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# The Reactions of Phosphorus- and Arsenic-Containing Multidentate Ligands with Some Iridium Complexes.
# Part III.[1,2] The Reaction with Ligands (o-$Ph_2LC_6H_4)_3L$ and (o-$Ph_2LC_6H_4)_2LPh$ (L = P and As)

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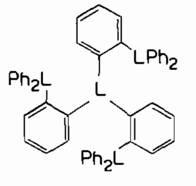
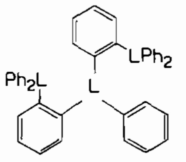
*The preparation of complexes [Ir(CO)(QL)]X, [IrCl(QL)] and [IrHCl(QL)][BPh$_4$] (QL = (o-Ph$_2$PC$_6$H$_4$)$_3$P and (o-Ph$_2$AsC$_6$H$_4$)$_3$As, X = Cl and [BPh$_4$], and of complexes [IrCl$_3$(TL)] (TL = (o-Ph$_2$PC$_6$H$_4$)$_2$PPh and (o-Ph$_2$AsC$_6$H$_4$)$_2$AsPh) and [IrX$_3$(o-Ph$_2$AsC$_6$H$_4$)$_2$AsPh] (X = Cl and Br) are reported. Their nmr and/or electronic spectra were used for their characterization.*

## Introduction

An earlier publication[2] reported the X-ray structure determination of the complex $[Ir(SnCl_3)(C_8H_{12})_2]$, its reaction with the ligand (*o*-$Ph_2AsC_6H_4)_3As$, QAS, (Ib), which gave five-coordinate $[Ir(SnCl_3)(QAS)]$, and its chlorine oxidation which gave six-coordinate $[IrCl(SnCl_3)(QAS)]Cl$. We report here reactions of other iridium olefin complexes and of Vaska's compound[4] with the ligands QAS, (*o*-$Ph_2PC_6H_4)_3P$, QP, (Ia), (*o*-$Ph_2PC_6H_4)_2PPh$, TP, (IIa), and (*o*-$Ph_2AsC_6H_4)_2AsPh$, TAS, (IIb).



(Ia) L = P; QP
(Ib) L = As; QAs



(IIa) L = P, TP
(IIb) L = As; TAs

## Experimental

### Preparation of the Ligands

The ligands (*o*-$Ph_2PC_6H_4)_2PPh$, TP, and (*o*-$Ph_2PC_6H_4)_3P$, QP, were prepared by the method of Chiswell and Venanzi,[5] and the ligands (*o*-$Ph_2AsC_6H_4)_2AsPh$, TAS, and (*o*-$Ph_2AsC_6H_4)_3As$, QAS, were prepared by the method of Howell, *et al.*,[6] using the method of Cannon, *et al.*,[7] for the preparation of *o*-$Ph_2AsC_6H_4Br$.

### Preparation of the Complex Intermediates

The complex $[IrCl(CO)(Ph_3P)_2]$ was prepared by the method of Chatt, *et al.*,[8] and complexes $[Ir_2Cl_2(C_8H_{12})_2]$ and $[Ir_2H_2Cl_4(C_8H_{12})_2]$($C_8H_{12}$ = 1,5-*cyclo*-octadiene) was prepared by the method of Winkhaus and Singer.[9]

### Preparation of the Complexes

[Ir(CO)(QP)]Cl: Complex $[IrCl(CO)(Ph_3P)_2]$ (0.39 g) and QP (0.45 g) were refluxed in chlorobenzene (30 ml) for 3 h. The orange solution was evaporated under reduced pressure and the yellow solid obtained was washed with ether and recrystallized from chlorobenzene.

[Ir(CO)(QP)][$BPh_4$]: The chloro-complex above (0.25 g) in ethanol (25 ml) was added to an ethanolic solution of sodium tetraphenylboron. The precipitate was filtered off and recrystallized from dichloromethane/ethanol. [Ir(CO)(QAS)]X (X = Cl and $BPh_4$) were prepared and purified as their QP analogues.

