iron(II) with cyanide and aromatic diimines shows no temperature dependence.[13]   A study of numerous ferrous low-spin complexes exhibiting large quadrupole splittings showed a small temperature dependence to the quadrupole splitting.[14] These results indicate that a significant temperature dependence to the "lattice" contributions is a rare occurrence. Since changes in the "lattice" contributions would be expected to accompany changes in the distortion parameters, these results imply that the distortion parameters are not normally significantly temperature dependent.

In the analysis described above, it was assumed that the radii of the three t_{2g} orbitals were identical.   The quadrupole splitting was also fitted allowing for as much as a 100% difference in the factor $\langle r^{-3}\rangle_{t_{2g}}$.   This large anisotropy has no significant effect on the overall analysis.   Inclusion of this anisotropy allows the parameter ΔE_i to be reduced and causes a small reduction in the average value of N^2.   Allowance for an anisotropy in k also has an insignificant effect on the analysis.

In this analysis of the epr and quadrupole splitting data, deviations from the crystal field model were treated in the simplest possible manner.   For this reason the parameters, k and N^2, should be treated as semiempirical parameters which reflect the ligand character of the molecular orbital and the extent of orbital delocalization, respectively.

In view of these difficulties it is probably not meaningful to discuss the results in Table II in terms of small differences among the four compounds studied.   However, it does appear clear fom the results in Table II that $\langle r^{-3}\rangle_{t_{2g}}$ for all these compounds is substantially reduced from the free ion value.   The spin–orbit coupling constant ζ falls in the range of 175–250 cm^{-1}.   This represents a reduction to 40–55% of the free ion value, 460 cm^{-1}.[15]   The "orbital reduction factor," as defined here, is 0.25–0.60, a reduction to 25–60% of the free ion value.

Ballhausen[16] derives a formula $k = 1 - \frac{1}{2}N^2 A_{\pi}{}^2$, where $\psi = N(\psi_{Fe} + A_{\pi}\psi_{lig})$.   With $k = 0.85$, neglecting overlap, this leads to $N^2 = 0.70$.   This value is not in good agreement with that found from the Mossbauer spectroscopy data.   No particular agreement is expected here, however, since π bonding is not the only mechanism for orbital delocalization.

The magnitude of the spin–orbit coupling constant provides the best measure of orbital delocalization.   The magnitude of N^2 depends on assumptions concerning the magnitudes of the quadrupole moment Q, the shielding factor, $(1 - R)$, and the free ion value of $\langle r^{-3}\rangle$.[17]   The magnitude of k is very sensitive to the manner in which configuration interactions are treated.

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Photoaquation of Some Complexes of Iridium(III)[1]

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Qualitative observations of the photochemistry of complexes of Ir(III) indicate that there is a close resemblance to the photochemistry of Rh(III).[3-8]   Complexes which, like their Rh(III) analogs, undergo photoaquation of halide include *trans*-Ir(en)$_2$X$_2{}^+$,[3-5] *cis*-Ir(phen)$_2$X$_2{}^+$,[6] and *cis*-Ir-(bipy)$_2$X$_2{}^+$,[6] where en is ethylenediamine, phen is 1,10-phenanthroline, bipy is 2,2'-bipyridyl, and X is Cl, Br, or I. Photoaquation of pyridine (py) has been observed both for the Rh(III) and Ir(III) complexes of the type *trans*-Ir(py)$_4$-X$_2{}^+$.[7,8]   It seemed of interest to obtain quantum yields for some of these Ir(III) systems for comparison with the analogous Rh(III) systems.[9]

Experimental Section

Physical Measurements. A Perkin-Elmer 202 spectrophotometer was used to obtain visible-uv absorption spectra and a Hitachi Perkin-Elmer 139 spectrophotometer was used to determine concentration from the absorbance values at selected wavelengths.   The molar conductance was determined with a Beckman RC16 B2 bridge and a dip-type cell with a cell constant of 1.022 cm^{-1}.   X-Ray powder diffraction photographs were obtained from a Philips Debye-Scherrer 5.73-cm camera with nickel-filtered Cu radiation (λ 1.5418 Å).

Materials. Solvents were glacial acetic acid, reagent grade thiophene-free benzene, and water distilled from an all-glass still.   Chemicals used in the preparation of complexes were reagent grade 2,2'-bipyridyl, reagent grade 1,10-phenanthroline, and ethylenediamine from Aldrich Chemical Co., K$_3$IrCl$_6$ from K & K Laboratories, IrCl$_3$ and IrBr$_3$ from Pfaltz and Bauer Co., and pyridine, which was refluxed 2 hr over BaO and distilled (bp 113–114°).

