Mössbauer Spectroscopy of Iridium Compounds. Part I. Some Iridium(III) Complexes

By **Alan F. Williams, Geoffrey C. H. Jones,** and **Alfred G. Maddock,*** The Chemical Laboratories, Lensfield Road, Cambridge CB2 1EW

Mössbauer spectra of 15 complexes of Ir^{III} have been recorded. Using these data, in addition to those of published work, it has been found that partial isomer-shift and partial quadrupole-splitting treatments are not very satisfactory for these complexes. One of the reasons is because the localised bonding that is the basis of such a treatment is less true for Ir^{III} than for Fe^{II} complexes. The interaction of one ligand bond with the others is also supported by n.m.r. data on complexes of ligands with phosphorus-donor atoms.

THE transition-metal iridium forms a very large number of complexes, in which it is octahedrally co-ordinated and assigned a formal oxidation state of III, with the electron configuration low-spin $5d^6$. The 73-keV Mössbauer transition of ^{193}Ir is a $\frac{1}{2} \longleftrightarrow \frac{3}{2}$ nuclear transition which gives readily measurable quadrupole splittings and centre shifts,[1] and may thus be used to study the electronic environment of the iridium atom.† In this paper we report Mössbauer parameters for a number of octahedral iridium complexes and discuss their relation to the stereochemistry and bonding. For octahedral Fe^{II} $3d^6$ low-spin complexes, a successful additive model for quadrupole splittings and centre shifts has been developed. This model has been reviewed recently by Bancroft,[2] and (more theoretically) by Clark.[3] In this

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† 1 eV ≈ 1.60 × 10^{-19} J.

[1] P. Rother, F. Wagner, and U. Zahn, *Radiochim. Acta*, 1969, **11**, 203.

[2] G. M. Bancroft, *Co-ordination Chem. Rev.*, 1973, **11**, 247.

[3] M. G. Clark in 'Molecular Structure and Properties,' ed. A. D. Buckingham, *MTP Internat. Rev. Sci.*, Physical Chemistry series 2, Butterworths, London, in the press.

paper its application to similar t_{2g}^6 iridium(III) complexes is discussed. If such a model is valid the splittings and shifts of complexes containing ligands whose partial Mössbauer parameters have been determined may be predicted and conclusions drawn about the relative σ- and π-bonding capacities of the ligands.

EXPERIMENTAL

All Mössbauer spectra were recorded at liquid-helium temperature using a conventional constant-acceleration spectrometer. The source was an ^{193}Os–Nb alloy described before,[4] and the γ rays were detected using a Ge(Li) detector enabling partial resolution of the *X*-ray background. All samples were randomly oriented polycrystalline compounds, containing, typically, 150 mg cm^{-2} of natural Ir metal. The spectra were computer fitted using a program written by A. J. Stone,[5] the errors quoted allowing for those in the fitting and instrumental. Phosphorus n.m.r. spectra were recorded on a Varian XL-100 Fourier-transform spectrometer using dichloromethane solutions. The complexes *mer*-$[IrCl_3(SMe_2)_3]$,[6] $[PhMe_2HP]$[*trans*-$IrCl_4(PMe_2Ph)_2$],[7] *mer*-$[IrCl_3(PMe_2Ph)_3]$,[7] $[IrHCl_2(PMe_2Ph)_3]$,[8] and $[Ir(CN)Cl_2(PMe_2Ph)_3]$ [8] were prepared by published methods. The complex *fac*-$[IrCl_3(PMe_2Ph)_3]$ was prepared by photolysing a dichloromethane solution of the *mer* isomer for a few minutes in u.v. light and leaving the solution to stand for 24 h. Evaporation of the solution gave a white precipitate of *fac*-$[IrCl_3(PMe_2Ph)_3]$.

Dimethylphenylarsonium trans-*Tetrachlorobis(dimethylphenylarsine)iridate*(III).—The salt $IrCl_3{\cdot}4OH_2$ (1.4 g) was dissolved in 2-methoxyethanol (75 cm^3) and concentrated hydrochloric acid (10 cm^3). Dimethylphenylarsine (2.5 g) was added and the mixture heated under reflux under N_2 for 45 min. The mixture was filtered and the residue extracted with benzene to leave crystals of $[PhMe_2HAs]$[*trans*-$IrCl_4(AsPhMe_2)_2$]. The complex *mer*-$[IrCl_3(AsPhMe_2)_3]$ was obtained by refluxing the initial solution for a longer period, extracting the residue with benzene several times, and concentrating the extract.

Dichlorobis(dimethylphenylphosphine)(pyridine)iridium(III) *Hexafluorophosphate*.—The complex *mer*-$[IrCl_3(PMe_2Ph)_3]$ (1 g) was dissolved in the minimum of dichloromethane and an excess of pyridine added. An excess of $Ag[PF_6]$ in dichloromethane was added with stirring, and the AgCl which formed immediately was removed by centrifuging. The complex crystallised on concentration and was recrystallised from dichloromethane as light green crystals.

