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The Reactions of Phosphorus- and Arsenic-Containing Multidentate Ligands with Some Iridium Complexes.
Part VI.[1] The Formation of Trigonal Bipyramidal Complexes $[Ir(Ph_3P)(L'L_3)]X$

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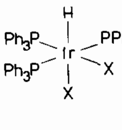
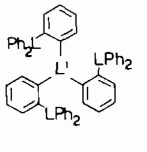
Complexes $[IrHX_2(Ph_3P)_3]$, $[IrX(Ph_3P)_3]$ ($X = Cl$ and Br), $[IrHCl(C_6H_4PPh_2)(Ph_3P)_2]$, and $[IrCl(Ph_3P)(C_8H_{12})]$ (C_8H_{12} = 1,5-cyclo-octadiene) were reacted with ligands $(o\text{-}Ph_2LC_6H_4)_3L'$ ($L' = P$ and As; $L = P$ and As), $L'L_3$. The isolation of complexes of the types $[IrHX(L'L_3)][BPh_4]$, octahedral, $[IrX(L'L_3)]$, trigonal bipyramidal, and unusual $[Ir(Ph_3P)(L'L_3)][BPh_4]$, also trigonal bipyramidal, is reported. The proton and phosphorus-31 n.m.r. spectra and the electronic spectra of some of the complexes are recorded.

Introduction

An earlier publication[3] described the reaction of $[IrHBr_2(Ph_3P)_3]$, isomer (Ib), with the quadridentate ligand tris-(*o*-diphenylphosphinophenyl)phosphine, QP, (II; L = L′ = P) from which one obtained a complex of composition $[IrHBr(Ph_3P)(QP)][BPh_4]$ which was assigned a seven-coordinate structure. We report here some reactions of complexes $[IrHX_2(Ph_3P)_3]$, isomers (Ia), (Ib) and (IIIa), $[IrX(Ph_3P)_3]$ (IV; X = Cl and Br), $[IrHCl(C_6H_4PPh_2)(Ph_3P)_2]$ (V), and $[IrCl(Ph_3P)(C_8H_{12})]$ (VI), (C_8H_{12} = 1,5-*cyclo*-octadiene) with ligands QP, tris-(*o*-diphenylphosphinophenyl)arsine, ASTP (II; L = P, L′ = As), tris-(*o*-diphenylarsinophenyl)phosphine, PTAS (II; L = As, L′ = P), and tris-(*o*-diphenylarsinophenyl)arsine, QAS (II; L = L′ = As).



X = Cl (Ia)
X = Br (Ib)



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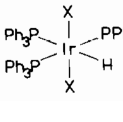

X = Cl (IIIa)
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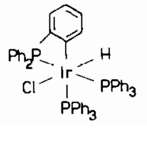


(V)

Experimental

Preparation of the Ligands

The ligand $(o\text{-}Ph_2PC_6H_4)_3P$, QP, was prepared by the method of Chiswell and Venanzi;[4] the ligands $(o\text{-}Ph_2PC_6H_4)_3As$, PTAS, and $(o\text{-}Ph_2AsC_6H_4)_3As$, QAS, were prepared as described elsewhere[5] and the ligand $(o\text{-}Ph_2PC_6H_4)_3As$, ASTP, was prepared by the method of Higginson, *et al.*[6]

