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

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Mössbauer spectra of 13 four-co-ordinate, formally Ir^{I}, species are reported. The comparatively small differences in the electronic environments of the iridium nuclei in these complexes are attributed to the interaction between the metal–ligand bonds in these molecules leading to compensation effects. This interpretation of the data is confirmed by changes in the ^{31}P n.m.r. parameters of the phosphine ligands and of ν(CO) in the carbonyl ligand.

SQUARE-PLANAR complexes of iridium(I) have been studied extensively since the discovery by Vaska of $[Ir(CO)Cl(PPh_3)_2]$.[1] There has been particular interest in the ability of these complexes to react with simple molecules such as Cl_2, H_2, O_2, and MeI to give adducts, of varying stability, in which a chemical bond in the adduct molecule is either broken (as in the Cl_2 adducts) or appreciably weakened (as in the O_2 adducts). Although much kinetic and structural data have accumulated, the electronic structures of these complexes are not well understood. The complexes are diamagnetic and the optical spectra are obscured by charge-transfer bands; spectroscopic studies have concentrated on the ligands, in particular carbonyl-stretching frequencies, but such information is only indirectly relevant to the electronic state of the metal atom. ^{193}Ir Mössbauer spectroscopy yields direct information about the atom, but only two papers on Ir^{I} complexes have appeared.[2,3] Here we report Mössbauer data for a number of complexes, and endeavour to relate our observations to other spectroscopic data and the reactivity of these molecules. The complexes studied are square planar, generally described as Ir^{I} d^8, and tetrahedral, described as Ir^{II} d^{10}, although these electronic configurations are idealised rather than actual.

The 73 keV Mössbauer transition of ^{193}Ir is between the excited, $I = \frac{1}{2}$, and ground, $I = \frac{3}{2}$, states.‡ Isomer shifts between -2 and $+4$ mm s^{-1} (with respect to iridium metal) have been measured,[4] and quadrupole splittings of the ground state of up to 8.8 mm s^{-1} reported; the spectra are thus sufficiently sensitive to chemical environment to be of use to the chemist. Unfortunately, however, the low magnetic moment of the ground state [5] and the relatively large linewidth (*ca.* 0.6 mm s^{-1}) prevent measurement of the sign of the quadrupole splitting (q.s.) by the magnetic-perturbation method [6] without use of very high magnetic fields (greater than 60 T) which are not at the moment readily available.

EXPERIMENTAL

The Mössbauer spectra were recorded at liquid-helium temperature using a standard constant-acceleration spectrometer and a ^{193}Os–Nb alloy source as described earlier.[7,8] The absorber contained typically 150 mg cm^{-2} of natural iridium metal. All the spectra were well resolved doublets, and thickness effects were ignored. The spectra were computer fitted using the procedure of Stone.[9] The quoted errors in the measurements allow for errors in the fitting and in the instrument. ^{31}P N.m.r. spectra were recorded using a Varian XL-100 Fourier-transform spectrometer.

The complexes were prepared by standard methods shown in Table 1, with the exception of the following.

Dinitrosylbis(triphenylphosphine)iridium Hexafluorophosphate.—Pure nitrogen oxide (NO) was bubbled through a refluxing solution of $[Ir(CO)_3(PPh_3)_2][PF_6]$ (1 g) in acetone (70 cm^3). The colourless solution rapidly became orange and then deep reddish black. After 6 h the flow of NO was stopped and nitrogen was passed through the solution for 10 min. The solution was taken to dryness and the crude $[Ir(NO)_2(PPh_3)_2][PF_6]$ thus obtained was recrystallised from dichloromethane–ethanol to give shiny black microcrystals, yield 0.85 g.

Bis[1,2-bis(diphenylphosphino)ethane]iridium Hexafluorophosphate.—Dppe (0.8 g) was added to a degassed frozen (−196 °C) solution of $[Ir(NO)_2(PPh_3)_2][PF_6]$ (0.8 g) in acetone (40 cm^3). After stirring the solution for 5 min (N_2O was evolved), $[Ir(dppe)_2][PF_6]$ (0.7 g) was precipitated on addition of diethyl ether.