Adducts of Bis[1,2-*bis(diphenylphosphino)ethane*]*iridium*(I).—The complex $[Ir(dppe)_2]^+$ was prepared by reaction of dppe ($Ph_2PCH_2CH_2PPh_2$) with the cation $[Ir(CO)(PPh_3)_2(CNMe)]^+$ (ref. 9) in refluxing solution under a steady stream of nitrogen. The O_2 and H_2 adducts were prepared by blowing O_2 or H_2 through ethanolic solutions of $[Ir(dppe)_2]^+$, filtering off the crude product obtained on cooling, and recrystallising from dichloromethane–cyclohexane–benzene. Attempted addition of Cl_2 under such conditions (or in dichloromethane solution) gave the HCl adduct. The Cl_2 adduct was prepared by adding a benzene solution of Cl_2 dropwise to a benzene solution of a salt of $[Ir(dppe)_2]^+$ under a steady stream of nitrogen, and recrystallising the light yellow product from dichloromethane–benzene–cyclohexane. The HCl adduct was prepared by blowing HCl through an ethanol solution of $[Ir(dppe)_2]^+$ and the HI adduct by addition of an ethanol solution of iodine to a similar solution of $[Ir(dppe)_2]^+$; both complexes were recrystallised from dichloromethane–benzene–cyclohexane.

All complexes were characterised by C, H, and halogen analysis, i.r. spectroscopy and, where appropriate, ^{31}P n.m.r. spectroscopy.

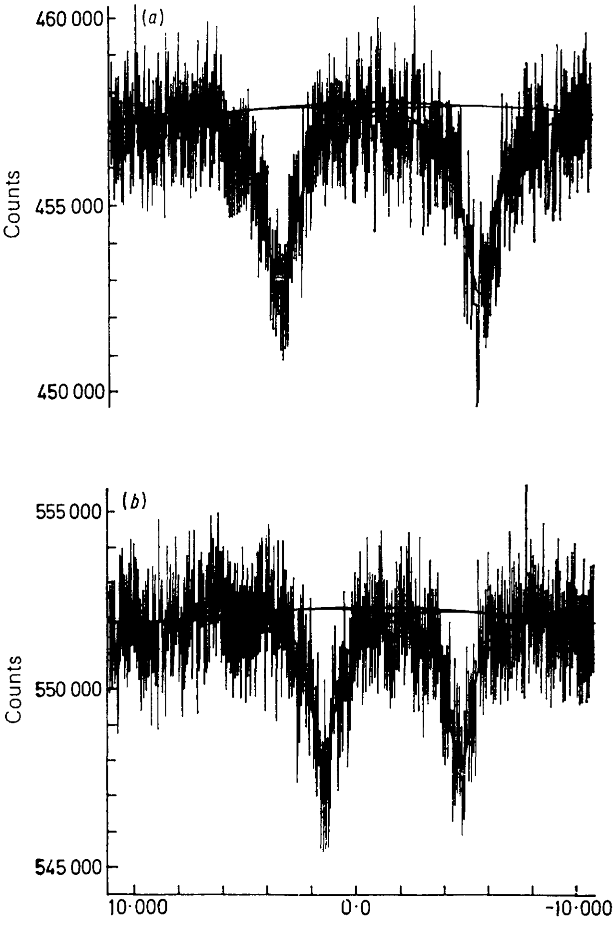

FIGURE 1 ^{193}Ir Mössbauer spectra of (*a*) *fac*-$[IrCl_3(PMe_2Ph)_3]$ and (*b*) $[IrHCl_2(PMe_2Ph)_3]$

RESULTS AND DISCUSSION

The Additive Model.—We have calculated a number of partial centre-shift (p.c.s.) and partial quadrupole-splitting (p.q.s.) values from our data and those of Wagner *et al.*[10,11] As pointed out by Clark,[3] the p.q.s. values may only be calculated as differences between values for two ligands rather than absolute values; we have thus taken the chloride ligand to have a p.q.s. of zero. The p.c.s. values were calculated relative to p.c.s. (Cl^-) = 0 since we regard $[IrCl_6]^{3-}$ as the complex

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[4] G. J. Davies, A. G. Maddock, and A. F. Williams, *J.C.S. Chem. Comm.*, 1975, 264.

[5] A. J. Stone, Appendix to *J. Chem. Soc.* (*A*), 1967, 1966.

[6] E. A. Allen and W. Wilkinson, *J.C.S. Dalton*, 1972, 613.

[7] J. Chatt, A. E. Field, and B. L. Shaw, *J. Chem. Soc.*, 1963, 3371.

[8] B. L. Shaw and J. M. Kenkins, *J. Chem. Soc.*, 1965, 6789.

[9] C. A. Reed and W. R. Roper, *J.C.S. Dalton*, 1973, 1365.

[10] F. E. Wagner, U. Wagner, W. Potzel, and H. H. Schmidtke, *Chem. Phys.*, 1974, **4**, 284.

