spectra, especially the inequality of the P sites and the large coupling constants, we propose that **1** is also an octahedral complex with a η^2-PCBr and a η^1-PCBr in trans configuration.

We believe that the existence of these new compounds confirms the expectation expressed by Crabtree et al.[3] that "the coordination chemistry of halocarbons will prove to be extensive, especially when part of a chelating ligand". It is worth noting that while the Crabtree compound had a P–C_6H_4Br chelating ligand, we have a P–C_6F_4Br ligand, where the donor ability of the bromine atom might be expected to be less. On the other hand, Crabtree was dealing with Ir^I while we have Ir^{III}, which would favor stronger $-Br \rightarrow Ir$ bonding in our case. Either these two factors are each of little importance or they offset each other fairly neatly, since the Ir–Br distances are virtually identical.

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Registry No. **1**, 103564-37-0; **2**, 103564-38-1.

Supplementary Material Available: Complete tables of bond distances and angles and anisotropic displacement parameters (3 pages); a listing of structure factors (12 pages). Ordering information is given on any current masthead page.

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Preparation and Properties of the Tribromide of *trans*-Dibromotetrakis(acetonitrile)vanadium(III), $[VBr_2(CH_3CN)_4]Br_3$. A Symmetric Br_3^- Ion

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Recently in this laboratory we have been endeavoring to establish some compounds containing vanadium(II) in forms suitable for further synthetic chemistry in nonaqueous media. Some of this work has entailed the reinvestigation of promising looking compounds previously mentioned in the literature. In some cases the reported compounds have been confirmed and further characterized, while in others the compounds have required reformulation.[1] We have been interested not only in establishing accurately the composition and structures of these compounds but also in confirming or finding convenient preparative procedures for them.

Table I

formula	$Br_5VN_4C_8H_{12}$
fw	614.70
space group	$C2/m$
syst absences	hkl, $h + k = 2n + 1$
a, Å	14.851 (2)
b, Å	10.401 (2)
c, Å	6.309 (1)
β, deg	104.35 (1)
V, Å^3	944.1 (3)
Z	2
d_{calcd}, g/cm^3	2.162
cryst size, mm	0.3 × 0.4 × 0.5
μ(Mo Kα), cm^{-1}	109.84
data colln instrum	Syntex P$\bar{1}$
radiation (monochromated in incident beam)	Mo Kα (λ = 0.71073 Å)
orientation reflcns, no., range	15, $30 < 2\theta < 50$
temp, °C	5
scan method	θ–2θ
data colln range deg	$4 < 2\theta < 50$
no. of unique data, total with $F_o{}^2 > 3\sigma(F_o{}^2)$	838, 669
no. of params refined	48
transmissn factors (exptl): max, min	0.998, 0.380
R[a]	0.031
R_w[b]	0.042
quality-of-fit indicator[c]	0.994
largest shift/esd, final cycle	0.02
largest peak, e/Å^3	0.507

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. [c] Quality of fit $= [\sum w(|F_o| - |F_c|)^2/(N_{observns} - N_{params})]^{1/2}$.

Table II. Positional Parameters and Their Estimated Standard Deviations for $[VBr_2(CH_3CN)_4]Br_3$[a]

atom	x	y	z
Br(1)	0.13205 (5)	0.000	0.3183 (1)
Br(2)	0.500	0.000	1.000
Br(3)	0.17379 (6)	0.500	1.1786 (1)
V	0.000	0.000	0.000
N	−0.0653 (3)	−0.1407 (4)	0.1450 (6)
C(1)	−0.1030 (3)	−0.2110 (5)	0.2278 (8)
C(2)	−0.1521 (5)	−0.3002 (6)	0.336 (1)

[a] Estimated standard deviations in the least significant digits are shown in parentheses.

The compound $VBr_2\cdot CH_3CN$ and the reported electrochemical preparation[2] of it were of interest in this regard, and we have examined this chemistry. As will be discussed in detail later, our work has led to the isolation of a crystalline compound that has been shown by X-ray crystallography to be $[VBr_2(CH_3CN)_4]Br_3$.

Experimental Section

All chemical operations were conducted in an atmosphere of argon. Acetonitrile was dried over P_2O_5, distilled immediately before use, and transferred via syringe. The vanadium rod was obtained from Alfa Products and measured 6.2 mm × 7.5 cm. The platinum wire was also obtained from Alfa Products and measured 0.25 mm × 15.5 cm. A power pack capable of delivering 5.0 V dc at 3.0 A was used.

Synthesis and Crystallization of $[VBr_2(CH_3CN)_4]Br_3$. The solution phase consisted of 60 mL of acetonitrile, 10 mg of tetrabutylammonium perchlorate, and 1 mL of bromine. The vanadium anode and platinum cathode were 1 cm apart, and the voltage was applied for 8–72 h, resulting in large orange-brown crystals on the surface of the anode as well as in the bottom of the reaction vessel. The composition and structure of this compound have been determined by X-ray crystallography, showing it to be $[VBr_2(CH_3CN)_4]Br_3$.

Structure Solution and Refinement. The positions of the vanadium and bromine atoms were located by using direct methods in the form of the MULTAN program. All other atoms were located in difference Fourier maps. In all, 48 variable parameters were fitted to 669 observations. The final least-squares cycles did not shift any parameter by more than 0.02

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0020-1669/86/1325-3528$01.50/0