[IrCl(QP)]: Complex $[Ir_2Cl_2(C_8H_{12})_2]$ (0.15 g) and QP (0.40 g) in chlorobenzene (25 ml) were refluxed for two hours. The solution was taken to dryness under reduced pressure and the residue was recrystallized from tetrahydrofuran/ethanol. The unsolvated material was obtained after drying for 24 h at 145°/0.1 mm.

[IrCl(QAS)] was prepared as above.

[IrHCl(QP)][$BPh_4$]: Complex $[Ir_2H_2Cl_4(C_8H_{12})_2]$ (1.25 g) and QP (2.72 g) in chlorobenzene (30 ml) were refluxed for $1^1/_2$ h. The precipitate was filtered off and recrystallized first from dichloromethane/acetone and then from dichloromethane/petroleum ether. This solid (solvated [IrHCl(QP)]Cl) was dissolved in ethanol and reacted with an ethanolic solution of sodium tetraphenylboron. The precipitate was recrystallized from acetone/ethanol.

[IrHCl(QAS)][$BPh_4$] was similarly prepared.

[$IrCl_3$(TP)]: Hydrated chloro-iridic acid (0.4 g) and TP (0.63 g) were refluxed in chlorobenzene (3.0 ml) for 3 h. The precipitate was filtered off and recrystallized from dichloromethane/ethanol.

[$IrCl_3$(TAS)]: An aqueous solution of hydrated sodium chloro-iridite (1.0 g) was passed through a cation exchange resin in the hydrogen form. The solution was evaporated to a very small volume, ethanol (60 ml) and TAS (1.1 g) were added and the mixture refluxed for 2 h. The precipitate was filtered off and recrystallized from dichloromethane/petroleum ether.

[$IrBr_3$(TAS)]: An aqueous solution of hydrated sodium chloro-iridite (0.69 g) and sodium bromide (1.3 g) were refluxed for 12 h in the presence of a little sodium chloro-iridate. The resulting solution was passed through a cation exchange resin in the hydrogen form, reduced to a small volume and then it was reacted with TAS (0.76 g) and the product purified as described above.

### *Analyses*

Carbon, hydrogen and halogen analyses were carried out by Dr. A. Bernhardt, Mikroanalytisches Laboratorium Max Plank Institut für Kohlenforschung, Mühlheim, West Germany; phosphorus[10] and iridium were determined spectrophotometrically, the latter by the following modification of Ayes and Bolleter's method:[11] The complex (*ca.* 10 mg) was decomposed by heating with a 50:50 mixture of concd. nitric acid and 72% perchloric acid (5 ml) and 85% phosphoric acid (10 ml), in a 100 ml Kjeldahl flask. During the heating, the colour of the solution changed from amber to purple, and then to pale yellow, when fumes of perchloric acid appeared. Heating was continued until all the perchloric acid had distilled off, as indicated by the cessation of vigorous boiling. The solution was cooled, and made up to 250 ml with distilled water. Several 5 ml portions were transferred to 25 ml flasks, and treated with freshly prepared Leuco-Crystal Violet (1 ml of 0.10% solution), and acetate buffer (10 ml). The solutions were made up to 25 ml and their absorbances were measured at 590 nm against a reagent blank. A calibration curve and constant were obtained using 'Specpure' ammonium chloro-iridate. The reagents were prepared as follows: (a) Leuco-Crystal Violet (4,4′,4″-Hexamethyltriaminotriphenylmethane) (20 mg) was dissolved in 10 ml of a 1*M* solution of phosphoric acid. Solutions were always prepared just before use, as they oxidize slowly in sunlight. (b) The acetate buffer solution was prepared by adding glacial acetic acid (700 ml) to a 6*M* sodium hydroxide solution (300 ml) to give a solution of pH 3.9.