[11] F. E. Wagner and U. Zahn, *Z. Physik.*, 1970, **233**, 1.

in which the iridium atom is closest to a pure t_{2g}^6 configuration. These two reference values have the additional advantage that almost all p.c.s. and p.q.s. values have the same sign. We calculated the p.c.s. value from data for the complex with the most negative centre shift (c.s.). Where the sign of the quadrupole splitting (q.s.) is in doubt {as in $[\mathrm{Ir(NH_3)_5(SCN)]Cl_2}$} we assumed that the p.c.s. and p.q.s. values follow a similar order to those of $\mathrm{Fe^{II}}$; thus as p.c.s. $(\mathrm{NH_3}) >$ p.c.s. (SCN), we assumed p.q.s. $(\mathrm{NH_3}) <$ p.q.s. (SCN). This problem arises only once or twice, and the assumption is justified by the general similarity of p.q.s. and p.c.s. values. Following Bancroft *et al.*[12] we assumed that the q.s. in *trans*-$[\mathrm{IrL_4X_2}]^-$ is positive. As the magnetic moment of the $I = \frac{3}{2}$ state is too low to allow determination of the sign of the quadrupole coupling by the magnetic-perturbation method, the sign of the q.s. is always unknown, that of the p.q.s. values is thus arbitrary.

TABLE 1

Mössbauer data at liquid-helium temperature for $\mathrm{Ir^{III}}$ complexes [a]

Complex	δ [b] (mm s^{-1})	Δ (mm s^{-1})	Γ (mm s^{-1})	χ^2 [c]
$\mathrm{IrCl_3 \cdot 4OH_2}$	-2.11	0	2.66	383 (391)
$[\mathrm{PhMe_2HP}]$-[*trans*-$\mathrm{IrCl_4(PMe_2Ph)_2}$]	-1.31	5.85	1.59	412 (390)
mer-$[\mathrm{IrCl_3(PMe_2Ph)_3}]$	-0.81	3.81	1.47	404 (390)
fac-$[\mathrm{IrCl_3(PMe_2Ph)_3}]$	-0.58	0	1.67	389 (391)
$[\mathrm{IrHCl_2(PMe_2Ph)_3}]$	-0.59	6.10	1.29	372 (392)
$[\mathrm{Ir(CN)Cl_2(PMe_2Ph)_3}]$	-0.30	4.83	1.77	383 (392)
mer-$[\mathrm{IrCl_3(SMe_2)_3}]$	-2.36	1.85	1.47	373 (390)
mer-$[\mathrm{IrCl_3(AsMe_2Ph)_3}]$	-1.46	1.06	1.64	443 (390)
$[\mathrm{PhMe_2HAs}]$-[*trans*-$\mathrm{IrCl_4(AsMe_2Ph)_2}$]	-1.60	2.70	1.63	385 (392)
$[\mathrm{IrCl_2(py)(PMe_2Ph)_3}][\mathrm{PF_6}]$	-0.80	4.01	1.26	385 (392)
[*trans*-$\mathrm{Ir(dppe)_2Cl_2}$]Cl	-0.82	3.48	1.61	427 (388)
[*trans*-$\mathrm{Ir(dppe)_2(H)Cl}$][$\mathrm{PF_6}$]	-0.12	1.01	1.18	312 (390)
[*cis*-$\mathrm{Ir(dppe)_2(H)_2}$][$\mathrm{ClO_4}$]	$+0.44$	1.92	1.52	384 (392)
[*trans*-$\mathrm{Ir(dppe)_2(H)I}$][$\mathrm{PF_6}$]	-0.09	0.98	1.32	393 (390)
[*cis*-$\mathrm{Ir(dppe)_2(O_2)}$][$\mathrm{PF_6}$]	-0.26	1.49	1.20	408 (390)

[a] Errors, ± 0.1 mm s^{-1}; quadrupole splittings of zero were constrained to be so during fitting. [b] With respect to iridium metal. [c] The number of degrees of freedom is given in parentheses.

TABLE 2

Mössbauer parameters at liquid-helium temperature from other work *

Complex	δ (mm s^{-1})	Δ (mm s^{-1})	Ref.
$[\mathrm{Ir(NH_3)_5I]Cl_2}$	-1.55	2.72	10
$[\mathrm{Ir(NH_3)_5Cl]Cl_2}$	-1.63	2.06	10
$[\mathrm{Ir(NH_3)_5(NO_2)]Cl_2}$	-1.25	0.70	10
$[\mathrm{Ir(NH_3)_5(NCS)][ClO_4]_2}$	-1.48	0.31	10
$[\mathrm{Ir(NH_3)_6]I_3}$	-1.51	0.14 ± 0.1	10
$[\mathrm{Bu^t{}_4N]_3[Ir(SCN)_6]}$	-1.65	1.67	10
[*cis*-$\mathrm{IrCl_2(py)_4}$]Cl	-1.30	1.50	10
[*trans*-$\mathrm{IrCl_2(py)_4}$]Cl	-1.30	2.60	10
[Hpy][*cis*-$\mathrm{IrCl_4(py)_2}$]	-1.67	1.44	10
[Hpy][*trans*-$\mathrm{IrCl_4(py)_2}$]	-1.73	3.16	10
$\mathrm{K_3[IrCl_6]}$	-2.26	0.52	11
$\mathrm{Na_3[Ir(NO_2)_4Cl_2]}$	-1.27	2.00	11
$\mathrm{K_3[Ir(CN)_6]}$	$+0.26$	0.30 ± 0.2	11

* Error, ± 0.05 mm s^{-1} unless otherwise stated.