The complexes were prepared and purified by known methods and characterized by their X-ray powder patterns, molar conductance, and visible-uv spectra, as summarized below.

trans-[Ir(py)$_4$Cl$_2$]Cl·5H$_2$O.[10] d spacings (all in angstroms): 12.63 s, 7.49 s, 6.91 w, 6.43 s, 6.08 w, 5.27 m, 4.45 w, 4.13 w, 3.95 w, 3.67 s, 3.22 m, 2.99 w; Λ_M (0.001 *M*, H$_2$O): 89 ohm^{-1} cm^2 mol^{-1}.   Vis-uv (H$_2$O) (nm): 410 (ϵ 24), 285 (7.3 × 10^3), 272 (1.2 × 10^4), 265 (1.5 × 10^4), 258 (1.6 × 10^4), 252 (1.8 × 10^4), 246 (1.9 × 10^4).   [Lit.[11] vis-uv (H$_2$O) (nm): 410 (ϵ 24), 285 (7.3 × 10^3), 272 (1.18 × 10^4), 264 (1.49 × 10^4), 258 (1.63 × 10^4), 250 (1.79 × 10^4), 246 (1.8 × 10^4).]

cis-[Ir(bipy)$_2$Cl$_2$]Cl·2H$_2$O.[11] d spacings: 12.90 vs, 8.93 vs, 6.88 m, 6.53 w, 5.92 s, 5.78 s, 5.58 m, 5.25 m, 4.68 w, 4.22 m, 4.07 w, 3.93 s, 3.78 s. Λ_M (0.001 *M*, H$_2$O):   85.5 ohm^{-1} cm^2 mol^{-1}. Vis-uv (H$_2$O) (nm).   448 (ϵ 130), 420 (420), 350 (2.4 × 10^3), 316 (2.2 × 10^4), 306 (2.0 × 10^4), 280 (1.8 × 10^4), 254 (2.4 × 10^4). [Lit.[11] d spacings: 12.9 vs, 9.02 vs, 6.96 m, 6.55 w, 5.90 s, 5.78 s, 5.32 m, 4.98 m, 4.50 w, 4.23 m, 4.11 w, 3.93 w, 3.78 s. Λ_M (0.001 *M*, H$_2$O):   83 ohm^{-1} cm^2 mol^{-1}. Vis-uv (H$_2$O) (nm):   448 (ϵ 130),

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420 (420), 350 (2.4 × 10³), 316 (2.2 × 10⁴), 306 (2.0 × 10⁴), 280 (1.8 × 10⁴), 254 (2.4 × 10⁴).]

cis-[Ir(bipy)₂Br₂]Br·3H₂O.[11] *d* spacings: 12.90 vs, 8.98 vs, 7.13 m, 6.72 w, 6.23 s, 5.77 s, 5.37 m, 4.99 m, 4.79 m, 4.26 m, 4.12 w, 4.00 s, 3.85s. Λ_M (0.001 *M*, H₂O): 99.5 ohm⁻¹ cm² mol⁻¹. Vis-uv (H₂O) (nm): 450 (ε 160), 420 (5.5 × 10²), 350 (2.6 × 10³), 317 (2.2 × 10⁴), 308 (1.9 × 10⁴), 285 (1.8 × 10⁴), 257 (2.2 × 10⁴). [Lit.[11] *d* spacings: 12.9 vs, 9.02 vs, 7.07, m, 6.80 w, 6.51 w, 6.23 s, 6.02 w, 5.78 m, 4.98 m, 4.79 m, 4.27 m, 4.11 w, 4.00 s, 3.86 s. Λ_M: 95.5 ohm⁻¹ cm² mol⁻¹. Vis-uv (H₂O) (nm): 450 (ε 160), 420 (550), 350 (2.6 × 10³), 317 (2.2 × 10⁴), 308 (1.9 × 10⁴), 285 (1.8 × 10⁴), 257 (2.2 × 10⁴).]