Preparation of the Intermediates

Complex (IIIa),[7] [ν(Ir–H) = 2199 cm^{-1}], was prepared by the method of Vaska and DiLuzio[8] using aqueous ethanol as a solvent. Complex (Ia) [ν(Ir–H) = 2228 cm^{-1}] was prepared as described by Vaska;[9] in our hands this method gave, in most preparations, a compound showing a band at 2345 cm^{-1} (see below) which, on recrystallization from CH_2Cl_2/EtOH and C_6H_6/EtOH gave isomer (Ia). In some preparations one obtained a mixture of products containing mostly that with the band at 2345 cm^{-1} and some isomer (IIIa). Recrystallization of the above mixture gave both isomers (Ia) and (IIIa) respectively. The two isomers were easily separated by fractional crystallization as follows: the mixture was dissolved in dichloromethane and ethanol was added. On evaporation of some solvent, a first crop of pure (Ia) was obtained. Further concentration gave (Ia) contaminated with some (IIIa) which could be eliminated by a second crystallization. Complex (Ib),[10] [ν(Ir–H) = 2224 cm^{-1}] was prepared by the Vaska[9] method using $K_2[IrBr_6]$ prepared by precipitation of "$Ir(OH)_4$" from $Na_2[IrCl_6]$ with sodium carbonate. The precipitate was redissolved in hydrobromic acid (47%), repeating the above procedure, adding KBr and some Br_2 to the solution and reducing to a small volume. Great care must be taken with the preparation of $K_2[IrBr_6]$ as mixed chloro–bromo species are easily obtained. The reaction of $K_2[IrBr_6]$ and Ph_3P, in either aqueous ethanol or 2-methoxyethanol, gave a solid with an infrared band at 2345 cm^{-1} which, on recrystallization from C_6H_6/EtOH produced isomer (Ib). The band at 2345 cm^{-1} in the intermediate was assigned to a vibration involving hydrogen as shown by the product obtained from the same reaction carried out in the presence of D_2O instead of H_2O. In this case, the product showed bands at 2345 and 1678 cm^{-1} (calc. for XD, relative to XH, 1658 cm^{-1}). On dissolution, this compound gave immediately isomer (Ib). The intermediate appears to have the same composition as (Ib). (Found: P, 8.25; calcd., P, 8.15%).

Complex $[IrCl(Ph_3P)(C_8H_{12})]$ was prepared by the method of Winkhaus and Singer,[11] while complexes $[IrCl(Ph_3P)_3]$, $[IrBr(Ph_3P)_3]$ and "$IrHCl(Ph_3P)_3$" were prepared as described by Bennett and Milner.[12]

Preparation of the Complexes

All these reactions were carried out in a nitrogen atmosphere. Unless otherwise stated, all the products were dried overnight at 110°/0.1 mm.

Method A

In a typical reaction isomers (Ia) or (IIIa) (0.60 g) and QP (0.50 g) in chlorobenzene (35 ml) were refluxed for 3 h. A yellow precipitate began to form after about 20 min. The reaction with evolution of HCl. In a quantitative experiment, 65% of the theoretical hydrochloric acid amount was recovered. The mixture was cooled, the precipitate filtered off and washed with a little chlorobenzene. The solid was dissolved in ethanol and treated with an ethanolic solution of sodium tetraphenylboron. The precipitate was filtered off, washed with ethanol and recrystallized from either CH_2Cl_2/EtOH or acetone/EtOH and was shown to be $[Ir(Ph_3P)(QP)][BPh_4]$. Yields varied between 70 and 80%.

There were no other iridium complexes in the mother liquor of the reaction with sodium tetraphenylboron. The mother liquor from the original reaction mixture was taken to dryness under reduced pressure and the residue was washed repeatedly with petroleum ether to remove the triphenylphosphine, dissolved in the minimum quantity of acetone and reprecipitated with benzene giving a yellow crystalline solid which, when turned into the corresponding tetraphenylboron salt, proved to be an additional amount (*ca.* 3%) of $[Ir(Ph_3P)(QP)][BPh_4]$. Examination of the mother liquors showed only small amounts of intractable gums to be present.

Method B

In later preparations, the whole reaction mixture was taken to dryness and the solid treated as described above. When the above preparation was carried out in toluene or *o*-xylene, it gave essentially the same results with the exception that, in toluene a 7% yield of $[IrHCl(QP)]Cl$ was also obtained. This product remained as an insoluble residue in the extraction with acetone of the reaction mixture after it had been taken to dryness. For its identification, see Part III.[1] Traces of this product, together with a normal yield of $[Ir(Ph_3P)(QP)][BPh_4]$, were also obtained when reaction as for Method A was carried out in a sealed tube.

Reactions of Isomer (Ia) with ASTP, PTAS and QAS

These were carried out using Method A and gave $[Ir(Ph_3P)(ASTP)][BPh_4]$ (88% yield) $[Ir(Ph_3P)(PTAS)][BPh_4]$ (30% yield for a 3 h reaction and 37% for a 6 h reaction) and $[Ir(Ph_3P)(QAS)][BPh_4]$ (35% yield), respectively. In all reactions, only intractable gums and unreacted ligands were obtained from the residues.