The method was found to be accurate to ± 2%, provided that a standardized procedure was followed. The length of the heating for the decomposition was found to be critical. Prolonged heating led to the formation of a 'jelly' of phosphoric acid, which could not be redissolved in water and produced inhomogeneity in the solution. On the other hand, insufficient heating resulted in the presence of perchloric acid, or its decomposition products, in the solution, which interfered with the oxidation of the dyestuff at the colour development stage. It was also found necessary to develop the colour within a few hours of the decomposition process, as 'aging' of the iridium solutions led to changes which affected the oxidation process. Once developed, however, the colour was stable for at least twelve hours.

### *Other Physical Measurements*

Conductivity measurements were made for approximately $10^{-3}M$ nitrobenzene solutions, using a Cambridge Instruments conductivity bridge and a cell with bright platinum electrodes. Infrared spectra were recorded on Perkin–Elmer Model 237 and 337 spectrometers using mulls of the complexes in either Nujol or hexachlorobutadiene. The visible and ultraviolet spectra were recorded on a Unicam Model SP 700 spectrophotometer using 1 cm fused silica cells; low temperature spectra were obtained using a VLT–2 unit manufactured by the Research and Industrial Instruments Co., Ltd., filtered with fused silica windows. The n.m.r. spectral measurements were done as described in Part IV.

## Results and Discussion

The complexes prepared and some of their physical properties are listed in Table I. Complexes [Ir(CO)(QL)]Y (QL = QP and QAS; Y = Cl and [$BPh_4$]) have been assigned trigonal bipyramidal coordination. The spin-decoupled $^{31}P-\{^1H\}$ nmr spectrum of [Ir(CO)(QP)][$BPh_4$], IIIa, shows a low field quartet assigned to the central phosphorus atoms, P′, and a highfield doublet, of three times the intensity, assigned to the terminal phosphorus atoms, P. The relevant data are:[12] $\delta_{P'} = +13.19$ (1), $\delta_P = +81.69$ (1) (both relative to $P_4O_6$) and $|^2J(P\text{–}Ir\text{–}P')| = 16.3$ Hz, consistent with the data observed for other trigonal bipyramidal complexes.[12,13] Complexes [Ir(CO)(QAS)]Y (Y = Cl and [$BPh_4$]), IIIb, are assumed to be isostructural with the QP complexes. Their electronic spectra are in agreement with the predictions made by

(IIIa): L = P, X = CO
(IIIb): L = As, X = CO
(IIIc): L = P, X = Cl
(IIId): L = As, X = Cl