The values so obtained are roughly in accord with those for $\mathrm{Fe^{II}}$ low-spin complexes,[13] with $\mathrm{H^-}$ and $\mathrm{Cl^-}$ at opposite ends of the two scales in both cases, but plots of the $\mathrm{Ir^{III}}$ values against those for $\mathrm{Fe^{II}}$ low spin were

TABLE 3

Partial Mössbauer parameters (mm s^{-1})

Ligand	Calculated from:	p.c.s.	p.c.s. ($\mathrm{Fe^{II}}$) [a]
$\mathrm{Cl^-}$	$\mathrm{K_3[IrCl_6]}$	0[b]	0.10
$[\mathrm{SCN}]^-$	$\mathrm{[Bu^t{}_4N]_3[Ir(SCN)_6]}$	$+0.10$	
$\mathrm{I^-}$	$\mathrm{[Ir(NH_3)_5I]Cl_2}$	$+0.12$	0.13
$\mathrm{NH_3}$	$\mathrm{[Ir(NH_3)_5Cl]Cl_2}$	$+0.13$	0.07
$[\mathrm{NO_2}]^-$	$\mathrm{Na_3[Ir(NO_2)_4Cl_2]}$	$+0.25$	0.05
py	$\mathrm{[Hpy][IrCl_4(py)_2]}$	$+0.28$	0.07
$\mathrm{Me_2S}$	$\mathrm{[IrCl_3(SMe_2)_3]}$	$+0.30$	
$\mathrm{AsMe_2Ph}$	$\mathrm{[PhMe_2HAs][IrCl_4(AsMe_2Ph)_2]}$	$+0.33$	
$\frac{1}{2}$dppe	$\mathrm{[Ir(dppe)_2Cl_2]Cl}$	$+0.36$	0.07
$\mathrm{PMe_2Ph}$	$\mathrm{[PhMe_2HP][IrCl_4(PMe_2Ph)_2]}$	$+0.48$	
$\mathrm{CN^-}$	$\mathrm{[Ir(CN)Cl_2(PMe_2Ph)_3]}$	$+0.52$	0.01
$\mathrm{H^-}$	$\mathrm{[Ir(dppe)_2(H)Cl][ClO_4]}$	$+0.70$	-0.08
		p.q.s.	p.q.s. ($\mathrm{Fe^{II}}$)
$\mathrm{I^-}$	$\mathrm{[Ir(NH_3)_5I]Cl_2}$	$+0.33$	-0.29
$\mathrm{Cl^-}$		0 [b]	-0.30
$\mathrm{Me_2S}$	*mer*-$\mathrm{[IrCl_3(SMe_2)_3]}$	-0.54	
$\mathrm{AsMe_2Ph}$	$[\mathrm{PhMe_2HAs}]$-[*trans*-$\mathrm{IrCl_4(AsMe_2Ph)_2}$]	-0.68	
py	[Hpy][*trans*-$\mathrm{IrCl_4(py)_2}$]	-0.79	-0.47
$\frac{1}{2}$dppe	$\mathrm{[Ir(dppe)_2Cl_2]Cl}$	-0.87	-0.68 [c]
$\mathrm{NH_3}$	$\mathrm{[Ir(NH_3)_5Cl]Cl_2}$	-1.03	-0.51
$[\mathrm{NO_2}]^-$	$\mathrm{[Ir(NH_3)_5NO_2]Cl_2}$	-1.38 [d]	-0.41
$\mathrm{PPhMe_2}$	$[\mathrm{PhMe_2PH}]$-[*trans*-$\mathrm{IrCl_4(PMe_2Ph)_2}$]	-1.46	-0.62 [e]
$\mathrm{H^-}$	[*cis*-$\mathrm{Ir(dppe)_2(H)_2}$][$\mathrm{ClO_4}$]	-1.83	-1.04

[a] From refs. 13 and 14. [b] By definition. [c] Bancroft and Libbey[13] suggested that a less negative value might be appropriate. However, Mays and Sears (P. L. Sears, Thesis, Cambridge, 1973) obtained splittings in four $[\mathrm{Fe^{II}(dppe)_2}]$ complexes which demand a value of at least -0.64 mm s^{-1}. [d] Assuming p.q.s. $(\mathrm{NO_2^-}) <$ p.q.s. $(\mathrm{NH_3})$ since p.c.s. $(\mathrm{NO_2^-}) >$ p.c.s. $(\mathrm{NH_3})$. When the opposite sign of Δ was chosen a p.q.s. of -0.68 mm s^{-1} was obtained. Neither value gave a calculated q.s. for $[\mathrm{Ir(NO_2)_4Cl_2}]$, supposing either *cis* or *trans* geometry, within 0.64 mm s^{-1} of the observed value. [e] Interpolated from data for $\mathrm{PPh_3}$, $\mathrm{PMePh_2}$, and $\mathrm{PMe_3}$ in refs. 13 and 14.