cis-[Ir(phen)₂Cl₂]Cl·3H₂O.[12] *d* spacings: 14.59 s, 11.18 vs, 9.45 s, 8.55 vs, 7.40 w, 6.68 vs, 6.28 w, 5.90 s, 5.46 m, 5.12 w, 4.74 w, 4.44 s, 4.24 m, 3.88 w, 3.70 w, 3.54 s, 3.14 m, 2.94 w. Λ_M (0.001 *M*, H₂O): 90.5 ohm⁻¹ cm² mol⁻¹. Vis-uv (H₂O) (nm): 452 (ε 60), 432 (220), 370 (3.5 × 10³), 300 (1.8 × 10⁴), 276 (5.0 × 10⁴). [Lit. *d* spacings:[13] 14.74 s, 11.27 vs, 9.51 s, 8.58 vs, 7.50 m, 6.69 vs, 6.32 w, 5.93 s, 5.44 m, 5.14 w, 4.74 m, 4.45 s, 4.27 m, 3.88 w, 3.73 w, 3.57 s, 3.14 m, 2.96 w. Vis-uv (H₂O) (nm):[11] 452 (ε 60), 432 (220), 370 (3.5 × 10³), 300 (1.75 × 10⁴), 276 (4.93 × 10⁴).]

trans-[Ir(en)₂Cl₂]ClO₄.[5] *d* spacings: 8.15 vs, 6.28 m, 5.94 m, 5.64 s, 5.06 m, 4.62 m, 4.48 s, 3.35 w, 3.14 s, 2.89 s, 2.83 m. Λ_M (0.001 *M*, H₂O) (nm); 96 ohm⁻¹ cm² mol⁻¹. Vis-uv (H₂O) (nm): 425 (ε 10.4), 345 (54.0), 273 (72.4). [Lit.[5] vis-uv (H₂O) (nm): 425 (ε 12.7), 345 (51.5), 273 (58.4).]

Photolyses. A detailed description of the experimental procedures appears elsewhere.[9] Photolyses were carried out in the Rayonet RPR-100 reactor equipped with the Rayonet lamps for 254 and 350 nm and with the MGM-100 merry-go-round accessory. The intensity of the incident light was determined by standard actinometric methods[14,15] and was checked by simultaneous photolysis of a previously studied complex of Rh(III) with the same halide ligand present. Halide salts of the complexes were converted to the nitrate form before photolysis on a Dowex 1-X8 column in the nitrate form. The concentration of the eluate was adjusted to 1.00 × 10⁻³ *M* and several 5-ml samples were placed in Pyrex or quartz test tubes which were then stoppered and treated with nitrogen. The duration of photolysis was adjusted to give no more than 20% reaction. The concentrations of halide and amine released were determined after photolysis and the spectrum of the reaction mixture was taken. Halide was measured with an Orion chloride or bromide electrode and a double-junction reference electrode and an Orion Model 404 meter. Pyridine, phen, and bipy were measured by extraction into benzene and titration with perchloric acid in glacial acetic acid.[16] Ethylenediamine was titrated potentiometrically in aqueous solution.

Results and Discussion

Photoaquation of chloride or bromide was observed for all the complexes in both wavelength regions. The quantum yields are listed in Table I. Only *trans*-Ir(py)₄Cl₂⁺ released a significant amount of amine during photolysis; none of the complexes with bidentate ligands gave any detectable free amine. (The limits of detection of free amine were 5 × 10⁻⁶ *M* or less for the amines.) The quantum yield for photoaquation of pyridine is also included in Table I. The determination of the fraction of the incident light absorbed was only approximate in the 350-nm region because the bandwidth of the incident light is large. Thus, while the relative values of the quantum yields in this region should be correct, the absolute values may be in error, and therefore relative values are reported here.[9] This uncertainty does not affect the comparisons to be made in this discussion.

The more difficult problem is the inability to determine the quantum yield for photoaquation of amine for the complexes with bidentate ligands.[9] This results from the fact

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Table I. Relative Quantum Yields for Photoaquation of Halide and of Amine

Complex	Φ_i	
	350 nm	254 nm
i = X⁻		
cis-Ir(bipy)₂Cl₂⁺	2.7ᵃ	3.2ᵃ
cis-Ir(bipy)₂Br₂⁺	7.0	5.1
cis-Ir(phen)₂Cl₂⁺	2.0	2.25
trans-Ir(en)₂Cl₂⁺	8.9	5.9
trans-Ir(py)₄Cl₂⁺	3.7	2.9
i = py		
trans-Ir(py)₄Cl₂⁺	1.0ᵇ	1.0ᶜ

