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*-$Ir(py)_4Cl_2^+$ [18] and for *cis*-$Ir(bipy)_2X_2^+$ and *cis*-$Ir(phen)_2Cl_2^+$ [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*-$[Ir(py)_4Cl_2]Cl$, 14077-29-3; *cis*-$[Ir(bipy)_2Cl_2]Cl$, 22710-60-7; *cis*-$[Ir(bipy)_2Br_2]Br$, 23329-12-6; *cis*-$[Ir(phen)_2Cl_2]Cl$, 15609-62-8; *trans*-$[Ir(en)_2Cl_2]ClO_4$, 20037-59-6.

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[20] D. H. W. Carstens and G. A. Crosby, *J. Mol. Spectrosc.*, **34**, 113 (1970).

[21] R. J. Watts and G. A. Crosby, *J. Amer. Chem. Soc.*, **93**, 3184 (1971).

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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), $(C_6H_8)Fe(CO)_2PPh_3$. 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

$$n\text{-BuCl} + e^- \rightarrow n\text{-Bu} + Cl^-$$

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, $A_{iso} = \pm 59$ G and $2B = \pm 9$ G. When combined with the theoretical values of the hyperfine couplings from ^{31}P of $A^\circ_{iso} = +3636$ 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

[1] P. B. Ayscough and C. Thomson, *Trans. Faraday Soc.*, **58**, 1477 (1962).

[2] Calculated from the wave functions given by C. Froese, *J. Chem. Phys.*, **45**, 1417 (1966).

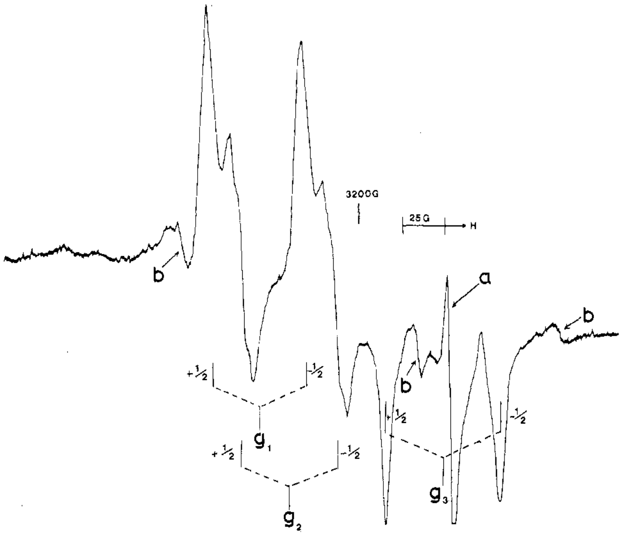

Figure 1. First-derivative X-band esr spectrum of γ-irradiated powdered dicarbonylcyclohexadienetriphenylphosphineiron(0). Line a is an unidentified singlet at free spin; lines b are extra unidentified lines. The main features marked $g_{1,2,3}$ having the normal form of a shoulder, a crossover, and a shoulder, respectively, are each split into two by hyperfine coupling to ^{31}P, the $M_I = \pm ^1/_2$ components being as indicated.

addition of the iron–cyclohexadiene compound, these characteristics are easily observed on irradiation. Furthermore, if the glassy solvent matrix is allowed to warm to the point at which the organic radicals produced from the solvent have decayed away, the remaining spectrum is the same as that in Figure 1. It is concluded that the electrons produced from the solvent and normally trapped in the glass have been captured by the organometallic substrate to give the species responsible for the spectrum in Figure 1. This species is then identified as the radical anion $[(C_6H_8)Fe(CO)_2(PPH_3)]^-$. This anion has a formal 3d^9 configuration on iron and even in the absence of X-ray structural data for the parent complex some partial conclusions can be drawn regarding its electronic structure. If we define the Fe-P direction as z, then the two most likely configurations are $d_{z^2}{}^2$, $d_{x^2-y^2}{}^1$ and $d_{x^2-y^2}{}^2$, $d_{z^2}{}^1$. Our data strongly favor the latter configuration. This conclusion is based on the form of the g tensor and the magnitude of the ^{31}P coupling. Thus, for either model, g_{zz} must lie along the direction of largest coupling to ^{31}P and hence $g_{zz} = 2.006$. This is close to the free-spin value, as required by the $d_{z^2}{}^1$ configuration, but not by the other. Furthermore, the total spin density of *ca.* 6% on phosphorus is reasonable for a delocalization mechanism, but very large indeed for a spin-polarization mechanism required by the $d_{x^2-y^2}{}^1$ configuration. Also in favor of the $d_{z^2}{}^1$ structure is the relatively large proton coupling. This also implies some direct delocalization onto the organic ligand which is only possible for this configuration.