Reaction of Isomer (Ib) with QP

This reaction was carried out using Method B, but no precipitate was formed during the reaction. On dissolution of the residue in acetone there remained a white crystalline solid which on recrystallization from CH_2Cl_2/acetone and transformation into the corresponding tetraphenylboron salt gave $[IrHBr(QP)][BPh_4]$ in 70% yield. The yield of $[Ir(Ph_3P)(QP)][BPh_4]$ in this reaction was 10%. This reaction was also carried out (1) in toluene, *o*-xylene and bromobenzene with similar results, (2) in the presence of excess of triphenylphosphine (3 moles/mole of complex) when $[Ir(Ph_3P)(QP)][BPh_4]$ (12% yield) and $[IrHBr(QP)][BPh_4]$ (58% yield) were obtained, (3) in the presence of an excess of Na_2CO_3 giving $[Ir(Ph_3P)(QP)][BPh_4]$ (42% yield) and $[IrBr(QP)]$ (2% yield).

Reactions of $[IrHBr_2(Ph_3P)_3]$ with ASTP, PTAS and QAS

These were carried out as for that with QP, (see Method A). Yellow precipitates were formed in these cases. The yield, after a six-hour reaction time, of products $[Ir(Ph_3P)(ligand)][BPh_4]$ (ligand = ASTP, PTAS and QAS) were: 80%, 35% and 41%, respectively. These reactions gave also products $[IrHBr(ligand)][BPh_4]$ as follows: ASTP 14%, PTAS traces, QAS none.

Reaction of $[IrCl(Ph_3P)_3]$ with QP

The complex (0.21 g) and QP (0.17 g) in chlorobenzene (24 ml) were refluxed for 3 h. A slight precipitate formed during the reaction. The mixture was taken to dryness under reduced pressure, the residue washed with petroleum ether and extracted with tetrahydrofuran. On addition of ethanol to the extract and concentration gave $[IrCl(QP)]$ in 26% yield. From the residue of the tetrahydrofuran extraction, $[Ir(Ph_3P)(QP)][BPh_4]$ in 26% yield was obtained as described under Method A.

Reaction of $[IrBr(Ph_3P)_3]$ with QP

This was carried out as above and gave $[IrBr(QP)]$ in 25% yield and $[Ir(Ph_3P)(QP)][BPh_4]$ in 3% yield.

Reaction of $[IrHCl(C_6H_4PPh_2)(Ph_3P)_2]$ *with QP*

The complex (0.21 g) and QP (0.17 g) in chlorobenzene (24 ml) were refluxed for 3 h. The reaction mixture was treated as described under Method A and gave $[Ir(Ph_3P)(QP)][BPh_4]$ in 50% yield. No other identifiable compound could be obtained from the residue.

Reaction of $[IrCl(Ph_3P)(C_8H_{12})]$ *and QP*

The complex (0.15 g) and QP (0.24 g) in chlorobenzene (30 ml) were refluxed for 3 h. The mixture was treated as indicated for the reaction of $[IrCl(Ph_3P)_3]$ with QP giving [IrCl(QP)] (53%) and $[Ir(Ph_3P)(QP)][BPh_4]$ (3.5%).

Reaction of [IrHCl(QP)]Cl *or* $[IrCl_2(QP)]Cl$ *with* $Na[BH_4]$

The iridium complex in ethanol was treated with an excess of the borohydride in ethanol. The mixture was hydrolysed with water and the precipitate, after washing with water and ethanol, was recrystallized from tetrahydrofuran/ethanol. The product, [IrCl(QP)], obtained in *ca.* 35% yield, was dried for 24 h at 145°/0.1 mm and proved to be identical with that obtained from the reaction of $[Ir_2Cl_2(C_8H_{12})_2]$ and QP.[1]

Reaction of [IrHBr(QP)]Br *with* $Na[BH_4]$

The complex [IrBr(QP)] was obtained in 38% yield by carrying out the reaction as described above.

Reaction of [IrHCl(QP)]Cl *and* Ph_3P

The complex (0.15 g) and Ph_3P (0.11 g) in chlorobenzene (20 ml) were refluxed for 3 h. There was a slow and continuous evolution of HCl and the solution became gradually orange. The solution was taken to dryness under reduced pressure and the residue extracted with tetrahydrofuran. The residue was [IrHCl(QP)]Cl, 51%, and the extract on addition of ethanol and slow evaporation, gave [IrCl(QP)], 35%.