ᵃ The values reported are averages of two or more determinations with deviations of 10% or less. They are relative to the value of Φ_py for *trans*-Ir(py)₄Cl₂⁺ at the same wavelength. ᵇ The absolute quantum yield is in the range of 0.01–0.018. ᶜ The absolute quantum yield is 0.0062.

that the primary products shown below can undergo subsequent reactions, the most important of which may be return to the initial complex. Thus, the fact that no significant amount of free amine was found for such complexes does not mean there was no photoaquation of amine. All that can be said on the basis of these results and the reports in the literature for these complexes[3-6] is that if there is photoaquation of amine, it results neither in displacement of the amine molecule nor in any rearrangement to a significant extent.
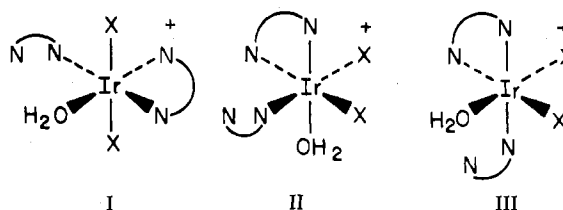
In spite of this problem, several interesting conclusions result from the data in Table I. The quantum yields for photoaquation of chloride varied as the amine changed in the same order observed for the Rh(III) complexes:[9] bipy > phen for the cis complexes and en > py for the trans complexes. The same relative order was observed for both wavelength regions, although the magnitudes of the quantum yields were smaller at 254 nm. This same behavior was observed for the Rh(III) complexes.[9,17] The yield for photoaquation of Br⁻ was greater than that for Cl⁻ as was observed for Rh(III). No photoisomerization reactions could be detected from the spectral data and no photoredox products were found, although the possibility that photoredox processes occur cannot be eliminated.[17]

For most of the complexes in both wavelength regions the quantum yields for photoaquation of halide of the Ir(III) complexes were slightly larger than for the corresponding Rh(III) complexes. The main difference observed between Ir and Rh was in the ratio of Φ_py to Φ_Cl, which was 1.6 for *trans*-Rh(py)₄Cl₂⁺ and 0.27 for *trans*-Ir(py)₄Cl₂⁺ at 350 nm. At 254 nm the ratios were 0.97 for *trans*-Rh(py)₄Cl₂⁺ and 0.34 for *trans*-Ir(py)₄Cl₂⁺.[9] Both complexes have internal ligand transitions in the 254-nm region but in the 350-nm region the transitions differ with d-d for the Rh complex and CT for the Ir complex.[18,19]

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As with Rh(III)[9] the relative order of quantum yields as halide and amine were varied remained unchanged as the wavelength was varied, which is interesting since the assignments of the transitions for *trans*-Ir(py)$_4$Cl$_2$$^+$ [18] and for *cis*-Ir(bipy)$_2$X$_2$$^+$ and *cis*-Ir(phen)$_2$Cl$_2$$^+$ [20,21] indicate that the wavelength regions used correspond to different types of transitions, including internal ligand,[18] charge transfer,[18,20,21] and d–d[18] transitions. Thus the qualitative behavior, at least, is apparently independent of the type of transition.

Registry No. *trans*-[Ir(py)$_4$Cl$_2$]Cl, 14077-29-3; *cis*-[Ir(bipy)$_2$Cl$_2$]Cl, 22710-60-7; *cis*-[Ir(bipy)$_2$Br$_2$]Br, 23329-12-6; *cis*-[Ir(phen)$_2$Cl$_2$]Cl, 15609-62-8; *trans*-[Ir(en)$_2$Cl$_2$]ClO$_4$, 20037-59-6.

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## Electron Spin Resonance Study of Free Radicals Produced in an Iron(0)–Diene System

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It is almost invariably found that organometallic complexes of transition metals are diamagnetic. One effective method for preparing paramagnetic derivatives is exposure to high-energy radiation, but this does not appear to have been exploited. In our studies of the radicals which may be produced from organometallic compounds, direct irradiation of pure material with ^{60}Co γ radiation has been the simplest and most productive means of generating paramagnetic species for esr study. In an attempt to expand the types of radical species obtainable in these systems, it was thought to be of interest to explore the area of radical attack on undamaged organometallic compounds.