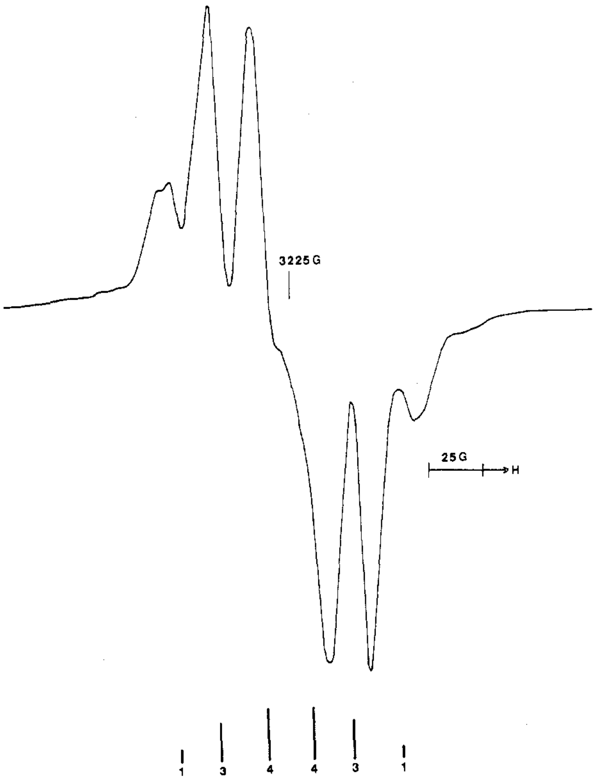

Figure 2. First-derivative esr spectrum of the n-Bu· radical, obtained from irradiation of a frozen solution of the iron(0)–diene complex in n-BuCl (*ca.* 80 K). The reconstruction gives $a(\alpha\text{-H}) = 23$ G, $a(\beta\text{-H}_1) = 23$ G, and $a(\beta\text{-H}_2) = 45$ G (see ref 1).

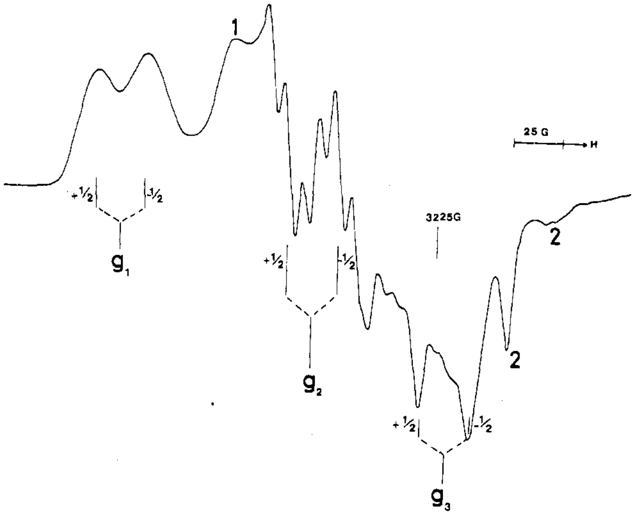

Figure 3. The spectrum of the frozen solution of Figure 2 after standing at *ca.* 110 K. Lines 1 and 2 are due to unrelated radical species, as shown by their thermal stabilities compared with the main features. These again, having the normal shape for three g features, comprise major doublets, the central (crossover) features showing an additional triplet splitting.