Reaction of [IrHBr(QP)]Br *and* Ph_3P

This reaction was carried out as above and the starting material was quantitatively recovered.

Reactions of [IrHX(QP)]X *or* $[Ir(Ph_3P)(QP)]X$ *(X = Cl and Br) with* X_2

The complexes in CH_2Cl_2 reacted instantaneously with the corresponding halogens in CH_2Cl_2 to give, in practically quantitative yields, the complex ions $[IrX_2(QP)]^+$ which were characterized as their tetraphenylboron salts.

Reaction between $[Ir(Ph_3P)(QP)]Cl$ *and* $Na[BH_4]$

The reagents were refluxed in ethanol for 30 min. The starting material was recovered unchanged after working up the mixture as described earlier.

Reactions of [IrCl(QP)] *with HCl,* Cl_2 *or* Ph_3P

The complex in tetrahydrofuran or CH_2Cl_2 reacts instantaneously with gaseous HCl or Cl_2 in CH_2Cl_2 to give [IrHCl(QP)]Cl and $[IrCl_2(QP)]Cl$, respectively, which were characterized as their tetraphenylboron salts. The complex [IrCl(QP)] was recovered unchanged after refluxing for 3 h in chlorobenzene with a three-fold excess of Ph_3P.

Analyses

Carbon, hydrogen and halogen analyses were carried out by Galbraith Laboratories, Knoxville, Tennessee. Phosphorus[13] was determined spectrophotometrically, arsenic[14] by atomic absorption using a Perkin–Elmer Model 303 spectrophotometer, and iridium was determined by the same method using the line at 264 nm in the atomic absorption spectrum of iridium; measurements were made on dimethylformamide solutions containing *ca.* 100 mg Ir/ml and the calibration curve was constructed using a pure specimen of $[Ir(Ph_3P)(QP)][BPh_4]$ which had been analysed for C, H, P and Ir, the latter element by a spectrophotometric method.[1]

N.m.r. Spectra[15]

P.m.r. spectra were recorded at 100 MHz on a Varian HA–100D spectrometer, using TMS as primary internal standard. The phosphorus-31 spectra were recorded at 40.48 MHz on the same instrument in 5 mm o.d. spinning tubes, with P_4O_6 as primary external standard. The homonuclear lock system of the instrument was employed, using the reference compound in a capillary. Phosphoric acid (85%) was used as a secondary reference ($\delta_{P_4O_6} = +\ 112.50 \pm 0.01$ ppm) where phase difference between lock resonance and the resonance to be observed was so large as to cause the lock to be unstable when the phase was correct for the observed signal. The phenyl protons of the ligands were decoupled from the phosphorus-31 spectra by taking the appropriate frequency, derived from a Hewlett–Packard Model 5105A frequency synthesizer and Model 5110B frequency synthesizer driver, amplified by a Hewlett–Packard 230A power amplifier. The V 4333 probe was double-tuned to accept both proton and phosphorus-31 frequencies. A Varian C–1024 time-averaging computer was used for spectral accumulation, which was required in nearly all cases. During accumulation the internal sweep oscillator of the spectrometer was replaced with a Hewlett–Packard Model 3310A function generator, using the ramp of the C–1024 computer to provide the external frequency control. In such cases, chemical shifts were obtained from averages of accumulated spectra for both increasing and decreasing frequency sweep obtained from positive- and negative-going ramps, respectively. Bulk magnetic susceptibility corrections were not made.

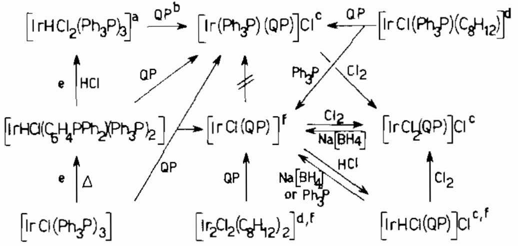
Other Physical measurements

Conductivities were measured for approximately 10^{-3} *M* nitrobenzene solutions using a Wayne–Kerr B 641 Bridge and cells with platinum black electrodes. Infrared spectra were recorded on a Perkin–Elmer Model 225 spectrophotometer using rock salt cells or plates. Visible and ultraviolet spectra of 10^{-3}–10^{-5} *M* solutions were recorded on a Cary 14 spectrophotometer using 1 cm fused silica cells; low-temperature spectra were obtained using a Beckman VLT–2 low-temperature accessory fitted with standard silica windows.