Hydroxonitrosylbis(triphenylphosphine)iridium Hexafluorophosphate.—The complex $[Ir(NO)_2(PPh_3)_2][PF_6]$ (1 g) was dissolved in acetone (150 cm^3) and irradiated with Pyrex-filtered sunlight, in the presence of air, for several hours until the solution changed colour to deep orange, and $[Ir(NO)(OH)(PPh_3)_2][PF_6]$ (0.7 g) was precipitated as orange crystals on addition of diethyl ether.

Interpretation of Centre Shifts and Quadrupole Splittings.—In the interpretation of isomer shifts of iridium complexes one cannot readily distinguish the effects of changes in occupation of the 6*s* orbital from those due to changes in the 5*d* and perhaps also 6*p*. A pure d^8 ion is expected to have a very negative isomer shift with respect to Ir by analogy with $[IrCl_6]^{3-}$, but all the complexes examined here have shifts close to zero. This must indicate a substantial

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† Part I is ref. 8.

‡ 1 eV ≈ 1.60 × 10^{-19} J, 1 Bohr ≈ 5.3 × 10^{-11} m.

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[2] H. H. Wickman and W. E. Silverthorn, *Inorg. Chem.*, 1971, **10**, 2333.

[3] F. Holsboer, W. Beck, and H. D. Bartunik, *J.C.S. Dalton*, 1973, 1828.

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

[5] A. Narath and D. C. Barham, *Bull. Amer. Phys. Soc.*, 1967, **12**, 314.

[6] R. L. Collins and J. C. Travis, 'Mössbauer Effect Methodology,' ed. I. J. Gruverman, Plenum Press, New York, 1967, vol. 3, p. 134.

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

[8] A. F. Williams, G. C. H. Jones, and A. G. Maddock, preceding paper.

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

departure from d^8 character, as might be expected for these highly covalent complexes, presumably as a result of σ donation into the 6*s* orbital and π acceptance from the 5*d* orbitals. Both these factors must be important since, if the 6*s* were unoccupied, the iridium atom would need to π donate a massive amount of electron density until its state was close to that in IrF_5, a compound with comparable isomer shift (δ +0.06 mm s^{-1}).[10] Conversely, if only 6*s* occupation were important, since our quadrupole-splitting data indicate a considerable occupation of the $5d_{x^2-y^2}$ orbital, the effect of 6*s* occupation would be to give the iridium atom an appreciable negative charge.

We assume that a positive increase in isomer shift is a result of both these effects. As the chemistry of Ir^I is concerned with soft π-accepting ligands, a mixture of these two effects is quite plausible. The quadrupole splitting (q.s.) arises from the asymmetries of both the valence shell of the iridium atom and of the charges on surrounding ligands.

This is a rather arbitrary distinction in covalent systems such as these, but Clark *et al.*[11] have shown for tin(IV) complexes that imbalance in the valence shell is the dominant term (unless it is close to zero), and for these iridium complexes we assume this to be true. This assumption is further justified by the fact that the ligands around the iridium are generally neutral or carry only a low charge. Since approximate calculations show that $\langle r^{-3}\rangle_{6p}$ is appreciably less than $\langle r^{-3}\rangle_{5d}$, the electric field gradient (e.f.g.) will be dominated by the 5*d* contribution. In tetrahedral symmetry the 6*p* orbitals will be approximately equally occupied and in the square-planar case the contribution will arise mainly from σ donation into $6p_x$ and $6p_y$ orbitals; this contribution will be identical in sign to that due to σ donation into the $5d_{x^2-y^2}$, and neglect of 6*p* orbitals will only result in assignment of a slightly larger occupation to $5d_{x^2-y^2}$.

For pure D_{4d} symmetry, $\eta = 0$, and even when η is as high as 1 the q.s. is only increased by 15%. We thus take the q.s. as a measure of *q*. If *q* arises only from the 5*d* orbital asymmetry, we may use expression (1),[12]

$$q = \frac{-4}{7}(1 - R_{5d})\langle r^{-3}\rangle_{5d}[(N_{z^2} - N_{x^2-y^2}) + \tfrac{1}{2}(N_{xz} + N_{yz} - 2N_{xy})] \quad (1)$$

where N_i is the occupation of the *i* 5*d* orbital, and $(1 - R_{5d})$ is a Sternheimer shielding parameter which may be assumed to be constant.