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

| Compound | Colour | Yield (%) | Decomp. Pt. | $\Lambda_M$[a] | $\nu_{CO}/\nu_{IrH}$ cm$^{-1}$ | C(%) Found | C(%) Calcd. | H(%) Found | H(%) Calcd. | P/As(%) Found | P/As(%) Calcd. | Ir(%) Found | Ir(%) Calcd. | Cl/Br(%) Found | Cl/Br(%) Calcd. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| [Ir(CO)(QP)]Cl[b] | Pale Yellow | 57 | 220–225° | 28.2 | 1995 | 61.6 | 61.7 | 4.1 | 4.0 | 11.5 | 11.6 | 17.6 | 17.9 | 3.2 | 3.3 |
| [Ir(CO)(QP)][BPh$_4$][b] | Pale Yellow | 63 | 260–262° | 15.4 | 1995 | 69.8 | 70.1 | 4.8 | 4.6 | 9.0 | 9.2 | 14.1 | 14.2 | | |
| [Ir(CO)(QAS)]Cl | Pale Yellow | 79 | 293–295° | 22.7 | 1981 | | | | | 23.9 | 24.1 | 15.4 | 15.4 | | |
| [Ir(CO)(QAS)][BPh$_4$] | Pale Yellow | 87 | 272–275° | 16.9 | 1989 | | | | | 19.4 | 19.6 | 12.5 | 12.6 | | |
| [IrCl(QP)] | Orange | 66 | 310–315° | 0.1[c] | | 62.0 | 62.2 | 4.1 | 4.1 | 18.6 | 18.4 | 11.9 | 11.9 | 3.3 | 3.4 |
| [IrCl(QAS)] | Orange | (d) | 255–260° | 0.3[c] | | 53.2 | 53.3 | 3.5 | 3.5 | | | 15.9 | 15.8 | 3.4 | 2.9 |
| [IrHCl(QP)][BPh$_4$][b] | Colourless | 83 | 180–185° | 16.3 | 2100 | 68.2 | 68.8 | 4.6 | 4.7 | 9.1 | 9.1 | 14.0 | 14.1 | | |
| [IrHCl(QAS)][BPh$_4$] | Colourless | 22 | 190–195° | 14.4 | 2080 | 60.1 | 61.0 | 4.2 | 4.1 | | | 12.6 | 12.5 | 2.7 | 2.3 |
| [IrCl$_3$(TP)] | Pale Yellow | 84 | 365–370° | 0.1 | | 54.3 | 54.3 | 3.8 | 3.6 | 10.0 | 10.0 | 20.5 | 20.7 | 10.0 | 11.4 |
| [IrCl$_3$(TAS)] | Yellow | 63 | 328–330° | 0.5 | | | | | | 20.9 | 21.2 | 18.1 | 18.1 | | |
| [IrBr$_3$(TAS)] | Orange | 71 | 298–303° | 1.0 | | | | | | 18.9 | 18.8 | 16.0 | 16.1 | | |

[a] In $\Omega^{-1}$cm$^2$*M*$^{-1}$ for approx. $10^{-3}$ *M* nitrobenzene solutions at 20°. [b] These compounds are diamagnetic. [c] These compounds are decomposed by the solvent. [d] Not recorded.

comparison with the spectra of the corresponding cobalt and rhodium complexes.[14] Unlike [Rh(CO)(QL)]Cl (QL = QP and QAS), complexes [Ir(CO)(QL)]Cl do not lose carbon monoxide either on heating or on irradiation. If forcing conditions are used, the complexes decompose. This behaviour, however, parallels that observed for complexes [Co(CO)(QL)][BPh$_4$],[16] and does not appear to be related to the CO stretching frequencies of the complexes of the three metals.

Complexes [IrCl(QL)] (QL = QP and QAS), IIIc and IIId respectively, are also assigned trigonal bipyramidal structure on the basis of their electronic spectra. The low-energy bands in these compounds, which are assigned to ligand field transitions, occur at the same energies as the corresponding transitions in the iso-electronic ions [PtCl(QL)]$^+$ (see Figure 1 for comparison of the QP complexes of the two metal ions) and show the same type of temperature dependence found in the platinum complexes.[17] This type of energy relationship in the ligand field spectra of iso-electronic complexes has already been observed for square planar species[18] and has been found to be valid to trigonal bipyramidal complexes of cobalt(I) and nickel(II),[14] and of rhodium(I) and palladium(II).[19] The iridium ligand field bands occur on the low-energy side of a high-intensity absorption band, or bands, which, on the basis of previous work on related compounds,[14] can be assigned to metal–to–ligand charge-transfer type transition, or transitions. It is interesting to note that the positions of the charge-transfer band, or bands, in complexes [IrCl(QL)] occur at very similar energies as those in trigonal bipyramidal complexes [Ir(CO)(QL)][BPh$_4$] (compare Figure 1 and Figure 4 of Ref. 14). Complexes [IrCl(QL)] are rather reactive