Results and Discussion

The reactions carried out on a number of chloro-complexes are shown in Scheme 1 and the resulting products, with some of their physical properties, are listed in Table I.

Scheme 1.
Some reactions of iridium chloro-complexes.



[a] The same reaction is given by (Ia) and (IIIa). [b] Ligands PTAS, ASTP and QAS react similarly. [c] The cation was fully characterized as its tetraphenylboron salt. [d] C_8H_{12} = 1,5-*cyclo*-octadiene. [e] See Ref. 12. [f] See Ref. 1.

TABLE I. Some physical and analytical data on complexes of iridium with quadridentate ligands.

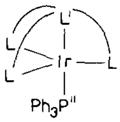
Compound	Color	Decomp. pt.	Λ_M[a]	C(%)		H(%)		Ir(%)		P(or As) (%)		Cl(or Br) (%)	
				Found	Reqd.	Found	Reqd.	Found	Reqd.	Found	Reqd.	Found	Reqd.
$[Ir(Ph_3P)(QP)][BPh_4]$	Yellow	280–285°	16.1	72.58	72.62	4.87	4.89	12.07	12.10	9.72	9.75		
$[Ir(Ph_3P)(ASTP)][BPh_4]$	Yellow	285–287°	16.1	70.62	70.64	4.95	4.75	11.77	11.77	(4.57)	(4.59)		
$[Ir(Ph_3P)(PTAS)][BPh_4]$	Yellow	325–330°	16.0	66.95	67.03	4.65	4.51	11.27	11.17	(13.22)	(13.06)		
$[Ir(Ph_3P)(QAS)][BPh_4]$	Yellow	318–321°	16.4	65.65	65.35	4.39	4.40	11.05	10.89	(16.40)	(16.99)		
$[IrHCl(QP)][BPh_4]$[b, c]	Colorless	250–254°	14.9	69.06	68.76	4.80	4.66	14.02	14.10	9.07	9.09	2.60	2.60
$[IrHBr(QP)][BPh_4]$[d]	Colorless	233–238°	16.5	66.22	66.58	4.59	4.51	13.76	13.66	8.65	8.80	(5.92)	(5.68)
$[IrCl_2(QP)][BPh_4]$	Colorless	315–318°	14.7	67.08	67.05	4.37	4.47	13.89	13.76	8.79	8.87	5.20	5.08
$[IrBr_2(QP)][BPh_4]$	Colorless	258–262°	15.7	62.98	63.02	4.35	4.21	12.97	12.94	8.33	8.34	(10.51)	(10.76)
$[IrCl(QP)]$[c]	Orange	310–315°	[e]	61.95	62.22	4.09	4.06	18.63	18.44	11.93	11.88	3.33	3.40
$[IrBr(QP)]$	Orange	343–346°	[e]	60.09	59.68	4.03	3.89	17.76	17.68	11.43	11.40	(7.23)	(7.35)

[a] For 10^{-3} *M* nitrobenzene solutions at 25° in Ω^{-1} cm^2 mole^{-1}. [b] $\nu_{Ir\text{-}H} = 2100$ cm^{-1}. [c] See also Reference 1. [d] $\nu_{Ir\text{-}H} = 2090$ cm^{-1}.
[e] Non-electrolyte, decomposes fairly rapidly in this solvent.

TABLE II. Phosphorus-31 nmr chemical shifts (δ, in ppm, relative to external P_4O_6) and coupling constants (J, in Hz) for dichloromethane solutions of $[Ir(Ph_3P)(L'L_3)][BPh_4]$.