For tetrahedral geometry and identical ligands *q* will be zero. In other complexes, where the geometry is not pure tetrahedral {such as $[Ir(PPh_3)_3(NO)]$ [13]}, an e.f.g. will arise from the relatively small variations in the occupation of the σ-bonding T_2 or π-bonding *E* orbitals. For a square-planar complex the d_{z^2} orbital will be effectively non-bonding while the $d_{x^2-y^2}$ will be σ bonding, and there will be an appreciable difference in their occupation.

For d^8 Ir^I, if we assume that the π-bonding *xy*, *xy*, and *yz* orbitals are approximately equally filled, then $q = \frac{-4}{7}(1 - R_{5d})\langle r^{-3}\rangle_{5d}(2 - N_{x^2-y^2})$. It is expected that, for Ir^I, $N_{x^2-y^2}$ is less than 2, and so square-planar complexes will have fairly large splittings; this affords a ready means of distinguishing the two geometries, and is confirmed by our data the square-planar complexes having, in general, a much higher q.s.

We may obtain a value for $(1 - R_{5d})\langle r^{-3}\rangle_{5d}$ either by calculation or by using the value obtained from tungsten

TABLE 1

Mössbauer [a] and i.r. data [b]

Complex	Preparation ref.	δ (mm s^{-1})	Δ (mm s^{-1})	Γ (mm s^{-1})	χ [c]	Ref.	$\bar{\nu}$(CO) (cm^{-1})	$\bar{\nu}$(NO) (cm^{-1})	I.r. ref.
$[Ir(CO)(PPh_3)_2Cl]$		−0.06	6.66	1.50	423 (392)		1 950		*d*
		−0.03	6.54			3			
		+0.04	7.74			2			
$[Ir(CO)(PPh_3)_2Br]$		+0.01	6.92			2	1 956		*d*
$[Ir(CO)(PPh_3)_2I]$	17	−0.02	6.65	1.31	428 (391)		1 955		*d*
$[Ir(CO)(PPh_3)_2F]$	17	+0.28	7.22	1.55	408 (391)		1 945, 1 960		17
$[Ir(CO)(PPh_3)_2(OH)]$	17	+0.28	7.17	1.87	410 (390)		1 930, 1 950		17
$[Ir(CO)(PPh_3)_2(SH)]$	17	+0.15	7.31	1.71	363 (390)		1 945		17
$[Ir(CO)(PPh_3)_2(O_2CCF_3)]$	17	+0.06	7.26	1.22	434 (390)		1 944, 1 970		17
$[Ir(CO)(PPh_3)_2(N_3)]$		+0.10	7.51			3	1 951		17
$[Ir(CO)(PPh_3)_2(SCN)]$		+0.08	7.42			3	1 970		17
$[Ir(CO)(PPh_3)_2(NCMe)][PF_6]$	17	+0.22	7.90	1.77	426 (390)		1 975		17
$[Ir(CO)(PPh_3)_3][PF_6]$	17	0.00	8.31	1.70	406 (389)		1 995		17
$[Ir(dppe)_2][PF_6]$		+0.4 ± 0.2	8.8 ± 0.2	1.6	452 (392)				
$[Ir(PMePh_2)_4][PF_6]$	17	+0.25	7.80	1.43	409 (390)				
$[Ir(CO)(PMe_2Ph)_2][PF_6]$		+0.32	7.49	1.59	424 (392)	*e*	1 959		*d*
$[Ir(NO)(PPh_3)_2(OH)][PF_6]$		+0.73	7.12	1.77	434 (387)			1 860	
$[Ir(NO)_2(PPh_3)_2][PF_6]$		−0.12	3.56	1.22	386 (388)			1 700, 1 765	
$[Ir(NO)(CO)(PPh_3)_2]$		−0.03	2.11			3		1 654, 1 660	*f*
$[Ir(PPh_3)_3(NO)]$		−0.30	1.27			3		1 600	*f*