When the iron–cyclohexadiene complex was dissolved in n-butyl chloride and the frozen solution irradiated at 77 K, a different set of esr spectra was obtained, as shown in Figures 2 and 3. The spectrum at 77 K is that of the n-butyl radical,[1] present in very high concentration. At approximately 100 K, the n-Bu· spectrum slowly disappeared, being replaced by the spectrum shown in Figure 3 in an approximately 1:1 manner. This spectrum is analyzed in terms of a species with an anisotropic g tensor ($g_1 = 2.11, g_2 = 2.04, g_3 = 2.00$) which also shows clearly resolved hyperfine structure on the g_2 line. All three g features are split into doublets, with a further 1:2:1 triplet hyperfine splitting on the g_2 feature. The occurrence of this line at $g = 2.04$ and the clear multiplet hyperfine splitting suggest that this spectrum is due mainly to an organic radical strongly bonded to the metal. The doublet splitting on $g_{1,2,3}$ is 26 G, and the triplet splitting on the g_2 line is 9 G. (This smaller coupling is not resolved on the g_1 and g_3 lines because of their excessive width.) Hence we conclude that there is considerable spin on iron, to cause the g shifts, but also considerable spin on the organic ligand, to cause proton hyperfine coupling which must at least ac-

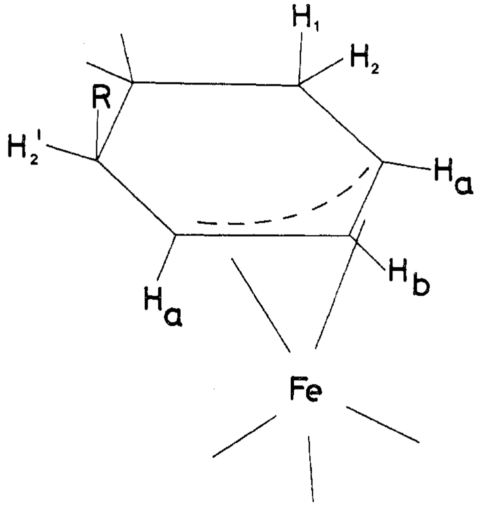

Figure 4. The coordinated allylic system.

count for the 9-G triplet if not also for the 26-G doublet (which could also be due to ^{31}P coupling).

One of the most likely modes of attack for the *n*-Bu radical on the cyclohexadiene ring is addition to the unsaturated system. This sort of attack at one of the unsaturated carbon atoms would probably occur from the side of the ring opposite to the metal atom, as has been observed repeatedly in such systems during nucleophilic attack on the ring.[3] If this were the case, the product would be the allylic radical shown in Figure 4.

The esr parameters to be expected from the allyl radical are 14 and 4 G for the five methylene and single methine protons, respectively.[4] The observed triplet splitting of 9 G is then assigned to the protons H_a, and this allows calculation of a spin density of ~65% in the allylic ring. Models indicate that the protons H_2 are very nearly in the plane of the allylic system, while proton H_1 (and the butyl group R) are *ca.* 90° out of this plane. As such, one expects the protons H_2 to be very weakly coupled to the allylic system, while H_1 would be strongly coupled with the unpaired spin. The maximum splitting from a proton such as H_1 under conditions of ideal geometry and unit spin density on the adjacent carbon is *ca.* 50 G.[5] Taking into account the spin density at the adjacent allylic carbon atom, the doublet splitting from H_1 should be $9\text{ G}/23\text{ G} \times 50\text{ G} = 20\text{ G}$, where 23 G is the splitting that H_a would cause if all the spin were localized on the one carbon atom.[6] This calculated value of 20 G is close to the doublet splitting of 26 G observed, and the increase can be accommodated if the allylic system has some cationic character.[7] Thus, for this model, the doublet splitting is assigned to a β proton rather than ^{31}P. This interpretation is also supported by the fact that the doublet hyperfine splitting is isotropic, which would be expected for a β-proton splitting, but not for a phosphorus splitting. Cationic character is expected if the metal acquires spin density by electron transfer from the allylic ligand.