$L'L_3$	$\delta_{P'}$	δ_P	$\delta_{P''}$	$J_{P'P}$	$J_{P'P''}$	$J_{PP''}$
QP	13.3(2)	95.3(1)	110.8(1)	13.4(1)	267(2)	31.7(2)
ASTP		89.8(1)	110.2(1)			
PTAS	2.5(3)		109.6(2)		282(5)	29.1(10)
QAS			109.6(1)			

Complex cations of the type $[Ir(Ph_3P)(L'L_3)]^+$ ($L'L_3$ = QP, ASTP, PTAS and QAS) have been assigned trigonal bipyramidal structure on the basis of their proton and phosphorus-31 n.m.r. spectra: (1) examination of the p.m.r. spectrum showed that only aromatic protons are present in this group of complexes, (2) the phosphorus-31 n.m.r. data, shown in Table II, are consistent only with trigonal bipyramidal coordination in the QP and ASTP complexes (VIa and VIb, respectively) while the spectra of the PTAS and QAS compounds are consistent with the same structural assignments. Comparison of chemical shifts and coupling constants for the four complexes allows the assignment of the low-field resonance to P′, as observed in other complexes of these ligands,[16] and the high-field resonance to P″. Irradiation of selected lines[15] showed that $J_{P'P}$ and $J_{PP''}$ have the same sign which is opposite to that of $J_{P'P''}$.



L′ = L = P; QP (VIa)
L′ = As, L = P; ASTP (VIb)
L′ = P, L = As; PTAS (VIc)
L′ = L = As; QAS (VId)

The trigonal bipyramidal coordination of the iridium atom $[Ir(Ph_3P)(QP)][BPh_4]$ has been confirmed by x-ray diffraction studies.[17] These are the first set of compounds of trigonal bipyramidal structure, containing only phosphorus or arsenic as donor atoms, to be characterized. Evidence[18] for the formation of $[Pt(Ph_3P)(QAS)]^{2+}$, however, has been obtained from a kinetic study of the reaction between $[PtBr(QAS)]^+$ and triphenyl phosphine in methanol solution. The abnormally slow rate for this reaction has been attributed[18] to steric crowding in the transition state. This is in agreement with the observation that compounds $[IrX(QP)]$ (X = Cl and Br) are recovered unchanged after refluxing for three hours in chlorobenzene with an excess of triphenylphosphine. Furthermore, compounds $[Ir(Ph_3P)(L'L_3)]X$ are remarkably inert, being unaffected by most chemical reagents with the exception of chlorine and bromine which react to give compounds $[IrX_2(QP)]X$ (X = Cl and Br, respectively).

It should be noted that while the micro-symmetry of the iridium atoms in complexes $[Ir(Ph_3P)(L'L_3)]X$ is similar to that found in a number of other iridium(I) complexes[19] as well as in $[Ir(CO)(QP)][BPh_4]$ and in $[Rh(CO)(QP)][BPh_4]$,[10] it is different from that found[21] in $[Ni(das)(tas)](ClO_4)_2$ [das = $(o\text{-}Me_2As)C_6H_4$; tas = $(o\text{-}Me_2AsC_6H_4)_2AsMe$] which is square pyramidal.

The reduction of the iridium which accompanies the formation of $[Ir(Ph_3P)(QP)]^+$ from $[IrHCl_2(Ph_3P)_3]$ may be of the type of a "reductive elimination" as during the reaction there is evolution of hydrogen chloride. In order to test this hypothesis and to understand the factors responsible for the formation of cations of the type $[Ir(Ph_3P)(L'L_3)]^+$, the ligand QP was reacted with a number of other substrates (see Scheme 1). The results of these experiments can be rationalized on the basis of the following set of reactions:

$$[IrHX_2(Ph_3P)_3] \underset{HX^{12}}{\overset{QP}{\rightleftarrows}} [IrX(Ph_3P)_3] + QP \cdot HX \qquad (1)$$

$$[IrX(Ph_3P)_3] + QP \rightarrow [IrX(QP)] + 3\ Ph_3P \qquad (2)$$

$$[IrX(Ph_3P)_3] \xrightarrow{\Delta^{12}} [IrHX(C_6H_4PPh_2)(Ph_3P)_2] \qquad (3)$$

$$[IrHX(C_6H_4PPh_2)(Ph_3P)_2] + QP \rightarrow [Ir(Ph_3P)(QP)]X + 2\ Ph_3P \qquad (4)$$

$$QP \cdot HX \xrightarrow{\Delta} QP + HX \qquad (5)$$

$$[IrX(QP)] \underset{Ph_3P^{22}}{\overset{HX}{\rightleftarrows}} [IrHX(QP)]X \qquad (6)$$

$$[IrHX(C_6H_4PPh_2)(Ph_3P)_2] + HX \xrightarrow{\Delta^{12}} [IrHX_2(Ph_3P)_3] \qquad (7)$$