[a] At liquid-helium temperature, with the exception of those from ref. 2 which were at 20 K. Centre shifts are quoted with respect to iridium metal. Errors, ±0.1 mm s^{-1} unless otherwise stated. [b] For Nujol mulls. [c] The number of degrees of freedom is given in parentheses. [d] J. Chatt, D. P. Melville, and R. L. Richards, *J. Chem. Soc.* (*A*), 1969, 2841. [e] J. Chatt, B. L. Shaw, and N. P. Johnson, *J. Chem. Soc.* (*A*), 1967, 604. [f] C. A. Reed and W. R. Roper, *J. Chem. Soc.* (*A*), 1970, 3054.

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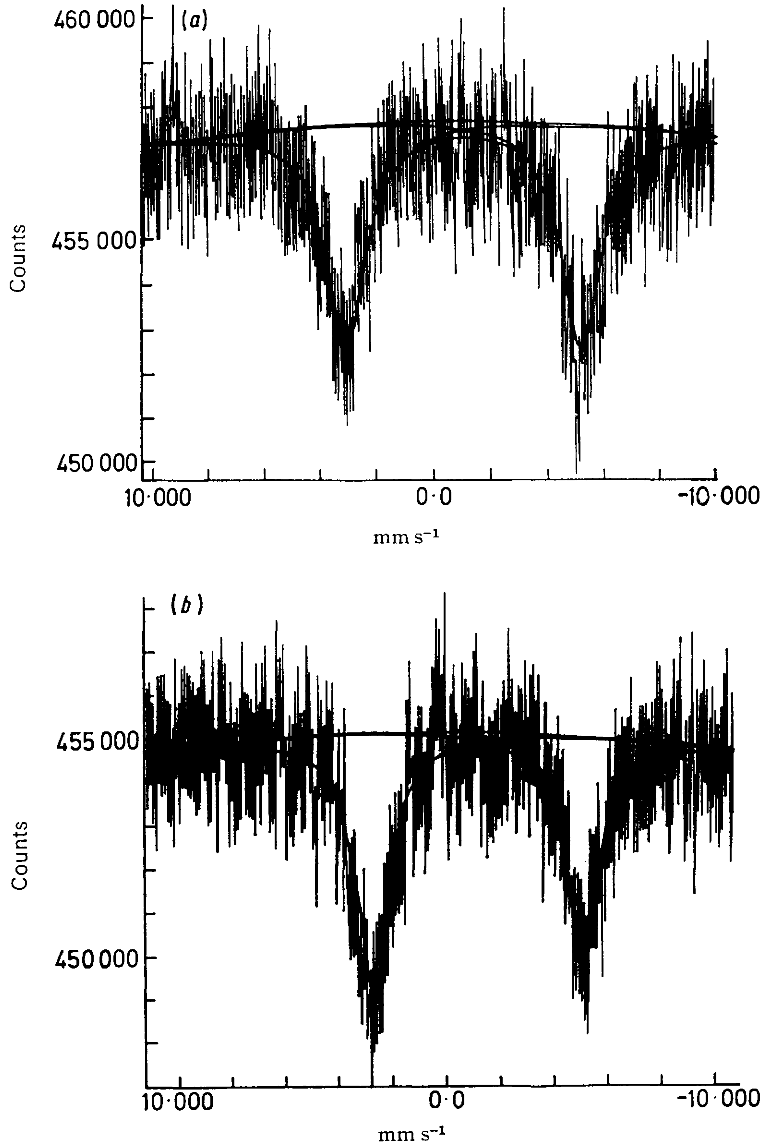
[10] F. E. Wagner and U. Zahn, *Z. Physik*, 1970, **233**, 1.

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

[12] M. G. Clark, ' Hyperfine Interactions and Molecular Structure ' in ' Molecular Structure and Properties,' ed. A. D. Buckingham, *MTP Internat. Rev. Sci.*, Physical Chemistry Series 2, in the press.

[13] C. P. Brock and J. A. Ibers, *Inorg. Chem.*, 1972, **11**, 2812.