TABLE 4

Calculated and observed Mössbauer parameters in mm s^{-1}

Complex	δ calc.	δ obs.	δ calc. — obs.
mer-$[\mathrm{IrCl_3(PMe_2Ph)_3}]$	-0.83	-0.81	-0.02
fac-$[\mathrm{IrCl_3(PMe_2Ph)_3}]$	-0.83	-0.58	-0.25
$[\mathrm{IrCl_2(H)(PMe_2Ph)_3}]$	-0.13	-0.59	$+0.46$
$[\mathrm{Ir(H)_2(dppe)_2][ClO_4]}$	$+0.58$	$+0.44$	$+0.14$
mer-$[\mathrm{IrCl_3(AsMe_2Ph)_3}]$	-1.27	-1.46	$+0.19$
$[\mathrm{IrCl_2(py)(PMe_2Ph)_3][PF_6]}$	-0.55	-0.80	$+0.25$
$\mathrm{K_3[Ir(CN)_6]}$	$+0.86$	$+0.26$	$+0.60$
$[\mathrm{Ir(py)_4Cl_2]Cl}$	-1.14	-1.30	$+0.16$
$[\mathrm{Ir(NH_3)_6]Cl_3}$	-1.48	-1.48	0
$[\mathrm{IrH(I)(dppe)_2][PF_6]}$	0.00	-0.09	$+0.09$
$[\mathrm{Ir(NH_3)_5NO_2]Cl_2}$	-1.38	-1.25	$+0.13$

Complex	Δ calc.	Δ obs.	Δ calc. — obs.
mer-$[\mathrm{Ir(PMe_2Ph)_3Cl_3}]$	5.05	3.77	$+1.28$
mer-$[\mathrm{IrCl_3(AsMe_2Ph)_3}]$	2.33	1.46	$+0.87$
[Hpy][*cis*-$\mathrm{IrCl_4(py)_2}$]	1.58	1.44	$+0.14$
[*cis*-$\mathrm{IrCl_2(py)_4}$]Cl	1.58	1.50	$+0.08$
[*trans*-$\mathrm{IrCl_2(py)_4}$]Cl	3.16	2.60	$+0.56$
$[\mathrm{Ir(dppe)_2(H)I][PF_6]}$	0.48	0.96	-0.48
$[\mathrm{Ir(dppe)_2(H)Cl][ClO_4]}$	0.18	1.05	-0.87
$[\mathrm{IrHCl_2(PMe_2Ph)_3}]$	6.21	6.10	$+0.11$
$[\mathrm{IrCl_2(py)(PMe_2Ph)_3][PF_6]}$	5.32	4.01	$+1.31$

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[12] G. M. Bancroft, R. E. B. Garrod, A. G. Maddock, M. J. Mays, and B. E. Prater, *Chem. Comm.*, 1970, 200.

[13] G. M. Bancroft and E. T. Libbey, *J.C.S. Dalton*, 1973, 2103.

not linear[2] [Figure 2(*a*) and (*b*)]. There seems to be some justification for using the p.q.s. values for one element to predict the splittings in complexes of neighbouring elements in the Periodic Table (for example Mn, Fe, and Co, and Sn and Sb), but not for elements as different as iron and iridium. If the iridium values are considered by themselves, there are some unexpectedly large differences in p.c.s. and p.q.s. values: the difference between I^- and Cl^- is surprisingly large (especially in the p.q.s. values), as is the very large difference between ½dppe and PMe_2Ph, considering the Fe^{II} values.

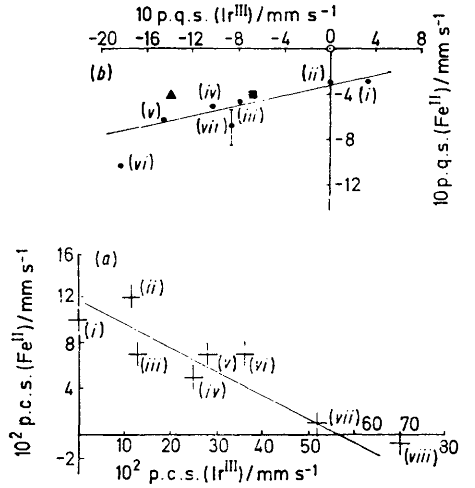

FIGURE 2 Plots of partial Mössbauer parameters for Ir^{III} against those for Fe^{II}: (*a*) partial centre shifts for Cl^- (*i*), I^- (*ii*), NH_3 (*iii*), $[NO_2]^-$ (*iv*), py (*v*) ½dppe, (*vi*), CN^- (*vii*), and H^- (*viii*); (*b*) partial quadrupole splittings for $[NO_2]^-$ (▲) and (■), I^- (*i*), Cl^- (*ii*), py (*iii*), NH_3 (*iv*), PMe_2Ph (*v*), H^- (*vi*), and extreme limits for ½dppe (*vii*)

TABLE 5

^{31}P N.m.r. data[a]

Compound	δ/p.p.m.	Relative intensity
PMe_2Ph	+46.9	
trans-$[IrCl_4(PMe_3Ph)_2]$	−36.7	
mer-$[IrCl_3(PMe_2Ph)_3]$	+41.2 (d)	2
	+50.3 (t)	1
	(*J* 17.1 Hz)	
dppe ($Ph_2PCH_2CH_2PPh_2$)	+13.5	
$[Ir(dppe)_2Cl_2]^+$	−1.8	
$[Ir(dppe)_2(H)Cl]^+$	−20.5	
$[Ir(dppe)_2(H)I]^+$	−15.6	
$[Ir(dppe)_2(H)_2]^+$	−31.0 (t)	1
	−19.5 (t)	1
	(*J* 7.8 Hz)	
$[Ir(dppe)_2(O_2)]^+$	−20.2[b]	1
	−12.9	1

[a] Recorded in CH_2Cl_2 at 40 °C. Both ^{191}Ir and ^{193}Ir have large nuclear quadrupole moments which will give quadrupole broadening. Proton resonances were decoupled with random noise. [b] No observable coupling, but broadened lines.