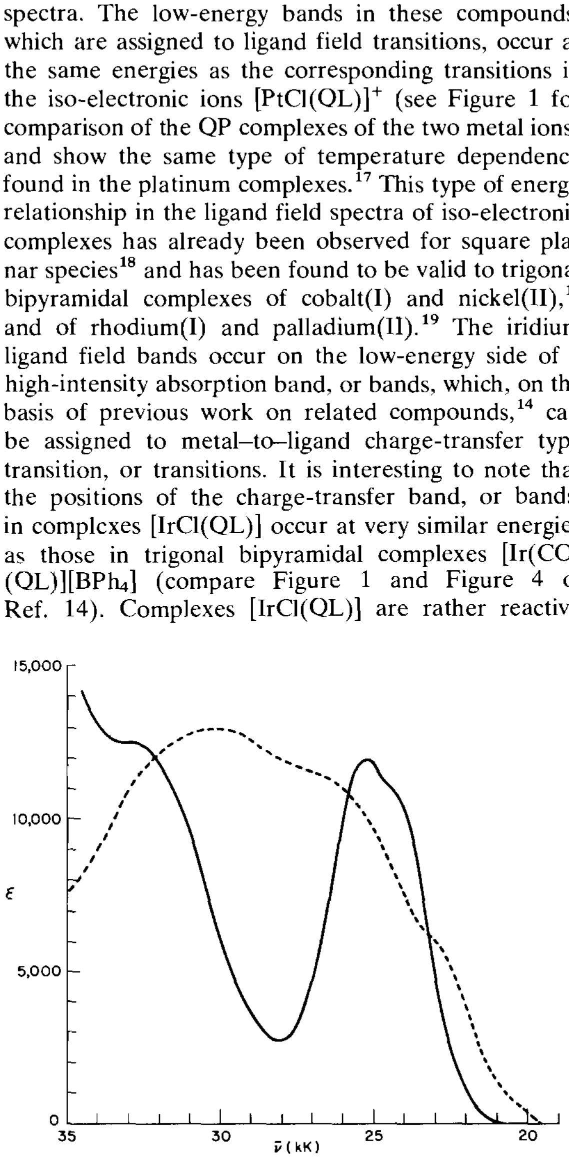


Figure 1. Electronic spectra of complexes (in dichloromethane/2-methyl-tetrahydroturan glasses at 100°K): [PtCl(QP)][BPh$_4$] (full line); [IrCl(QP)] (broken line).

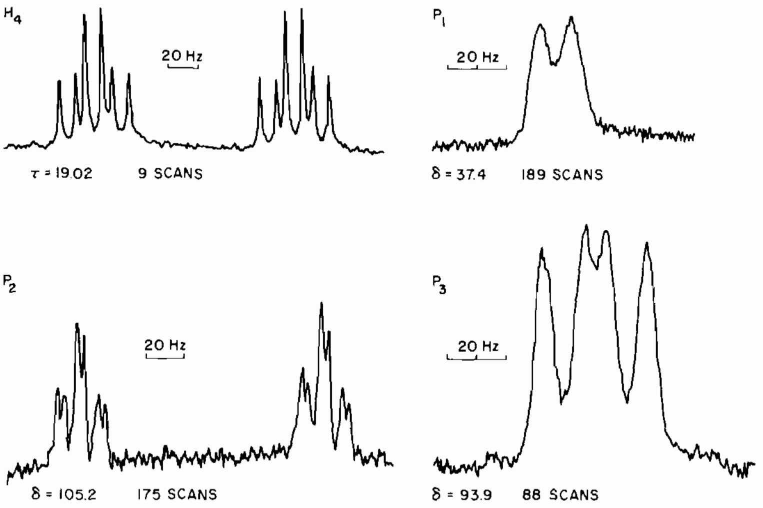
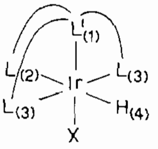


Figure 2. Nmr spectrum of [IrHCl(QP)][BPh$_4$].

and undergo oxidative addition reactions with ease (see Part IV). The complex with QAS appears to be less reactive than QP analogue.