Mössbauer spectroscopy of 5.3 Bohr.[14] This agrees fairly well with the value calculated by Froese for ^{193}Ir,[15] and gives $\Delta = 8.5\ (2 - N_{x^2-y^2})(1 + \frac{\eta^2}{3})^{\frac{1}{2}}$ mm s^{-1}. For [Ir(dppe)$_2$]-[PF$_6$], $\Delta = 8.8$ mm s^{-1} implying $N_{x^2-y^2} \approx 1$ ($\eta = 0$ for pure D_{4d} symmetry), and that each phosphorus atom donates *ca.* 0.25 electron into the $5d_{x^2-y^2}$ orbital. We do not wish to deduce too much from this approximate value, but it is reasonable to suggest that our interpretation of the q.s. is correct. The actual charge on each phosphorus (which centre-shift values suggest is also donating into the 6*s* orbital) will of course be reduced by π acceptance from the iridium atom.



^{193}Ir Mössbauer spectra of [Ir(PMePh$_2$)$_4$][PF$_6$] (a) and [Ir(CO)(PPh$_3$)$_3$][PF$_6$] (b)

RESULTS AND DISCUSSION

Mössbauer and other relevant spectroscopic data are given in Table 1. The most remarkable feature is the constancy of the Mössbauer parameters; the centre shifts only cover a range of 1.2 mm s^{-1}, while for Ir^{III} octahedral complexes a range of over 2.5 mm s^{-1} is spanned. If the carbonyl complexes alone are considered, the shifts are all within 0.6 mm s^{-1}, and for the square-planar complexes the quadrupole splittings vary by just over 2 mm s^{-1} compared with 6 mm s^{-1} for Ir^{III} complexes.[8] These facts indicate that the iridium is in an essentially constant electronic environment in the square-planar complexes. The extremes of the c.s. and q.s. ranges are occupied by non-carbonyl complexes; as the carbonyl complexes all give similar results we shall discuss them separately.

[Ir(CO)(PPh$_3$)$_2$X]$^+$ *Complexes*.—These complexes,

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[14] M. G. Clark, R. Gancedo, A. G. Maddock, and A. F. Williams, *J.C.S. Dalton*, 1975, 120.

[15] C. Froese and G. Malli, *Abs. Internat. J. Quantum Chem. Symp.*, 1967, 103.

which are all assumed to be square planar, are yellow crystalline solids [except where X = PPh_3 (light orange)], and show similar addition reactions, although the rates and equilibrium positions vary. The Mössbauer parameters are remarkably constant, and the small variations in c.s. observed are often in the opposite sense to that suggested by the donor power of the ligand. Thus on changing X from F^- to PPh_3 the shift falls and the q.s. rises, implying that F^- is a better σ donor and π acceptor than PPh_3; since this seems improbable, we must assume there is another effect present and the most obvious is the varying of the carbonyl ligand. The carbonyl-stretching frequencies in these two complexes are 1 945 and 1 995 cm^{-1} respectively, indicating a considerable change in the iridium–carbonyl bonding. Changes in the metal–carbonyl bond are expected and the effects on the Mössbauer spectra of Fe^{II} complexes have already been noted.[16] We were, however, surprised to find the change to be sufficiently great to maintain the iridium atom in an effectively constant electronic environment. The slight variations in the Mössbauer parameters are thus the result of the difference between the effect due to a change in X and that of the carbonyl-group adjustment.

Wherever the X ligand is capable of π acceptance the q.s. is slightly above the average value and the carbonyl-stretching frequency rises. These two observations may be related by assuming that the CO group now π accepts less charge [raising ν(CO)], and consequently σ donates less charge to the $5d_{x^2-y^2}$ orbital. The high c.s. of the fluoride and hydroxide complexes may be explained by strong π donation from the fluoride or hydroxide through the iridium to the carbonyl, lowering ν(CO),[17] with a consequent increase in σ donation. If we accept Bent's rule [18] that the bond to the most electropositive element will have the greatest *s* character, when the carbonyl is *trans* it will bond strongly with the 6*s* orbital, affecting the c.s.; when it is *trans* to a phosphine it will bond strongly with the $5d_{x^2-y^2}$ orbital affecting the q.s. Thus the high q.s. of $[Ir(PPh_3)_3(CO)][PF_6]$ is due to weak σ donation (into $5d_{x^2-y^2}$) of a carbonyl *trans* to a phosphine. If the *cis*-phosphine ligands are altered, as in going from $[Ir(CO)Cl(PPh_3)_2]$ to $[Ir(CO)(PMe_2Ph)_2Cl]$, the Mössbauer parameters change in the expected fashion, the softer, more basic alkylphosphine bonding strongly with the 6*s* orbital giving a higher c.s. and q.s.