The method employed in these studies is a pseudo-matrix-isolation technique. The organometallic substrate is dissolved in a suitable solvent, which is chosen for its ability to (i) dissolve the compound, (ii) form a glass when frozen, and (iii) generate clean, large quantities of known, reactive, organic radicals on short exposure to ^{60}Co γ radiation. The solution is frozen in the form of small beads to liquid nitrogen temperature and γ-irradiated. At this temperature the radicals produced are trapped in the glassy matrix, but as the temperature is raised in a controlled fashion, reactive radicals are able to seek out the nearest available site for radical attack.

The organometallic compound chosen for our initial study was dicarbonylcyclohexadienetriphenylphosphineiron(0), (C$_6$H$_8$)Fe(CO)$_2$PPh$_3$. This compound was irradiated in the pure solid state, as well as in glassy *n*-butyl chloride and 2-methyltetrahydrofuran. The first of these solvents generates the *n*-butyl radical (*n*-Bu) on irradiation at 77 K

$$n\text{-BuCl} + \text{e}^- \rightarrow n\text{-Bu} + \text{Cl}^-$$
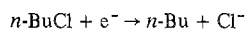
and the esr spectrum is dominated by features from the *n*-Bu radical.[1] The latter produces large numbers of physically trapped electrons (e$_t^-$) which normally give rise to an intense blue color and esr singlet, but which are readily added to any substrate present.

Experimental Section

The organometallic compound used in this study, dicarbonyl-1,3-cyclohexadienetriphenylphosphineiron(0), was donated in a state of high purity by Dr. L. A. P. Kane-Maguire, of the University of Cardiff, Cardiff, Wales. The organic solvents employed were of reagent grade and were used without special purification.

The γ-ray source was a Vickrad cobalt-60 radiation bomb, generating approximately 4 Mrads hr^{-1}. The material to be irradiated was typically exposed for approximately 1 hr, while suspended in a dewar vessel filled with liquid nitrogen.

Electron spin resonance spectra of the irradiated materials were recorded on a Varian E.3 spectrometer, fitted with the standard variable-temperature accessory. With this unit, the temperature could be varied smoothly from near liquid nitrogen temperature upward.

Results and Discussion

The esr spectrum obtained after irradiation of the pure organometallic compound is shown in Figure 1. This spectrum is assigned to a single species, with three g values ($g_1 = 2.075$, $g_2 = 2.062$, $g_3 = 2.006$). Each of these lines exhibits a clear doublet splitting from ^{31}P, the measured values of the hyperfine splittings being $A_1 = 56$ G, $A_2 = 54$ G, and $A_3 = 68$ G. The relatively large g-value variation clearly indicates that the unpaired electron has appreciable metal character, as it is the orbital angular momentum the electron gains while on the metal that causes this g-value shift from free spin. The ^{31}P hyperfine coupling parameters indicate that the coupling is nearly axial ($A_1 \cong A_2 < A_3$), and in this approximation it is possible to calculate values for A_{iso} and $2B$. With $A_\perp(A_1, A_2)$ and $A_\parallel(A_3)$ given the same sign, $A_{\text{iso}} = \pm 59$ G and $2B = \pm 9$ G. When combined with the theoretical values of the hyperfine couplings from ^{31}P of $A^\circ_{\text{iso}} = +3636$ G and $2B^\circ = +204$ G,[2] one finds 1.6% s character and 4.2% p character for the electron when on the phosphorus atom. This gives a p:s ratio of 2.6 which is acceptably close to the near sp^3 hybridization expected for phosphorus in triphenylphosphine and a total spin density on phosphorus of ~6%. The other sign possibility for $A_\parallel$ and $A_\perp$ gives chemically unacceptable results.

One further feature of this spectrum merits comment. Careful examination of the g_2 features reveals poorly resolved structure on each of the lines of the doublet. Because it is difficult for noise to seize control of rapidly falling features such as these, it is suggested that this structure is hyperfine splitting arising from hydrogen nuclei on the cyclohexadiene ring. There is coupling to at least two protons, since a triplet is clearly present, and further unresolved splitting is possible. The apparent hyperfine splitting is approximately 4 G.

Unfortunately, no structural reports on this compound have been published, and without further structural information, it is not possible to make any detailed assessment of the spin density in the cyclohexadiene ring. It is possible, however, to decide whether the species observed is an electron-excess or -deficit radical. If the cyclohexadiene compound is dissolved in 2-methyltetrahydrofuran, irradiation of the frozen glassy solutions at 77 K produces neither the blue-black color characteristic of the trapped electron nor the trapped electron signal in the esr spectrum. Without

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