We calculated centre shifts and quadrupole splittings using our p.c.s. and p.q.s. values, and the results obtained are not very encouraging. To compare discrepancies between observed quadrupole splittings and those calculated from p.q.s. values for Fe^{II} and Ir^{III} complexes one must take in account that the same amount of electron transfer from ligand to metal, or *vice versa*, should produce a splitting in the iridium complex that is

$$\{Q(\mathrm{Ir}^{193})\langle r^{-3}\rangle_{5d}(\mathrm{Ir^{III}})[I - R(^{193}\mathrm{Ir})]E\gamma(^{57m}\mathrm{Fe})/ \\ Q(^{57}\mathrm{Fe})\langle r^{-3}\rangle_{3d}(\mathrm{Fe^{II}})[I - R(^{57}\mathrm{Fe})]E\gamma(^{193m}\mathrm{Ir})\}$$

times that in the Fe^{II} complex. This factor is not very accurately known, but is *ca.* 3. For a group of Fe^{II} complexes, analogous to those of iridium in Table 4, $(\Delta_{obs.}{}^2 - \Delta_{calc.}{}^2)^{\frac{1}{2}}$ is 0.10 mm s^{-1} (compounds nos. 30—40 in table 44 of ref. 14): the nine Ir^{III} complexes in Table 4 give a value of 0.92 mm s^{-1}. It will be noted that larger average discrepancies are found with Fe^{II} complexes that depart substantially from octahedral symmetry or contain ligands such as CO.[13]

The discrepancies between observed and calculated isomer shifts are rather larger for the Ir^{III} complexes than the Fe^{II} data would suggest. Particularly disturbing are the differences between the observed and calculated values for the $[IrCl_3(PPhMe_2)_3]$ complexes and for $[Ir(py)_4Cl_2]Cl$ studies by Wagner *et al.*[10] For the phosphine complex we would expect the calculated c.s. and q.s. values to be accurate to within 0.3 mm s^{-1} and for the py complex to be still more accurate; yet the c.s. of the *fac*-phosphine complex differs by 0.25 mm s^{-1} from that of the *mer* isomer, and the q.s. of the latter deviates by 1.28 mm s^{-1} from the predicted value. The q.s. of *trans*-$[Ir(py)_4Cl_2]^+$ is 0.56 mm s^{-1} smaller than the predicted 3.16 mm s^{-1}. We regard the quantitative failure of the model in the prediction of the effect of changing one ligand as a serious deficiency, especially as it is this sort of change that is predicted so satisfactorily for Fe^{II} in similar complexes.

Two reasons for the failure of the model are proposed: (*i*) the breakdown of the localisation condition suggested by Clark *et al.*[15] as a result of extensive π bonding with the ligands; and (*ii*) the breakdown of the assumption that a given metal–ligand bond is independent of the other ligands surrounding the metal. Such interligand effects are commonly acknowledged in the *cis* and *trans* effects. The first possibility might appear more attractive, as the iridium 5*d* orbitals are known to be more diffuse than the iron 3*d*, but it might equally be argued that the higher formal charge of the iridium atom decreases the π donation to the ligands even giving rise to some π acceptance. We do not discount this explanation but feel that the second factor is of great importance. In a series of Ir^{I} complexes $[Ir(CO)(PPh_3)_2X]$[16] it has been found that the iridium Mössbauer parameters remained essentially constant for a wide variety of X ligands, the other ligands adjusting to maintain the shift of the iridium close to that of Ir metal; this is confirmed by the variation in carbonyl-stretching frequency and ^{31}P n.m.r. chemical shifts.

We recorded the phosphorus n.m.r. spectra of several of our samples and the variation in shifts was quite

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[14] G. M. Bancroft and R. H. Platt, *Adv. Inorg. Chem. Radiochem.*, 1972, **15**, 59.

[15] M. G. Clark, A. G. Maddock, and R. H. Platt, *J.C.S. Dalton*, 1972, 281.

[16] A. F. Williams, S. Bhaduri, and A. G. Maddock, following paper.

considerable, suggesting that the metal–phosphine bond is by no means constant. Thus the rather surprising result for the relative p.c.s. and p.q.s. values of $\frac{1}{2}$dppe and PMe_2Ph may be explained by the fact that the dppe results were obtained from a complex with a large number of phosphine donors around the iridium atom, so that the individual contribution from each phosphine is less, while the PMe_2Ph values were obtained from the more ionic situation with only one other phosphine bonded to the iridium.

There is evidence for this alteration of bonding properties (which we shall refer to as compensation) from deviations between the predicted and observed c.s. and q.s. values. Most of the q.s. values are overestimated by the additive model, suggesting that the ligands adjust slightly to reduce the asymmetry about the iridium nucleus. Similarly, the c.s. values are (with two exceptions) overestimated; as the p.c.s. value was derived from the complex with the lowest isomer shift, this positive deviation in the predicted values implies that as the c.s. of the complex rises the p.c.s. values of the ligands decrease slightly. The negative deviations shown by the phosphines may be explained by the fact that p.c.s. (PMe_2Ph) was derived from a complex where the phosphine is *trans* to another phosphine, while in *fac*-$[IrCl_3(PMe_2Ph)_3]$ the phosphines are all *trans* to chlorides, and if the *trans* effect is assumed to be greater than the *cis* they might be expected to have a greater p.c.s. value.