Thus, on this hypothesis, the species observed has partial allyl radical character, but with considerable spin density on iron, and little, if any, on phosphorus. This excludes the participation of the d_{z^2} orbital, but suggests that there is bonding between the π_2 orbital of the allylic system and an orbital such as d_{xz} on iron. The very large g_1 value can then be understood if this is g_{zz}, since coupling between d_{xz} and d_{yz} is likely to be facile.

Another possible mode of radical attack, namely, hydrogen atom abstraction from the diene ring to give a coordinated cyclohexadienyl radical, must also be considered. This alternative, however, is less likely than that first discussed, as it would require that the hyperfine coupling from the CH_2 protons in the cyclohexadienyl radical be reduced from *ca.* 50 to *ca.* 9 G by delocalization onto iron. This implies that the 26-G doublet must arise only from ^{31}P. However, a phosphorus splitting should be anisotropic, as found for the anion, whereas in fact it is almost completely isotropic. On this basis, the former scheme involving radical attack at an unsaturated carbon atom is favored.

Registry No. $(C_6H_8)Fe(CO)_2PPh_3$, 12213-19-3; $[(C_6H_8)Fe(CO)_2(PPh_3)]^-$, 39797-00-7; *n*-butyl radical, 2492-36-6.

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[3] J. K. Stille and R. A. Morgan, *J. Amer. Chem. Soc.*, 88, 5135 (1966); J. D. Munro and P. L. Pauson, *J. Chem. Soc.*, 3475, 3479, 3484 (1961); I. U. Khand, P. L. Pauson, and W. E. Watts, *J. Chem. Soc. C*, 2024 (1969), and references therein.

[4] R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, 39, 2147 (1963).

[5] M. C. R. Symons, *Advan. Phys. Org. Chem.*, 1, 284 (1963).

[6] I. A. Zlochower, W. R. Miller, and G. K. Fraenkel, *J. Chem. Phys.*, 42, 3339 (1965); G. B. Garbutt, H. D. Gesser, and M. Fujimoto, *ibid.*, 48, 4605 (1968).

[7] R. Hume and M. C. R. Symons, *J. Chem. Soc.*, 446 (1966).

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Reactions of Octacyanomolybdate(IV). II. Coordination to Iron(III) and H$^+$ in Aqueous Solution

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The octacyanomolybdate(IV) ion generally forms insoluble complexes with divalent transition metal cations. However, if the transition metal cation is trivalent, formation of a soluble complex results on mixing aqueous solutions of each species.[1,2] Malik and Ali studied the reaction of Fe(III)[1] and Cr(III)[2] with the octacyanomolybdate(IV) ion in aqueous solution and found that, in both cases, soluble complexes are formed. Using Job plots, the complexes were shown to be stoichiometrically 1:1, *i.e.*, of composition, $M^{III}Mo(CN)_8^-$, where M^{III} is Fe(III) or Cr(III). A reexamination of the system in acid solution to avoid hydrolysis of Fe^{3+} and an attempt to isolate salts of $Fe\text{-}NCMo(CN)_7^-$ have been made.

Experimental Section

$K_4Mo(CN)_8 \cdot 2H_2O$ was prepared by the method of Furman and Miller.[3] $Mo(CN)_8^{4-}$ solutions were stored in the dark for no more than 24 hr. Reagent grade $FeCl_3 \cdot 6H_2O$ was used to prepare Fe(III) solutions. Suitable H^+ concentrations were maintained with standardized $HClO_4$. Ionic strength was maintained at 1.0 with $NaClO_4$ when $[H^+]$ was varied. Elemental analyses were performed by the Microanalytical Laboratory of the University of Illinois. All spectra were recorded, using a Cary 14 recording spectrophotometer.

Results and Discussion

Mixing aqueous solutions of *ca.* 5×10^{-3} *M* Fe(III) and $Mo(CN)_8^{4-}$ and 1 *M* H^+ changed the colors of the reagents from yellow to blue, indicating interaction between Fe(III)

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[1] W. U. Malik and S. I. Ali, *J. Inorg. Nucl. Chem.*, 20, 155 (1961).

[2] W. U. Malik and S. I. Ali, *Talanta*, 8, 737 (1961).

[3] N. H. Furman and C. O. Miller, *Inorg. Syn.*, 3, 160 (1950).