We have concentrated our discussion on the relation between carbonyl-stretching frequency, c.s., and q.s., principally because of the ease of measurement of ν(CO) and its ready interpretation, but the *cis*-phosphine ligands also adjust significantly as may be seen from the ^{31}P n.m.r. shifts of the four complexes examined. The shifts generally follow the carbonyl-stretching frequency and the expected effects due to the electronegativity of the *cis*-X ligand. While the interpretation of the n.m.r. shifts is not straightforward,[19] they do serve to emphasise a change in the iridium–phosphine bond. We have observed similar effects with Ir^{III} complexes.[8] The differing methods of measurement used do not enable us to distinguish the relative strengths of *cis* and *trans* effects.

The multiplicity of effects influencing δ and Δ allows some ambiguity of detailed interpretation, but the results certainly confirm other evidence that: (*a*) the carbonyl and phosphine ligands are able to adjust their bonding character to compensate almost completely for any change in the electronic environment of the iridium atom due to change in the X ligand (The carbonyl group appears to be particularly effective.); (*b*) the carbonyl-stretching frequency will provide little information on the electronic state of the iridium atom, rather it reflects the nature of the other ligands around the metal atom; and (*c*) the compensation, which has been observed to a lesser extent with Ir^{III} complexes, is a reflection of the delocalised nature of the bonding in iridium chemistry. (The low symmetry results in almost all the Ir orbitals being allowed to mix, giving a varied hybridisation of metal–ligand bonds.)

TABLE 2

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

Compound	δ [b]/p.p.m.	
$[Ir(CO)(PPh_3)_2F]$	−24.4	*J*(PF) 19.7 Hz
$[Ir(CO)(PPh_3)_2Cl]$	−22.5	
$[Ir(CO)(PPh_3)_2I]$	−19.5	
$[Ir(CO)(PPh_3)_2(NCMe)][PF_6]$	−23.2	
$[Ir(CO)(PPh_3)_3][PF_6]$	−14.5(d) −17.0(t)	*J*(PP) 27 Hz
PPh_3	+6.0	
$[Ir(PMePh_2)_4][PF_6]$	+11.5	
$PMePh_2$	+28.0	
$[Ir(CO)(PMe_2Ph)_2Cl]$	+7.1	
PMe_2Ph	+46.9	

[a] In benzene solution at 40 °C; $[PF_6]^-$ absorptions have been omitted. Proton resonances were decoupled. [b] Relative to 85% H_3PO_4.

Nitrosyl and Phosphine Complexes.—If carbonyl is exchanged for a nitrosyl $\{[Ir(NO)(OH)(PPh_3)_2][PF_6]\}$ or phosphine group $\{[Ir(dppe)_2]^+\}$ there is a considerable change in c.s. and q.s., showing the dominating effect of the CO group. The positive shift of the NO complex is accounted for by the very strong π-acceptor properties of the nitrosyl group. Similarly, the negative shift and large q.s. of the phosphine complex may be explained by weaker σ-donor and π-acceptor properties. These trends are similar to those found for low-spin Fe^{II} complexes.

It is interesting to note the difference in c.s. and q.s. between $[Ir(dppe)_2]^+$ and $[Ir(PMe_2Ph)_4]^+$ which is tetrahedrally distorted.[20] When a correlation diagram between D_{4d} (square-planar) and T_d (tetrahedral)

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

[17] C. A. Reed and W. R. Roper, *J.C.S. Dalton*, 1973, 1365, 1370.

[18] H. A. Bent, *Chem. Rev.*, 1961, **61**, 275.