The failure of the assumption of constant metal–ligand character need not imply that these iridium complexes are more covalent than Fe^{II} complexes, but that the bonding is delocalised over several formal bonds. This need not be the result of π bonding, although the strongest effects were seen with π-accepting ligands (phosphines in this paper, CO in another) since these generally give the largest variations from the chloride complex we have taken as our reference and thus discrepancies are more readily observed. These interligand effects are noticeably more important in the iridium results and may even be the reason for the very large number of iridium complexes that may be prepared.

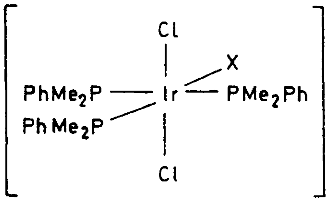
As the additive model gives only a rough estimate of the c.s. and q.s. values in iridium complexes, we shall devote the remainder of the discussion to comparisons of similar complexes.

trans-$[IrCl_4(PMe_2Ph)_2]^-$ *and* mer-$[IrCl_3(PMe_2Ph)_3]$, trans-$[IrCl_4(AsMe_2Ph)_2]^-$ *and* mer-$[IrCl_3(AsMe_2Ph)_3]$.—For these pairs the differences in bonding properties of the neutral and chloride ligands are sufficiently great for large changes in c.s. and q.s. to be observed on exchanging ligands; the additive model is poor for these systems. The q.s. of *mer*-$[IrCl_3(PMe_2Ph)_3]$ is smaller than expected, presumably due to the decrease in p.q.s. of the *trans* phosphines as a result of the greater charge donated to the metal by the third phosphine replacing a chloride ligand. The ^{31}P n.m.r. shifts also suggest that the phosphine ligands are not equivalent, and are both different from that in $[IrCl_4(PMe_2Ph)_2]^-$.

This difference in bonding power is also suggested by the more positive c.s. of *fac*-$[IrCl_3(PMe_2Ph)_3]$ where the phosphines are now all *cis* to each other. Unfortunately this complex was too insoluble to give an n.m.r. spectrum. The greater c.s. implies a stronger phosphorus–metal interaction when the phosphines are not mutually *trans*; a similar effect has been observed in *J*(Pt–P) in *cis*- and *trans*-$[PtCl_2(PR_3)_2]$ complexes.[17] It should be noted that the zero (or unresolved) q.s. of this *fac* complex is a consequence of the symmetry and not of the additivity of ligand quadrupole contributions; if the chlorine or phosphine ligands are distorted out of pure *fac*-octahedral geometry, then a q.s. will be seen. The broad linewidth of this spectrum may be due to distortion resulting from mutual repulsion by the bulky phosphine ligands.

Similar effects to the phosphine complexes are seen with the arsines, but now the c.s. change on moving from the bis to the tris arsine is much less, implying considerable compensation, in agreement with the low q.s. of the tris complex.

$[IrCl_3X_3]$ *Complexes*.—All the complexes with a *mer* configuration have a resolvable q.s., and this offers a convenient method of identifying their configuration. Dimethyl sulphide has similar partial Mössbauer parameters to $AsMe_2Ph$, but gives a slightly larger q.s. and c.s. which implies that it is a better σ donor. The larger q.s. may be a result of either more compensation by $AsMe_2Ph$, or less π acceptance by Me_2S since the c.s. is a measure of $(\sigma + \pi)$ interactions while the q.s. is a measure of $(\sigma - \pi)$ interactions. If compensation is a result of π delocalisation these causes are equivalent. Dimethylphenylarsine might be expected to be a stronger π acceptor as a result of the attached Ph group.



(A)

$[IrCl_2X(PMe_2Ph)_3]$ *Complexes*.—These have the configuration shown in (A) with the X ligand *trans* to a phosphine. In accord with predictions, the q.s. is greater than for *mer*-$[IrCl_3(PMe_2Ph)_3]$, although less than would be expected; the c.s. values also indicate that the ligands are compensating.

Exchanging py for chloride has almost no effect on the c.s., and the hydride ligand which, in these systems and for Fe^{II} complexes, has a large p.c.s. value, gives little change in the chemical shift. The effect of the CN ligand is more pronounced, possibly as a result of π acceptance which is possible for this ligand.

Adducts of $[Ir(dppe)_2]^+$.—The remaining complexes were all prepared by addition of small molecules to

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[17] J. F. Nixon and A. Pidcock, *Ann. Rev. N.M.R. Spectroscopy*, **1969**, **2**, 345.

$[Ir(dppe)_2]^+$, a square-planar complex of Ir^I with c.s. -0.4 mm s^{-1} and q.s. 8.8 mm s^{-1}.[16] Hydrogen chloride, HI, and Cl_2 all give *trans* adducts (the IrP_4 plane remaining unchanged) while O_2 and H_2 give *cis* adducts.