Complexes [IrHCl(QL)][BPh$_4$] (QL = QP and QAS), IVa and IVb, respectively, have been assigned octahedral structure. The high-resolution phosphorus-31 nmr spectrum of [IrHCl(QP)][BPh$_4$] (see Figure 2 and Table II) confirms the earlier structural assignment,[13] i.e., that the isomeric form isolated is that shown in IVa.



(IVa): L = L′ = P; X = Cl
(IVb): L = L′ = P; X = Br
(IVc): L = P; L′ = As; X = Cl
(IVd): L = L′ = As; X = Cl

The pmr spectrum of [IrHCl(QP)][BPh$_4$] (see Figure 2) shows coupling to one *trans*-phosphorus atom and to three *cis*-phosphorus atoms, one of which is coupled more weakly.

Irradiation at 40.482 87 MHz (corrected for TMS resonating at exactly 100 MHz in the same field) produced collapse of the weakest coupling to give a doublet of triplets. Since the resonant frequency for $^{31}$P in 85% H$_3$PO$_4$ in the same field is 40.480 74 MHz,[20] the chemical shift of the phosphorus atom giving rise to the weak coupling is approximately −76.3 ppm relative to 85% H$_3$PO$_4$. This is in the region expected for the central phosphorus atom of QP.[13] Further irradiation showed that the resonances of the other phosphorus atoms are to higher field. Therefore, these data permit assignment of structure IVa to the compound.[21] This is also in agreement with the phosphorus-31 nmr spectrum and with the previous assignment. In both the $^1$H and $^{31}$P nmr spectra, the coupling constants involving the central phosphorus atoms are smaller than the comparable coupling constants involving other phosphorus atoms.

The nmr spectra of compounds [IrHBr(QP)][BPh$_4$] and [IrHCl(ASTP)][BPh$_4$] are also consistent with structures IVb and IVc, respectively, and it is assumed

TABLE II. Nmr parameters for the complexes [IrHX(L'L$_3$)][BPh$_4$].

Chemical Shifts

| L'L$_3$ | X | Solvent | $\tau_4$ | $\delta_1$, ppm[a] | $\delta_2$, ppm[a] | $\delta_3$, ppm[a] |
|---|---|---|---|---|---|---|
| QP | Cl | CH$_2$Cl$_2$ | 19.02 ± 0.01 | 37.4 ± 0.2 | 105.2 ± 0.2 | 93.9 ± 0.1 |
| QP | Br | CH$_2$Cl$_2$ | 19.45 ± 0.01 | 34.6 ± 0.3 | 107.7 ± 0.2 | 95.2 ± 0.1 |
| ASTP | Br | CH$_2$Br$_2$ | 20.61 ± 0.01 | – | 102.7 ± 0.2 | 91.8 ± 0.2 |

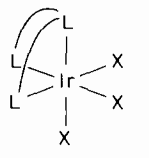
Coupling Constants (in Hz)

| L'L$_3$ | X | $J_{12}$ | $J_{13}$ | $J_{14}$ | $J_{23}$ | $J_{24}$[b] | $J_{24}$[c] | $J_{34}$ |
|---|---|---|---|---|---|---|---|---|
| QP | Cl | 3.6[d] | nr | 11.0[e] | 10.8[f] | 132.5[e] | 128.2[g] | 17.4[e] |
| QP | Br | nr | nr | 10.5[h] | 9.8[i] | 127.5[i] | 125.5[i] | 17.6[g] |
| ASTP | Br | – | – | – | 9.4[i] | 128.0[g] | 125.0[j] | 18.2[g] |

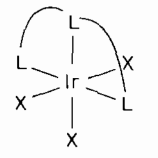
[a] Chemical shifts relative to external P$_4$O$_6$. [b] From pmr spectrum. [c] From phosphorus-31 spectrum.
[d] ± 0.3. [e] ± 0.2. [f] ± 0.4. [g] ± 0.5. [h] ± 0.8. [i] ± 1.0. [j] ±1.5. nr = not resolved.

that [IrHCl(QAS)][BPh$_4$] has structure IVd. The electronic spectra of these complexes are very similar and are related to those of complexes [RuX$_2$(L'L$_3$)],[21] which are known to have distorted octahedral structures.