The observation that the reaction of $[IrHCl(C_6H_4PPh_2)(Ph_3P)_2]$ with QP gives only $[Ir(Ph_3P)(QP)]Cl$ suggests that this product requires the above substrate for its formation. This hypothesis is supported by the following observations: (1) complex $[IrCl(Ph_3P)_3]$ reacts with QP to give an equimolecular mixture of $[Ir(Ph_3P)(QP)]Cl$ and $[IrCl(QP)]$ which is compatible with the results of Bennett and Milner[12] who find that the rate of hydrogen abstraction from $[IrCl(Ph_3P)_3]$ has a $t_{1/2}$ of 57 min in benzene at 39.5°, (2) complex $[IrCl(Ph_3P)(C_8H_{12})]$ reacts with QP to give, in addition to $[IrCl(QP)]$, a small amount of $[Ir(Ph_3P)(QP)]Cl$ which, presumably, originates from $[IrCl(Ph_3P)_3]$ which is formed according to the reaction sequence:

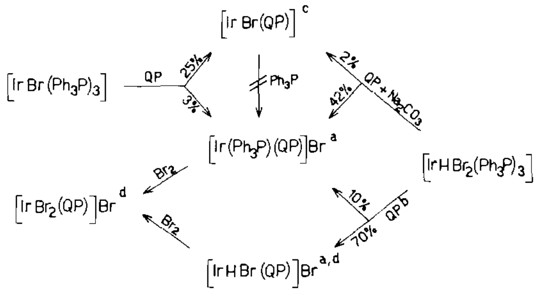
$$2[IrCl(Ph_3P)(C_8H_{12})] + 2\ QP \rightarrow 2[IrCl(QP)] + 2\ Ph_3P + 2\ C_8H_{12}$$

$$[IrCl(Ph_3P)(C_8H_{12})] + 2\ Ph_3P \rightarrow [IrCl(Ph_3P)_3] + C_8H_{12}{}^{12}$$

(3) complex $[IrCl(QP)]$ is unaffected by triphenylphosphine under the reaction conditions used.

To obtain additional evidence on the reaction path leading to the formation of the complex cation $[Ir(Ph_3P)(QP)]^+$ the reactions between some iridium bromo-complexes and QP were studied. These are shown in Scheme 2 and the products obtained are listed in Table I.

Scheme 2.
Some reactions of iridium bromo-complexes.



[a] The cation was fully characterized as its tetraphenylboron salt. [b] When this reaction was carried out in the presence of an excess of Ph_3P, the yields of $[Ir(Ph_3P)(QP)][BPh_4]$ and $[IrHBr(QP)][BPh_4]$ were 12 and 58%, respectively. [c] Reacts with HBr to give $[IrHBr(QP)]Br$. [d] Reacts with $Na[BH_4]$ to give $[IrBr(QP)]$.

As can be seen, there are considerable differences in patterns of reactivity between the chloro- and bromo-systems. The latter results, however, are also consistent with the postulated reaction scheme if one takes into account the following: (1) phosphonium chlorides have a higher vapor pressure than phosphonium bromides,[25] and (2) hydrogen bromide is more soluble than hydrogen chloride in aromatic hydrocarbons.[24] This difference causes a less rapid evolution of hydrogen bromide and, therefore, because of reaction (7), a reduction in the amount of $[IrHBr(C_6H_4PPh_2)(Ph_3P)_2]$ present in solution. When, however, the reaction between $[IrHBr_2(Ph_3P)_3]$ is carried out in the presence of carbonate, reaction (7) is prevented and a good yield of $[Ir(Ph_3P)(QP)]^+$ is obtained.

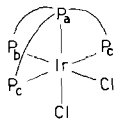
The formation of a small amount of $[IrHCl(QP)]Cl$ in the reaction between $[IrHCl_2(Ph_3P)_3]$ and QP in toluene may be due to its lower boiling point (110.6° while chlorobenzene has a b. pt. of 132°) and the higher solubility of hydrogen chloride in toluene ($\lambda_{20°} = 12.6$ while that for chlorobenzene is 6.27)[25] resulting in a higher concentration of hydrogen chloride in solution, i.e., reaction (7) would compete more effectively with reaction (4) for $[IrHCl(C_6H_4PPh_2)(Ph_3P)_2]$ as is found to be the case in the corresponding bromo-system.