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

[20] G. R. Clark, C. A. Reed, W. R. Roper, B. W. Skelton, and T. N. Waters, *Chem. Comm.*, 1971, 758.

symmetry is drawn it is found that the $5d$ orbitals mix with the $6p$ and there should be a reduction in c.s. and q.s. as a result of the lower shielding and $\langle r^{-3} \rangle$ values of the $6p$; this is indeed observed.

The tetrahedral nitrosyl complexes show similar shifts to the square-planar carbonyls and lower shifts than the square-planar nitrosyl; this is possibly due to the slightly greater occupation of the Ir $5d$ orbitals in a system with two more valence electrons. The changes are, however, small and suggest that the two extra electrons are localised on to the ligands, as is suggested by the noticeably lower ν(NO) stretching frequency. It is possible that tetrahedral geometry is assumed as a result of greater ligand–ligand repulsion.

Many reactions of these complexes involve attack on the NO group rather than the iridium atom, emphasising that it is the former and not the latter that is activated.[21] The greater q.s. of the dinitrosyl complex is presumably a result of its distortion towards square-planar geometry.[22]

Reactivity.—It had been hoped that the Mössbauer data on the Vaska-complex analogues would correlate with their oxidative-addition reactivity, and throw light on the mechanism of this reaction. This hope has hardly been realised as most of the carbonyls studied have very similar Mössbauer parameters. In the absence of CO the Mössbauer parameters change, and there is a corresponding change in reactivity; $[Ir(dppe)_2]^+$ is very reactive towards oxygen, while $[Ir(NO)(OH)(PPh_3)_2]$ does not undergo the addition reaction.[23] The square-planar dicarbonyl and tricarbonyl complexes have centre shifts close to zero and small quadrupole splittings {5 mm s^{-1} for the dicarbonyls,[24] 2 mm s^{-1} for $[Ir(CO)_3Cl]$ [25]}. They do not undergo addition of oxygen, but show metal–metal interaction in the solid state.

The data suggest some correlation between reactivity and q.s. This might be expected on a simple electrostatic model: if the reaction is initiated by nucleophilic attack by the iridium atom,[26] the reactivity might be expected to be greatest when the electron density is concentrated above the plane of the complex and this will correspond to a large q.s.

Extensive kinetic studies have been made of the addition reactions of *trans*-$[Ir(CO)L_2X]$ complexes, and show that the entropies of activation remain roughly constant for a given reaction, while the activation energies vary considerably.[26,27] The activation energies have been correlated with the electron-donor abilities of the ligands, and also with the Hammett σ_p constant for complexes *trans*-$[Ir(CO)Cl\{P(C_6H_4X\text{-}p)_3\}_2]$.[27,28] Previous Mössbauer studies have shown that the c.s. of the products is close to that of the initial complex.[2,8]

We suspect that the iridium atom provides only a suitable co-ordination site, and that the variation in reactivity arises from the varying capacity of the ligands to stabilise (by electron donation) the product or any intermediate. There may be a relation between the entropy of activation and the q.s. {both roughly constant for $[Ir(CO)XL_2]$}, the possibility of nucleophilic attack being greater for the more asymmetric species, while the activation energy is a function of the ligands. The iridium atom does not appear to be any more or less ' basic ' in any of these complexes.

The tetrahedral nitrosyls have a very low q.s. which suggests that the oxidative addition shown by square-planar complexes will not occur. This is generally found, and there is some evidence that the addition reactions that occur do so after dissociation,[21,29] presumably to a planar intermediate with a large q.s.

Conclusions.—As with Ir^{III} complexes, the formal oxidation state of iridium has little relevance to the population of the atomic orbitals as measured by the c.s. The phenomenon of compensation found for Ir^{III} is even more pronounced for the Ir^{I} carbonyl species, leading to an almost constant environment for the iridium atom and changes in the C–O bonding. Mössbauer spectroscopy appears to be an extremely powerful means of studying electron distribution in these otherwise rather intractable complexes.

We thank Dr. T. W. Matheson for the ^{31}P n.m.r. spectra, G. C. H. Jones for preparing a sample of $[Ir(CO)(PMePh_2)_2Cl]$, Johnson, Matthey Ltd. for a loan of iridium, and the Cambridge Philosophical Society for support (to A. F. W.).

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