Complexes [IrX$_3$(TL)] (TL = TP and TAS; X = Cl and Br) are also assigned octahedral structures. They were isolated in one isomeric form which could have either *vicinal* or *meridional* arrangement of the X donor atoms.



vic-[IrX$_3$(TL)]



mer-[IrX$_3$(TL)]

The assignment of isomeric structure to these complexes was attempted using their electronic spectra. The *vic*-isomers have a micro-symmetry which approaches $C_{3v}$ while the *mer*-isomers are closer to $C_{2v}$ symmetry. This latter micro-symmetry is also applicable to complexes [MX$_2$(QL)] and the resultant splitting of band due to $({}^1A_2 + {}^1B_1 + {}^1B_2) \leftarrow {}^1A_1$ has already been discussed in complexes of ruthenium(II).[22]

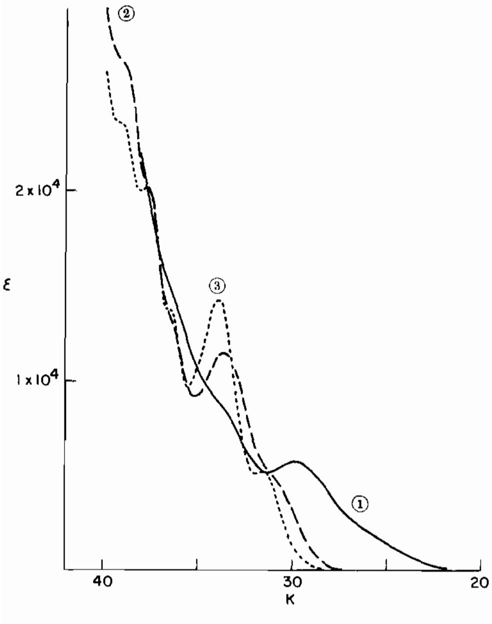


Figure 3. Electronic spectra of complex: ① [IrBr$_3$(TP)] (in dichloromethane solution at 295° K); ② [IrBr$_2$(QP)][BPh$_4$] (in 2-methyltetrahydrofuran solution at 295° K); ③ [IrBr$_2$(QP)][BPh$_4$] (in a 2-methyltetrahydrofuran glass at 100° K).

On the other hand, if the symmetry is close $C_{3v}$ one expects no significant splitting of the ${}^1T_{1g} \leftarrow {}^1A_{1g}$ and ${}^1T_{2g} \leftarrow {}^1A_g$ bands in $O_h$ symmetry, only their labels would change, i.e., they would become $({}^1A_2, {}^1E) \leftarrow {}^1A$ and $({}^1A_1, {}^1E) \leftarrow {}^1A$, respectively. The spectra of complexes [IrX$_3$(TL)] are very similar to those of species [IrX$_2$(QP)]$^+$ (see Part IV and Figure 3) showing the splitting already observed in complexes [RuX$_2$(QL)],[22] indicating that compounds [IrX$_3$(TL)] may be the *meridional* isomers.

## Acknowledgements

The authors are indebted to Dr. E. F. Trogu for the preparation of samples of [IrHX(QP)][BPh$_4$] (X = Cl and Br) used for nmr measurements and for a gift of [IrHCl(ASTP)][BPh$_4$] (ASTP = (*o*-Ph$_2$PC$_6$H$_4$)$_3$As) and to Drs. J.W. Dawson and R.J. Mynott for the nmr measurements. D.G.E.K. and R.J.M. carried out the work during the tenure of S.R.C. Fellowships and A.S. during the tenure of a N.A.T.O. Fellowship.

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