It is proposed that compounds $[IrX(Ph_3P)_3]$ and $[IrHX(C_6H_4PPh_2)(Ph_3P)_2]$ react with QP giving different products, [see reactions (2) and (4)] because all the phosphine ligands in the first complex are monodentate while in the latter case one of them is acting as a bidentate ligand and thus, it would be displaced with greater difficulty. Furthermore, Bennett and Milner[12] report that $[IrHCl(C_6H_4PPh_2)(Ph_3P)_2]$ reacts with carbon monoxide, undergoing a "C–H recombination reaction", to give $[IrCl(CO)(Ph_3P)_2]$. A C–H recombination reaction must also occur during reaction (4). The evidence presented here indicates that this reaction occurs as a last step: if it were to occur earlier in the phosphine substitution sequence of reaction (4), i.e., if after the C–H recombination a compound of the type $[IrX(Ph_3P)_n(QP^*)]$ (n = 1 or 2 and $QP^* = QP$ acting as tridentate or bidentate ligand, respectively) were to be formed, this would give $[IrX(QP)]$ as (i) the above intermediate must also be formed during reaction (2) which gives $[IrX(QP)]$ and (ii) it is known that this compound does not react with triphenylphosphine to give $[Ir(Ph_3P)(QP)]X$.

It should be pointed out here that a number of the products described in this paper could be formed by reactions which are different from those given above. These, however, are preferred on the grounds that they fit best all the available data. Lastly, while in many reactions the total yields of products are relatively low, the residues of each reaction contained only small amounts of intractable gums in addition to triphenylphosphine and, occasionally, small amounts of the appropriate quadridentate ligand.

Complex $[IrBr(QP)]$, like complexes $[IrCl(QL)]$ (QL = QP and QAS),[1] has been assigned trigonal bipyramidal structure on the basis of its electronic spectrum. It proved to be too insoluble for the measurements of its phosphorus-31 n.m.r. spectra. It is a rather reactive compound which easily undergoes oxidative-addition reactions.

The iridium atoms in complex cations $[IrX_2(QP)]^+$ (X = Cl and Br) have been assigned octahedral coordination on the basis of their phosphorus-31 n.m.r. spectra which shows a general resemblance to those of other octahedral complexes containing QP.[16] The compound $[IrCl_2(QP)][BPh_4]$ was examined in detail. Its low-field singlet was assigned to P_a on the basis of its chemical shift. The peaks at higher field have the appearance of a weakly coupled AB_2 system. No coupling to P_a is resolved, although the line-widths of the P_c doublet are significantly larger than those of the P_b triplet. Calculations show that this effect is due to unresolved $J_{P_aP_c}$ coupling. The relevant parameters are: $\delta_a = 36.5 \pm 0.2$, $\delta_b = 101.5 \pm 0.1$, $\delta_c = 103.5 \pm 0.1$ ppm, $|J_{P_bP_c}| = 11.9 \pm 0.5$ Hz.



Complexes $[IrHX(QP)]X$ and $[IrX_2(QP)]X$ undergo an interesting reaction with sodium borohydride: on addition of this reagent, a palecolored solution is obtained from which, within a short time, the orange compounds [IrX(QP)] separate out. The pale-colored solution is likely to contain $[IrH_2(QP)]X$ from which compounds [IrX(QP)] could be formed by loss of molecular hydrogen. In this context, it is interesting to recall that the hydrido-ligands in $[RuH_2(Ph_3P)_4]$ undergo facile exchange with molecular deuterium.[26]

During the course of the present investigation, we found no evidence indicating the formation of compounds of composition $[IrHX(Ph_3P)(QP)]X$, described in an earlier publication,[3] although many experiments were conducted under apparently identical conditions to those that led to the isolation of the above species. This discrepancy is still under investigation as the pmr spectra of complexes formulated as $[IrHX(Ph_3P)(QP)]X$ differ significantly from those of any of the other iridium complexes we have obtained and thus, whether their formulation is correct or not, are different chemical species from those described in this paper.

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