The process of oxidative addition might be expected to involve removal of electrons from the $5d_{z^2}$ orbital with some σ donation into the 6*s*; this should raise the c.s., and reduce the quadrupole splitting, since the large splitting in $[Ir(dppe)_2]^+$ arises from the imbalance in population between the $5d_{z^2}$ and $5d_{x^2-y^2}$ orbitals. All the adducts studied do in fact have higher c.s. and lower q.s. values than $[Ir(dppe)_2]^+$. In $[Ir(dppe)_2Cl_2]^+$ the q.s. is presumably positive, with a greater charge density in the *XY* plane arising from the strong σ-donor power of the four phosphine groups. For the two monohydrides the p.q.s. values suggest that the q.s. changes sign, with greater charge density on the *Z* axis as a result of the strong σ-donor power of the H^- ligand; this explains the magnitude of the difference in q.s. of the Cl_2 and HCl adducts. The trends roughly parallel those reported for $[Ir(CO)Cl(PPh_3)_2]$ adducts,[18] the discrepancies probably arising from the very strong compensating powers of the carbonyl ligand and the asymmetry in the $[IrCl(CO)(PPh_3)_2]$ plane.

The ^{31}P n.m.r. shifts for those complexes are interesting: apart from distinguishing between *cis* and *trans* adducts (showing two and one phosphine resonances, respectively), they also show that there is considerable compensation by the phosphines. The interpretation of these n.m.r. shifts is not straightforward, but there is evidence that a shift downfield arises from the sum of functions of σ donation from, and π acceptance on to, the phosphorus. It is surprising that the difference in n.m.r. shift between the Cl_2 and HCl adduct is so great, and we suspect that there must be appreciable interaction with the hydride ligand; this is confirmed by the still more negative shift of the dihydride. We cannot conclude much from the n.m.r. results, but clearly the varying n.m.r. shifts show that the Ir–P bond itself is far from constant. The shift of 5 p.p.m. between the HCl and HI adducts is also interesting since the chloride and iodide ligands have virtually identical p.c.s. and p.q.s. values with Fe^{II} and Sn^{II} complexes.

The structure of $[Ir(dppe)_2(O_2)][PF_6]$ has been determined by *X*-ray diffraction to be a flat square pyramid with the phosphorus atoms as the base and the iridium atom at the apex, the oxygen molecule being co-ordinated above the iridium atom.[19] The O–O distance is the longest known for this type of adduct, close to that in O_2^- ions. The ^{31}P n.m.r. spectrum showed two triplets with very different shifts, presumably corresponding to phosphorus atoms *cis* and *trans* to the O_2 group. The similarity of this n.m.r. spectrum to that of $[Ir(dppe)_2(H)_2]^+$ shows the *cis* structure of the hydrogen adduct. The high c.s. of the H_2 adduct shows the strong σ-donor power of the hydride ion, but rather more surprising is the relatively high c.s. of the adduct with the electronegative O_2 molecule; it has been suggested that this complex is a five-co-ordinate derivative of Ir^{III}, but in fact the c.s. increases rather than decreases on addition of O_2. This would be compatible with loss of 5*d* electrons increasing δ, but the low n.m.r. shifts of the phosphines and the splitting of the resonance into two lines suggests that the phosphines interact fairly strongly with the oxygen atom.

In the light of these observations we feel inclined to regard oxidative addition less as a reaction involving loss of electrons than one in which a molecule with a vacant co-ordination site and a large electronic asymmetry (and, consequently, a large q.s.) attacks a small molecule to give a product with a small q.s. and more symmetrical electron distribution. The large asymmetric charge distribution of the initial complex might be expected to make the species a good nucleophile; any actual charge transfer to the small molecule is at least partially compensated by the other ligands around the metal. Using this hypothesis, one may suggest that the species $[AuX_4]^-$ (X = halogen), which have almost zero quadrupole splittings[20] and do not undergo oxidative-addition reactions, may be inhibited by the absence of a nucleophilic asymmetric distribution of electrons.

Conclusions.—The Ir^{III} complexes studied show a very wide range of centre shifts and quadrupole splittings, with centre shifts overlapping those of Ir^I and Ir^{-I} complexes.[16] Rother *et al.*[1] have shown that the c.s. changes by *ca.* 1 mm s^{-1} on moving from d^n to $d^{n\pm1}$ complexes of halogen or oxygen ligands. Since the Ir^{III} complexes span a range of c.s. of over 2.6 mm s^{-1}, we must assume that there is another factor in the bonding besides partial removal of 5*d* electrons. Our data indicate that this is the varying bonding participation of the 6*s* orbital, which would be expected to have a greater direct effect on the c.s. Even so, it is doubtful whether the formal oxidation state of iridium has much relevance to the electronic environment in its complexes.

Oxidation states are indeed normally chosen by an arbitrary assignment of charge to the ligands, and, in cases where this is not clear (such as nitrosyl complexes), by the stereochemistry of the complex; we question the use of this assignment in interpreting the chemistry of the resulting complex. Further doubt arises from the range of quadrupole splittings of Ir^{III}, from zero to a value not far below those of formally d^8 square-planar complexes, and also from the change in Mössbauer parameters on additively oxidising Ir^I to Ir^{III}.

In conclusion, despite the inadequacies of a simple quantitative treatment, Mössbauer spectroscopy still offers a useful method of exploring the bonding and structure in iridium complexes.

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